



Institut für Festkörperforschung

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related intermetallic phases***

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Berichte des Forschungszentrums Jülich ; 4099
ISSN 0944-2952
Institut für Festkörperforschung Jül-4099
D 82 (Diss., Aachen, RWTH, 2003)

Zu beziehen durch: Forschungszentrum Jülich GmbH · Zentralbibliothek
D-52425 Jülich · Bundesrepublik Deutschland
☎ 02461 61-5220 · Telefax: 02461 61-6103 · e-mail: zb-publikation@fz-juelich.de

Plastic behaviour of quasicrystals and related intermetallic phases

In the present work, the plasticity of quasicrystals, metallic glasses and structurally complex alloy phases was investigated. The concepts of plasticity for simple crystalline materials cannot be applied to these materials without substantial modification.

Plastic deformation experiments and subsequent microstructural investigations by means of transmission electron microscopy (TEM) were performed on icosahedral Zn-Mg-Dy and Al-Pd-Mn single quasicrystals. A constitutive model approach describing the plasticity of icosahedral quasicrystals was applied to a wide range of experimental deformation parameters. In both materials plastic deformation depends on the interaction of dislocation storage and recovery and the strain driven disordering and diffusion driven reordering of the material.

The plastic deformation behaviour of Pd-Ni-Cu-P bulk metallic glass was studied in creep experiments at three different temperatures and in a wide range of creep stresses. The transition between steady-state creep and accelerating creep was studied. Based on the free-volume description a constitutive model was developed, which comprehensively describes the salient features of metallic-glass plasticity for various deformation conditions.

Furthermore dislocation-like defects in the structurally complex alloy phases ξ' -Al-Pd-Mn and c_2 -Al-Pd-Fe were investigated. New types of defects, which are present in the materials after plastic deformation, were found and characterized by means of TEM. It was shown that the basic concepts of dislocation-like defects show clear similarities in both structurally complex phases.

Plastisches Verhalten von Quasikristallen und verwandten intermetallischen Phasen

In der vorliegenden Arbeit wurde das plastische Verhalten von Quasikristallen, metallischen Gläsern und strukturell komplexen intermetallischen Phasen untersucht. Die Konzepte zur Beschreibung der Plastizität von einfachen kristallinen Materialien können auf diese Materialien nicht ohne grundlegende Modifikation übertragen werden.

Plastische Verformungsexperimente und mikrostrukturelle Untersuchungen wurden an Zn-Mg-Dy und Al-Pd-Mn Quasikristallen mit Hilfe der Transmissionselektronenmikroskopie (TEM) durchgeführt. Ein konstitutives Modell der Quasikristallplastizität wurde auf einen großen Bereich von experimentellen Verformungsparametern angewendet. In beiden Materialien wird die plastische Verformung durch die Wechselwirkung von Versetzungserzeugung und -erholung und die dehnungsinduzierte Entordnung und diffusionsbedingte Wiederherstellung der Ordnung im Material gesteuert.

Das plastische Verformungsverhalten von massiven metallischen Pd-Ni-Cu-P Gläsern wurde in Kriechexperimenten bei drei verschiedenen Temperaturen in einem großen Kriechspannungsbereich untersucht. Der Übergang zwischen stationärem Kriechen und beschleunigtem Kriechen wurde untersucht. Basierend auf der *free-volume Theory* wurde ein konstitutives Modell entwickelt, welches die plastischen Eigenschaften von metallischen Gläsern bei unterschiedlichen experimentellen Verformungsbedingungen beschreibt.

Weiterhin wurden versetzungsartige Defekte in den strukturell komplexen Legierungsphasen ξ' -Al-Pd-Mn und c_2 -Al-Pd-Fe untersucht. Es wurden neue Arten von strukturellen Defekten entdeckt, welche nach der plastischen Verformung in den Materialien vorhanden sind. Diese Defekte wurden theoretisch sowie mit Hilfe von TEM untersucht. Es wurde gezeigt, dass die grundlegenden Konzepte der versetzungsartigen Defekte in beiden strukturell komplexen Phasen deutliche Ähnlichkeiten zeigen.

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Introduction

Plasticity is the irreversible deformation of matter under an applied stress and is connected to the relative permanent displacement of parts of the material. In most materials, plasticity is mediated by the movement of defects like dislocations or vacancies, which are one- and zero-dimensional defects in the structure, respectively. The plasticity of simple crystals has been investigated since the 1930s and a variety of model descriptions has been proposed. Simple crystals, particularly metals, deform plastically by the movement of dislocations. Nevertheless, plastic deformation is a highly complex process, which is not fully understood. A critical point is that different mechanisms taking place on different length scales ranging from atomic to mesoscopic, are simultaneously involved. Therefore, up to now the understanding of plastic deformation processes of metallic alloys is limited to simple crystals. Few, or in some cases essentially nothing, is known about other classes of materials like metallic glasses, quasicrystals and structurally complex alloy phases (SCAPs).

The plastic deformation properties of metallic glasses have been the subject of numerous publications since the 1960s. However, these studies were limited to the investigation of rapidly quenched ribbons. The discovery of metallic-glass forming alloys like Pd-Ni-Cu-P (He *et al.* 1996) or Zr-based metallic glasses (Peker and Johnson 1993, Inoue *et al.* 1993), possessing low critical cooling rates enabled the production of bulk-metallic-glass samples. This made more accurate investigations of the plastic deformation properties of metallic glasses possible, because of the high structural stability and crystallization resistivity of these phases and the possibility to form glass ingots of up to some cubic centimetres in volume. Plastic deformation experiments under various conditions were performed mainly on metallic glass ribbons, and attempts for model descriptions were made. However, no comprehensive description of the plastic deformation behaviour under consideration of structural disordering of the material could be established, yet.

The plasticity of quasicrystals is investigated since the late 1980s. A deformation mechanism based on the movement of dislocations was found despite the lack of translational symmetry of these materials. Most of the studies were performed on polycrystalline materials containing some amount of secondary foreign phases. The intrinsic plastic deformation properties of icosahedral quasicrystals were studied since the 1990s mainly on Al-Pd-Mn single-grain quasicrystals. The microstructural and macroscopic deformation properties were investigated and yielded a model description of quasicrystal plasticity (Feuerbacher *et al.* 1997b, Feuerbacher *et al.* 2001a). However, these investigations are limited to a narrow range of experimental deformation conditions and to only one icosahedral single-quasicrystalline phase. In order to test if these models describe the plastic properties of a class of materials rather than merely those of a single phase, the investigation of single quasicrystals of other icosahedral phases became increasingly necessary.

Little is known about the physical properties of SCAPs. The plastic deformation behaviour of these materials is of particular interest because of the occurrence of large lattice parameters. It is not straightforward to apply the dislocation concept to these materials since the elastic energies of dislocations are expected to be very high. Indeed an investigation into the plasticity of a structurally complex phase, orthorhombic ξ' -Al-Pd-Mn, has revealed a novel mechanism of plastic deformation (Klein *et al.* 1999).

The topic of the present work is the investigation of the plastic deformation properties and structural defects in these three classes of materials, metallic glasses, quasicrystals and SCAPs.

Chapter 1 gives a short introduction into the structure and the current understanding of the plasticity of quasicrystals. In Chapters 2 to 4 the macroscopic and microstructural features of the plasticity of icosahedral Zn-Mg-Dy quasicrystals are presented in detail for the first time. The results of plastic deformation experiments are presented as well as the observation and characterization of planar defects, the evolution of the dislocation density and the determination of the mode of dislocation motion. Chapter 5 presents plastic deformation experiments on icosahedral Al-Pd-Mn under variation of experimental conditions in a wide range. The evolution of the dislocation density and the structural order and their influence on the stress-strain behaviour during plastic deformation is studied. These experimental results are described in the framework of a quasicrystal plasticity model, which has been proposed by Feuerbacher *et al.* (2001a). Chapter 6 contains a generalizing discussion about the plasticity of Zn-Mg-Dy and Al-Pd-Mn quasicrystals with the background of different diffusion dynamics in both materials.

Chapter 7 describes compression experiments under constant-true-stress conditions, performed on Pd-Ni-Cu-P bulk metallic glasses for the first time. Structural disordering upon plastic deformation, which is a very stress-sensitive process, was studied accurately. A quantitative model, based on the free-volume description by Cohen and Turnbull (1959), is elaborated which describes the plastic deformation behaviour of metallic glasses. Chapter 8 discusses the similarities and differences of the macroscopic plastic deformation properties of icosahedral quasicrystals and bulk metallic glasses.

In Chapter 9 an introduction to metadislocations, a novel type of structural defects governing plastic deformation in the structurally complex ξ' -Al-Pd-Mn phase (Klein *et al.* 1999) is given. A new ansatz for a deformation mechanism in ξ' -Al-Pd-Mn on the basis of local metadislocation networks is presented and discussed. Chapter 10 presents a detailed microstructural investigation on deformed c_2 -Al-Pd-Mn, which is another structurally complex phase possessing a large unit cell with a lattice constant of 15.52 Å. Dislocation-like defect structures possessing large Burgers vectors are observed and characterized. Evidence is furnished that structural modifications at the dislocation core lower the elastic energy of these defects. The basic common concept of structural defects in ξ' -Al-Pd-Mn (Klein *et al.* 1999) and c_2 -Al-Pd-Fe is discussed in Chapter 11.

Quasicrystals and metallic glasses cannot be treated in terms of a unit-cell description, as e.g. simple metals. While quasicrystals and metallic glasses possess no translational symmetry at all, SCAPs possess such large lattice constants that conventional unit-cell based descriptions reach their limit of validity, because of e.g. energetical problems. Consequently, the simple concept of dislocations for the description of their plastic behaviour cannot be applied, at least not without severe modifications. Moreover, all three materials possess icosahedral cluster-based local coordinations, which define types of short-range order which do not exist in simple crystalline materials but, as will be demonstrated, determine their macroscopic physical properties to a wide extend. Furthermore, it is discussed that disordering plays a major role in the description of the physical properties of quasicrystals and metallic glasses due to their lack of translational symmetry.

1. Quasicrystals

Besides crystalline and amorphous material, quasicrystals represent a third independent structural state of matter. As amorphous materials, quasicrystals do not possess conventional translational symmetry. Nevertheless, electron or x-ray diffraction patterns of quasicrystals show sharp diffraction spots, which provides direct evidence for the presence of long-range orientational order. The most striking feature of quasicrystals is the occurrence of symmetries which are forbidden in terms of classical crystallography, e.g. fivefold or tenfold rotational axes. A diffraction pattern corresponding to an icosahedral point group containing fivefold rotation axes was firstly observed by Shechtman *et al.* (1984) in a rapidly quenched Al-Mn alloy. Since that time a large number of metastable and stable quasicrystal phases have been found. The most prominent stable icosahedral quasicrystals are Al-Cu-Fe, Al-Pd-Mn and Zn-Mg-RE (RE: rare earth elements) which were discovered by Tsai *et al.* in 1987 and 1990 and by Luo *et al.* in 1993.

Since it is known that the existence range of stable quasicrystalline phases is limited to certain ranges of the average number of valence electrons per atom and the relative ratios of atomic radii (cf. Tsai 1999), a well-directed search for new quasicrystalline phases became possible. Recently, stable icosahedral quasicrystals in the binary systems Cd-Yb and Cd-Ca (Guo *et al.* 2000, Tsai *et al.* 2000) and in the systems Ag-In-Ca, Ag-In-Yb, Ag-In-Ca-Mg, Ag-In-Yb-Mg, Cd-Ca-Mg and Cd-Yb-Mg were discovered (Guo *et al.* 2002).

1.1 The structure of quasicrystals

The lack of translation symmetry impedes the construction of a quasicrystal lattice by periodic translation of a unit cell. Using the so-called cut procedure, which was introduced by Katz and Duneau (1984), a quasicrystal structure can be constructed from a higher-dimensional periodic hyperlattice. In Figure 1.1 this method is illustrated for the construction of an one-dimensional quasiperiodic chain from a two-dimensional periodic hyperlattice.

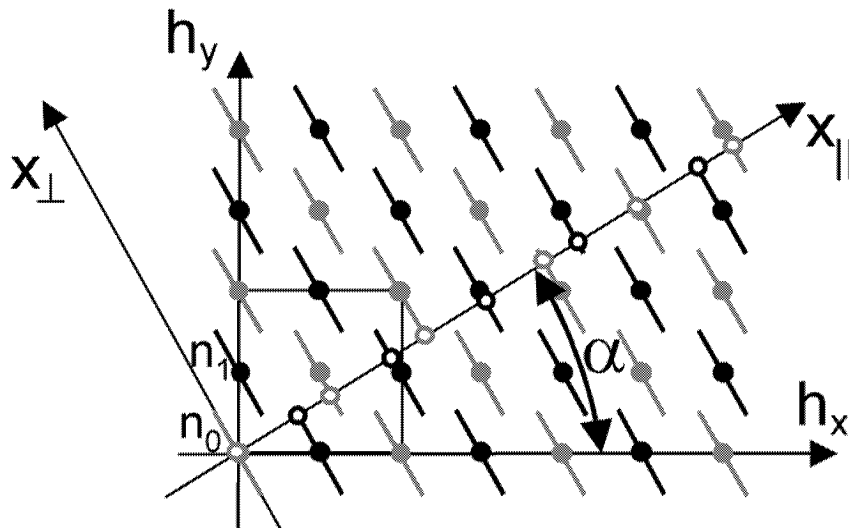


Figure 1.1: Illustration of the construction of an one-dimensional quasiperiodic chain from a two-dimensional lattice by the cut method. The axes h_x and h_y span the hyperlattice, which contains two orthogonal subspaces $x_{\parallel}$ and $x_{\perp}$. The hyperlattice points are divided into two subsets of nodes, which are denoted n_0 and n_1 .

The unit cell of the hyperlattice is indicated as a square. The axes h_x and h_y span the two-dimensional hyperlattice, which contains two orthogonal subspaces $x_{\parallel}$ and $x_{\perp}$. The axes $x_{\parallel}$ and $x_{\perp}$ represent the so-called physical and perpendicular space, respectively. The axis $x_{\parallel}$ is tilted with respect to h_x in a way that the angle α fulfils the condition $\tan \alpha = \tau^{-1}$, where $\tau = \frac{\sqrt{5}+1}{2}$ is the irrational number of the golden mean. The hyperlattice points (filled circles) are decorated with line segments, the hypersurfaces, which have an extension only in the perpendicular space. The cut of these hypersurfaces with the physical space defines the quasiperiodic arrangement of points in $x_{\parallel}$ (open circles). Furthermore, the hyperlattice points are divided into two subsets of nodes, which are denoted n_0 and n_1 . These nodes are decorated with different hypersurfaces referring to different atomic species, which is indicated in Figure 1.1 by a different shading of the line segments. Cutting of the respective type of hypersurface with $x_{\parallel}$ leads to the creation of two different types of lattice points in the quasiperiodic chain (open circles) which are then decorated with different elements.

Using the cut method a three-dimensional quasicrystal lattice can be produced from a six-dimensional periodic lattice in analogy to the two-dimensional example described before. The hypersurfaces are then represented by three-dimensional polygons, which are for the sake of simplicity and faster calculation frequently approximated by spheres. The three-dimensional physical space is embedded into the six-dimensional hyperspace in such a way that the six orthogonal vectors spanning the basis of the hyperspace are projected onto six fivefold axes of an icosahedron in the physical space. In a lattice possessing icosahedral symmetry there are six fivefold axes, ten threefold axes and fifteen twofold axes. The electron diffraction patterns corresponding to these symmetry axes show ten-, six- and twofold symmetry due to Friedel's law. Figure 1.2 shows electron-diffraction patterns of an icosahedral Zn-Mg-Dy quasicrystal showing (a) ten-, (b) six- and (c) twofold symmetry corresponding to five-, three- and twofold symmetry of the corresponding autocorrelation functions, i.e. the symmetry of the real-space structure.

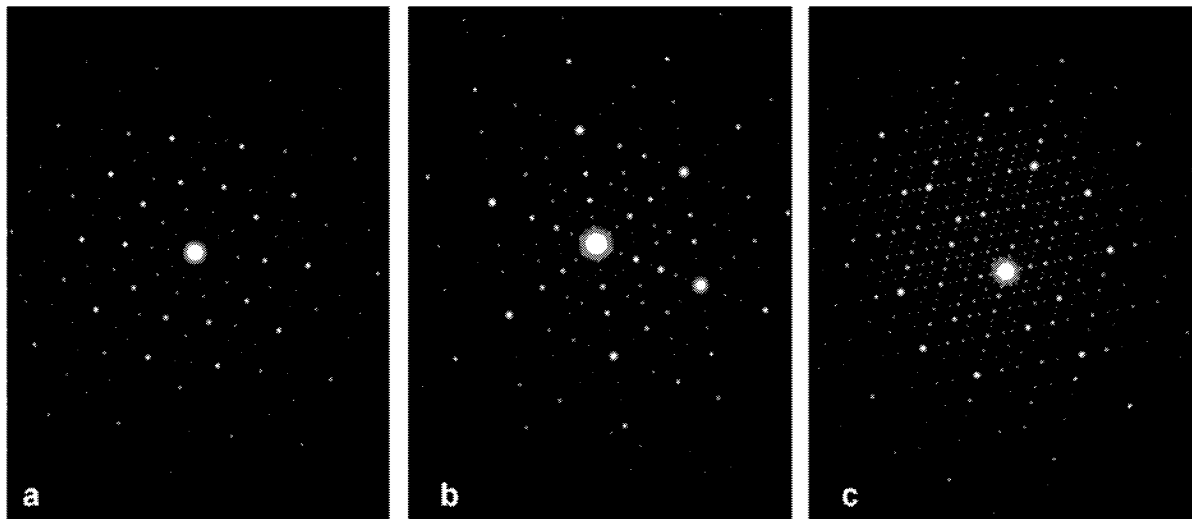


Figure 1.2: Electron-diffraction patterns of an icosahedral Zn-Mg-Dy quasicrystal showing (a) ten-, (b) six-, and (c) twofold symmetry.

Due to the occurrence of irrational aspect ratios of the distance of spots in the diffraction patterns, an indexing of the icosahedral quasilattice is not possible using three integer numbers. For the indexing of a three-dimensional quasilattice six integer indices are required. The indexing of the quasilattice can be performed with regard to the basis of the six-dimensional hyperspace. Figure 1.3 a shows the projection of the six basis vectors of the hyperlattice onto six fivefold axes of an icosahedron in the three-dimensional physical space. An indexing system which is based on the six-dimensional hyperlattice has been developed by Elser (1985). However, different indexing systems based on the six-dimensional hyperlattice are used in literature, according to the choice of the basis. In the present work a six-dimensional notation according to Cahn *et al.* (1986) is used. A reciprocal vector in the six-dimensional notation is written

$$(n_1, n_2, n_3, n_4, n_5, n_6). \quad (1.1)$$

Cahn *et al.* (1986) developed an indexing system which is based on three orthogonal basis vectors in the physical space. Figure 1.3 b shows the arrangement of three orthogonal vectors along three twofold axes of an icosahedron. A lattice point is indexed with two integer numbers along a vector of the basis where both portions are related by a factor of τ . Hence, a lattice vector of the reciprocal space is indexed by $(h + \tau h', k + \tau k', l + \tau l')$. This reciprocal vector is written

$$(h/h', k/k', l/l'). \quad (1.2)$$

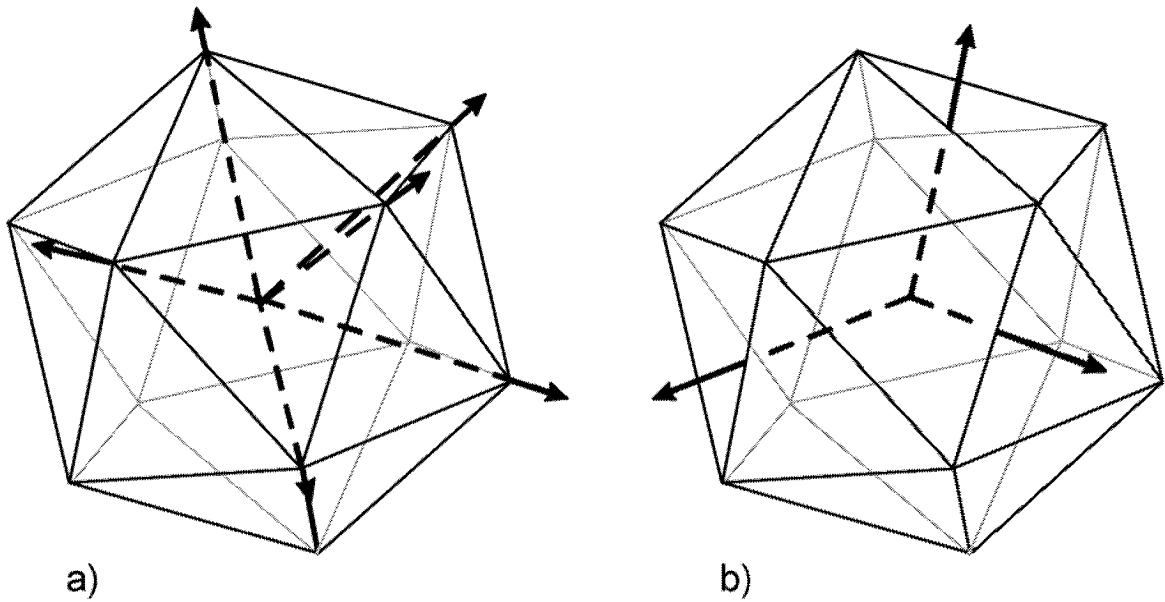


Figure 1.3: Arrangement of vectors in an icosahedron. (a) Three orthogonal vectors are arranged along three twofold directions and (b) six vectors are arranged along six fivefold directions.

The notations are converted by the Equations

$$\begin{aligned} h &= n_1 - n_4, \quad h' = n_2 + n_5, \\ k &= n_3 - n_6, \quad k' = n_1 + n_4, \\ l &= n_2 - n_5, \quad l' = n_3 + n_6. \end{aligned} \tag{1.3}$$

In the present work the notation corresponding to Equation (1.2) is mainly used. In some occasions where it is helpful for the understanding the six-dimensional notation according to Equation (1.1) is used.

The icosahedral quasicrystal phases in the systems Zn-Mg-Dy and Al-Pd-Mn possess chemical long-range order (Niikura *et al.* 1994a, Tsai *et al.* 1994, Boudard *et al.* 1992). A quasiperiodic structure possessing chemically ordered quasilattice positions can be constructed if different hypersurfaces on subsets of lattice nodes are used (cf. Figure 1.1). In the Al-Pd-Mn and Zn-Mg-RE alloy system there are face-centred icosahedral phases, which means that their six-dimensional periodic hyperlattice possesses face-centred order. The ordered lattice is referred to as a superlattice, while the basic lattice points, without the introduction of chemical order, is referred to as the fundamental lattice. The ordering of the hyperlattice can be seen in analogy to the structure of ordered alloys like Cu₃Au or β -brass. In Appendix A a simple three-dimensional example is given for an ordered and disordered structure, which is in direct analogy to the six-dimensional description used in the present Chapter.

Figure 1.4 shows calculated diffraction patterns along the twofold [0/0, 0/0, 0/2] direction of a simple-cubic (a) and a face-centred (b) icosahedral structure according to Devaud-Rzepski *et al.* (1989). The diffraction spots of the simple-cubic structure are referred to as fundamental reflections, the additional spots in the diffraction pattern of the face-centred structure are referred to as superstructure reflections. The extinction rules for indexing of the icosahedral reciprocal lattice for simple cubic (SC) and face centred cubic (FCC) direct hyperlattices are given in Table 1.1. The simple cubic lattice has a lattice parameter of a_0 . The chemically ordered lattice fulfils the extinction conditions of a face centred lattice with lattice parameter $2a_0$. However, for the direct comparison of both diffraction patterns, both indexing systems are related to the same lattice parameter of $2a_0$ (cf. Appendix A). The reciprocal lattices of the direct SC and FCC lattice are SC and body centred cubic (BCC), respectively.

direct lattice	reciprocal lattice	$n_1, n_2, n_3, n_4, n_5, n_6$	$h/h', k/k', l/l'$
SC (a_0)	SC (a_0)	all n_i even	$h+k', k+l', l+h'$ even
FCC ($2a_0$)	BCC (a_0)	all n_i even or all n_i odd	all integer

Table 1.1: The extinction rules for indexing of the reciprocal lattices for simple cubic (SC) and face centred cubic (FCC) direct hyperlattices. The reciprocal lattices are SC and body centred cubic (BCC). The indexing is given in the systems according to Equations 1.1 and 1.2.

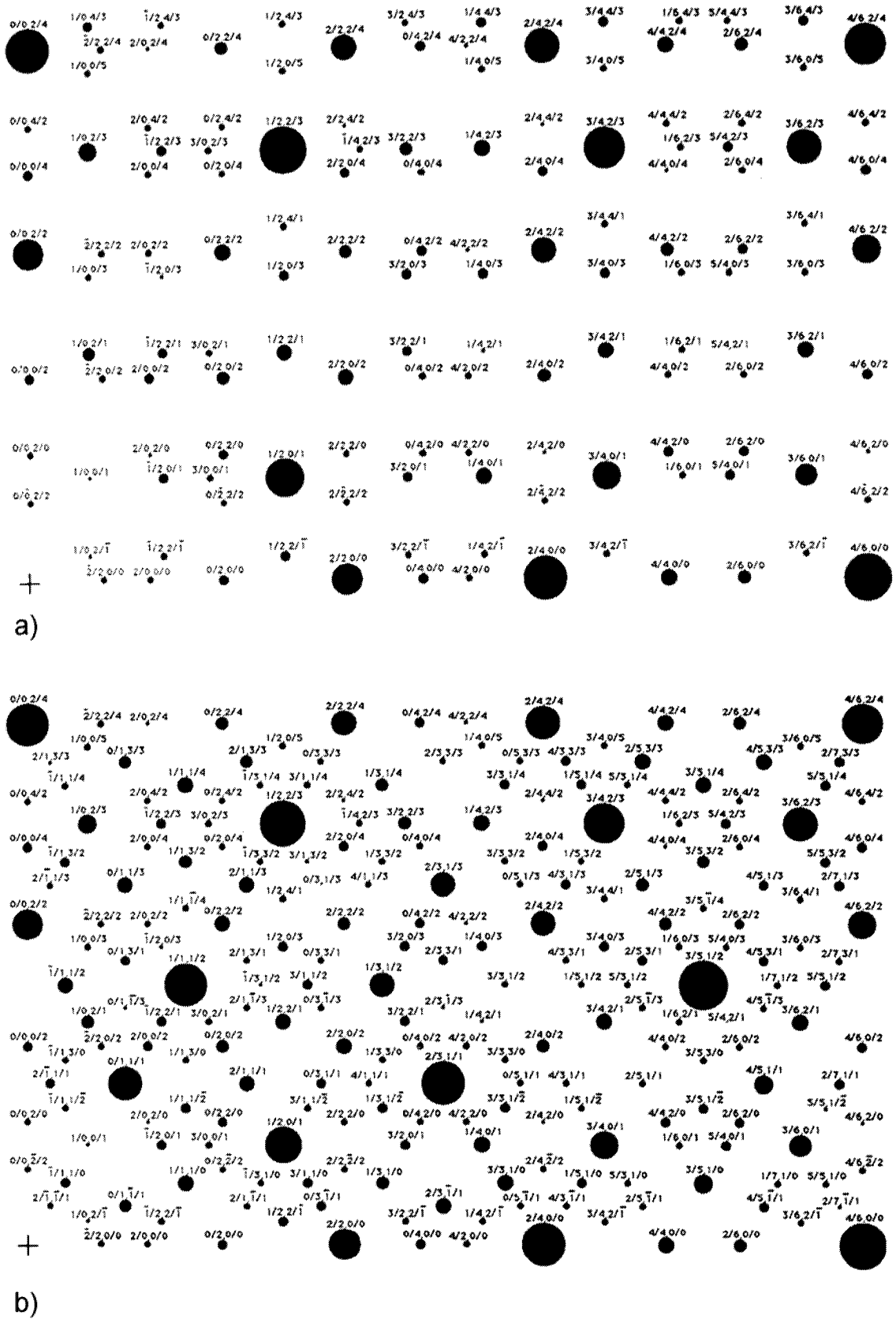


Figure 1.4: Calculated diffraction patterns along the twofold $[0/0, 0/0, 0/2]$ -direction of (a) a simple-cubic Hyperlattice and (b) a face-centred Hyperlattice. The diffraction spots are indexed $h/h', k/k'$ (Devaud-Rzepski et al. 1989)

Icosahedral Al-Pd-Mn

Compared to other quasicrystalline phases, icosahedral Al-Pd-Mn has been studied most intensively during the past ten years. The main reason for this is that the technique to grow large high-quality single grains is well established. The icosahedral phase with a composition around $\text{Al}_{70.5}\text{Pd}_{21.0}\text{Mn}_{8.5}$ is stable up to the melting temperature of about 870 °C (Dong *et al.* 1991). The phase diagram was investigated in detail by Audier *et al.* (1993), Gödecke and Lück (1995), and Grushko *et al.* (1999), which enabled the growth of quasicrystals of many centimetres in size using the Czochralski technique (Yokoyama *et al.* 1992, Boudard *et al.* 1994) and the Bridgman technique (de Boissieu *et al.* 1992).

The structure of icosahedral Al-Pd-Mn was determined by means of x-ray and neutron diffraction (Boudard *et al.* 1991, Boudard *et al.* 1992, de Boissieu *et al.* 1994). Comparing experimental diffraction data and calculations computed on the basis of a six-dimensional structure model, the model parameters were modified to achieve the best fit. Figure 1.5 shows a cut of the six-dimensional unit cell with a plane, which is spanned by the axes $[1, 0, 0, 0, 0, 0]$ and $[0, 1, 1, 1, 1, \bar{1}]$.

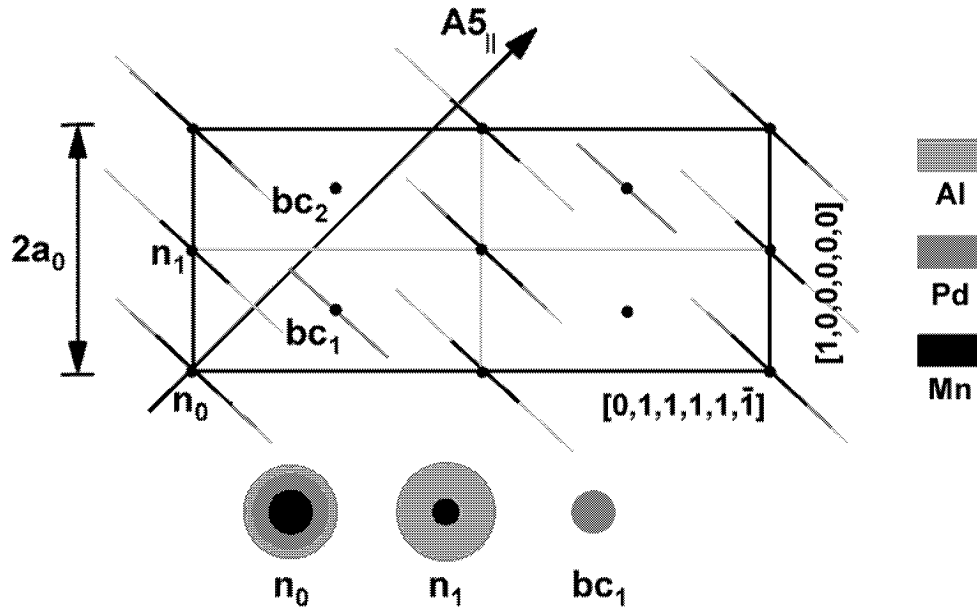


Figure 1.5: Cut through the six-dimensional unit cell according to the Al-Pd-Mn structure model by de Boissieu *et al.* (1994). The hyperlattice is decorated alternately with different hypersurfaces on the hyperlattice nodes n_0 , n_1 and bc_1 . The hyperlattice node bc_2 is not occupied. $A5_{||}$ denotes a fivefold axis in physical space.

The lattice parameter of the superlattice is $2a_0$. $A5_{||}$ denotes a fivefold axis in physical space. The lattice is decorated with three kinds of atomic hypersurfaces, which are approximated by spheres. The hypersurfaces consist of different shells assigned to different atomic species. The hyperlattice is decorated alternately with different hypersurfaces on the hyperlattice nodes n_0 and n_1 leading to face-centred ordering. The lattice position bc_1 is occupied by the hypersurface (bc_1), the lattice position bc_2 is unoccupied. Using this hypercell the physical space structure of icosahedral Al-Pd-Mn can be generated following the cut method. This structure model for Al-Pd-Mn, which is referred to as the Boudard model, has a

reliability factor of $R = 0.09$. Usually, a reliability factor of $R < 0.05$ is referred to as a good standard for structural models¹.

The basic structural building block of the icosahedral Al-Pd-Mn quasicrystal in the three-dimensional physical space is a Mackay-type cluster, which consist of about 51 atoms. It is constructed of surrounding shells of one central atom, an imperfect dodecahedron (8 atoms on average), an icosahedron, and an icosidodecahedron (Janot 1996). The physical properties of quasicrystals are in many respects directly connected to the cluster structure of the material. The Mackay-type clusters, for example, have shown to be mechanically stable units in the structure (Ebert *et al.* 1996) and have crucial influence on the electronic properties (Janot 1996 a, b).

Icosahedral Zn-Mg-RE

Among the class of icosahedral quasicrystals, which is predominated by Al-based alloys, the Zn-based icosahedral Zn-Mg-RE quasicrystalline phases are quite exceptional. Shortly after the first observation of icosahedral quasicrystals in the Zn-Mg-RE system (RE = Y, Tb, Dy, Er, Ho) by Luo *et al.* (1993), a highly ordered face-centred icosahedral phase (Niikura *et al.* 1994a, Tsai *et al.* 1994) coexisting with a simple-cubic icosahedral phase (Niikura *et al.* 1994b) was observed. The formation of the simple-cubic and face-centred phase was shown to depend on the growth conditions (Niikura *et al.* 1994b) and on the content of rare-earth elements (Rodewald *et al.* 1997). Single-quasicrystal growth became possible on the basis of systematic phase-diagram investigations of the Zn-Mg-Y alloy system by Langsdorf *et al.* (1997). Large single quasicrystals of face-centred icosahedral Zn-Mg-Dy were grown using the self-flux technique (Fisher *et al.* 1998, Heggen *et al.* 2000a).

Icosahedral Zn-Mg-RE quasicrystals are referred to as Bergman-type quasicrystals (Tsai *et al.* 1994) contrary to Mackay-type quasicrystals like icosahedral Al-Pd-Mn. The basic structural element is the Bergman cluster, which consists of 117 atoms. The atoms are situated on the vertices of concentric polyhedra: A central atom is surrounded by an icosahedron, a pentagonal dodecahedron, an icosahedron, a truncated icosahedron and an icosahedron (Bergman *et al.* 1957). Among other quasicrystals of the Bergman-type as Al-Li-Cu, Mg-Ga-Zn and Mg-Al-Pd, icosahedral Zn-Mg-RE quasicrystals show an exceptionally high degree of structural perfection (Tsai *et al.* 1994). In x-ray diffraction studies Tsai and coworkers have demonstrated that a high degree of chemical ordering with correlation lengths of 100 nm is present in Zn-Mg-RE quasicrystals. Further investigations have shown that the structure of the icosahedral Zn-Mg-RE-phase is very complex and differs from other Bergman-type quasicrystals (Yamamoto *et al.* 1995). The works about the cluster structure of Zn-Mg-RE quasicrystals published so far are disagreeing: According to Tamura (1996) the three-dimensional structure cannot be constructed by Bergman clusters but by smaller clusters such as icosahedra and Friauf-polyhedra. Kramer *et al.* (2002) studied the cluster structure of Zn-Mg-Dy by means of high-resolution transmission electron microscopy. Results of this work indicate that there are even larger clusters than the Bergman cluster consisting of five concentric polyhedra with 124 atoms: an icosahedron, a dodecahedron, an icosahedron, a truncated icosahedron and a dodecahedron.

¹ The reliability factor $R = \sum \|F_{\text{exp}}\| - \|F_{\text{mod}}\| / \sum \|F_{\text{exp}}\|$ is a measure of the precision of a structure model, where F_{exp} and F_{mod} are the amplitudes of the experimentally measured and the calculated diffracted beams.

A six-dimensional structure model for icosahedral Zn-Mg-Ho was suggested by Ohno and Ishimasa (1997). Figure 1.6 shows a cut of the six-dimensional unit cell with a plane, which is spanned by the axes $[1, 0, 0, 0, 0, 0]$ and $[0, 1, 1, 1, 1, 1]$. Here, the lattice is decorated with five different kinds of atomic hypersurfaces. The hypersurfaces on the lattice nodes n_0 , n_1 , bc_1 and bc_2 are spherical, the hypersurface on the lattice node ec is ellipsoidal, with a short axis oriented along a fivefold axis in physical space. This structural model, however, only has a reliability factor of $R = 0.24$. Hence, in contrast to the Boudard model for Al-Pd-Mn, the structure of Zn-Mg-RE is still uncertain.

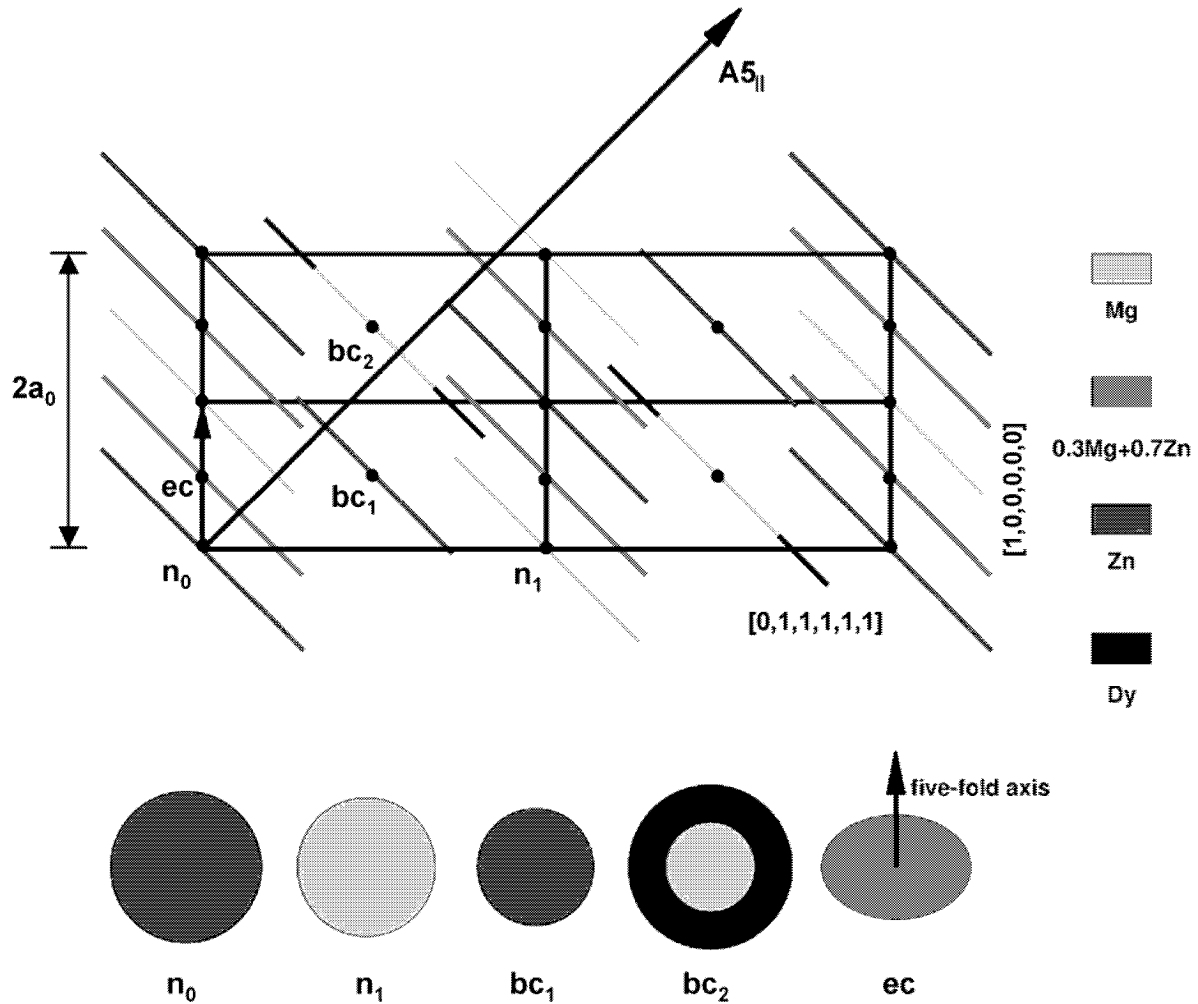


Figure 1.6: Cut through the six-dimensional unit cell according to the Zn-Mg-RE structure model by Ohno and Ishimasa (1997). The hyperlattice is decorated with different hypersurfaces on the hyperlattice nodes n_0 , n_1 , bc_1 , bc_2 and ec . $A5_{||}$ denotes a fivefold axis in physical space.

1.2 Defects in quasicrystals

Dislocations can be defined in a quasicrystal, in analogy to crystals, as line defects. The introduction of dislocations into a quasicrystalline structure is generally described with reference to the hyperlattice by introduction of a high-dimensional displacement field (Wollgarten *et al.* 1991)

$$\vec{U} = \vec{u}_{\parallel}(\vec{x}_{\parallel}) + \vec{u}_{\perp}(\vec{x}_{\parallel}), \quad (1.4)$$

where $\vec{u}_{\parallel}$ and $\vec{u}_{\perp}$ denote the displacement field in the physical and the perpendicular space, respectively. Figure 1.7 shows the effect of the components of the high-dimensional displacement field $\vec{u}_{\parallel}(\vec{x}_{\parallel})$ and $\vec{u}_{\perp}(\vec{x}_{\parallel})$ on lattice positions in the physical space according to Figure 1.1. In Figure 1.7 a and b hyperlattice positions (and the hypersurfaces) are displaced parallel to $\vec{x}_{\parallel}$ and $\vec{x}_{\perp}$, respectively. The displacement of hyperlattice positions is indicated by black arrows. Displaced hyperlattice positions are grey while the original hyperlattice positions are black. The displacement of lattice positions in the physical space (open circles) is indicated by grey arrows. Figure 1.7 a shows that the introduction of a displacement field $\vec{u}_{\parallel}(\vec{x}_{\parallel})$ leads to continuous local deviations from the ideal lattice positions in the physical space, i.e. the occurrence of phonon strain as in conventional crystals.

Figure 1.7 b shows that the introduction of a displacement field $\vec{u}_{\perp}(\vec{x}_{\parallel})$, on the other hand, may lead to the creation and annihilation of sites in the physical space quasicrystal structure. However it has to be provided that sites in the physical space are created and annihilated simultaneously and so the number of atomic sites is constant (closeness condition, Katz and Gratias 1994). Hence the introduction of a displacement field $\vec{u}_{\perp}(\vec{x}_{\parallel})$ leads to the jumps of atoms to new lattice sites in the physical space (grey arrow in Figure 1.7 b). These atomic jumps are called phason jumps. The corresponding strain introduced into the structure is termed phason strain. The introduction of phason strain represents a distortion of the ordered ideal structure and can be understood as the introduction of structural disorder. The displacement fields $\vec{u}_{\parallel}$ and $\vec{u}_{\perp}$ do not depend on $\vec{x}_{\perp}$ since this would lead to a dependence of the structure on the position of $\vec{x}_{\parallel}$ in the hyperspace which has to be considered unphysical.

Dislocations

In a crystalline lattice a perfect edge dislocation can be introduced by the Volterra process. From the ideal lattice (Figure 1.8 a) an atomic half-plane is removed (Figure 1.8 b). The parts of the lattice are closed and the lattice is relaxed elastically (Figure 1.8 c). At the end of the remaining half-plane a line defect is created (with line direction perpendicular to the image plane in Figure 1.8 c). Around the dislocation core the strain field $\vec{u}(\vec{r})$ describes the shift of each lattice point from its original position. The line direction $\vec{l}$ of a dislocation is a vector parallel to the line, where the strain field of the dislocation is invariant.

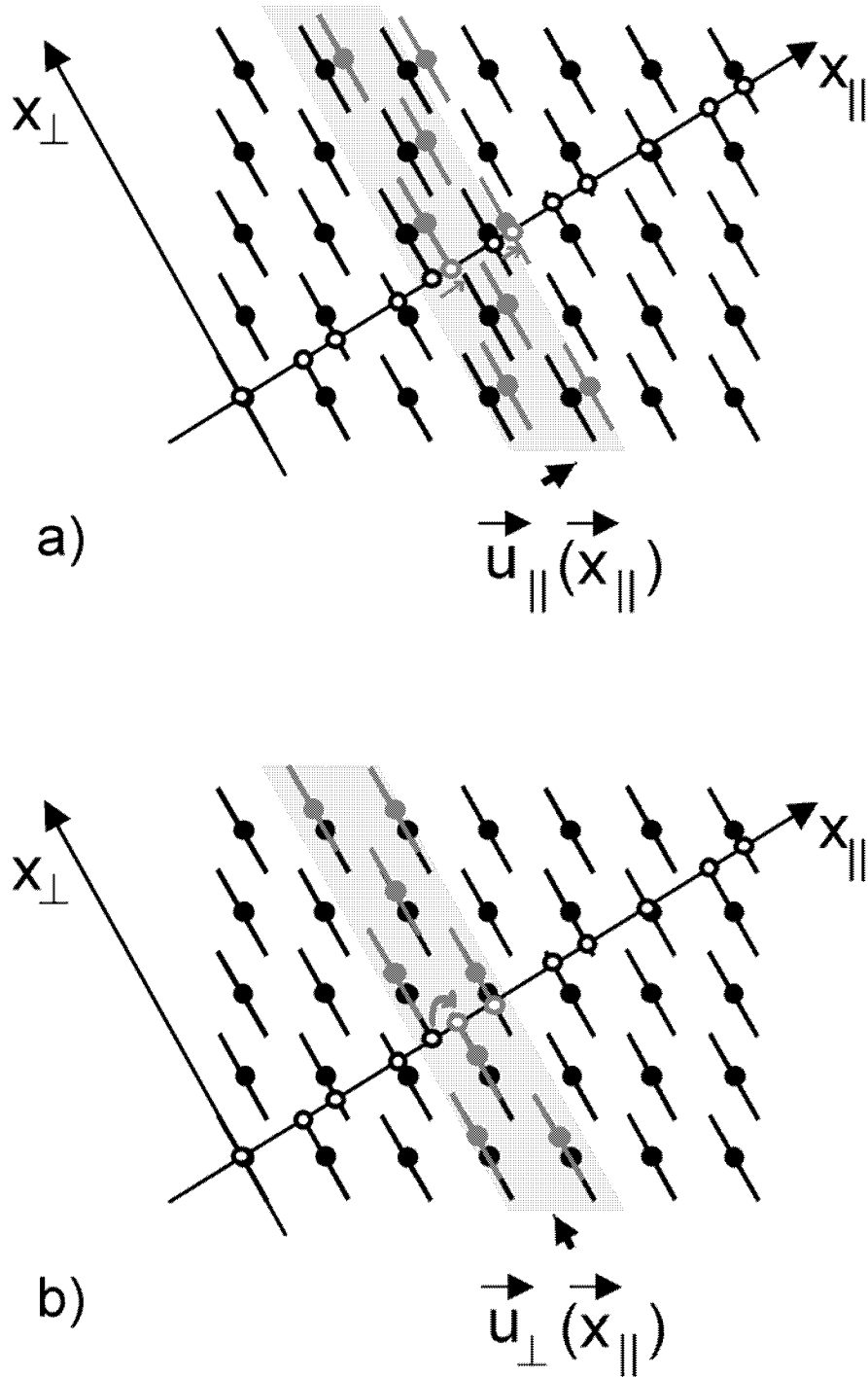


Figure 1.7: Hyperlattice positions (and the hypersurfaces) are displaced parallel to (a) $\vec{x}_{\parallel}$ and (b) $\vec{x}_{\perp}$, respectively. The displacement of hyperlattice positions is indicated by black arrows. Displaced hyperlattice positions are grey while the original hyperlattice positions are shown in black. The displacement fields $\vec{u}_{\parallel}$ and $\vec{u}_{\perp}$ only depend on $\vec{x}_{\parallel}$. In the present example they are confined to the light grey stripes. The displacement of lattice positions in the physical space (open circles) is indicated by grey arrows.

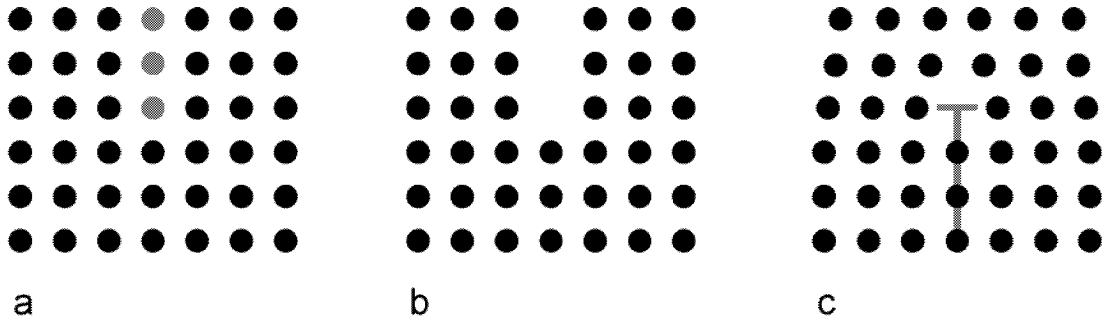


Figure 1.8: Volterra process: (a) The ideal lattice. Atoms of an atomic half plane are indicated as grey circles. (b) The atomic half-plane is removed. (c) The parts of the lattice are closed and the lattice is relaxed elastically. The dislocation is indicated.

The Burgers vector $\vec{b}$ of a dislocation is determined by a Burgers circuit. Around the dislocation core a closed Burgers circuit C is performed in clockwise direction² (Figure 1.9 a). The start and finish points of the circuit are marked by a circle and a cross. The sequence of basic steps of this Burgers circuit is transferred to the ideal crystal (Figure 1.9 b). The Burgers vector is the vector which connects the finish point and the start point of the Burgers circuit. In the literature this procedure is termed FS/RH (finish-start/right hand) rule (Hirth and Lothe 1982). A dislocation is characterized by its Burgers vector and line direction. A dislocation with $\vec{b}$ perpendicular to $\vec{l}$ is called an edge dislocation. A dislocation with $\vec{b}$ parallel to $\vec{l}$ is called a screw dislocation (cf. Hirth and Lothe 1982).

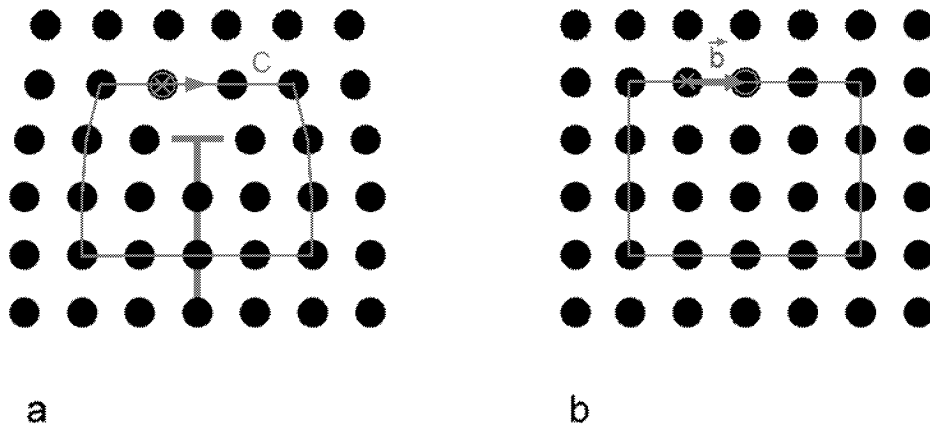


Figure 1.9: Determination of the Burgers vector $\vec{b}$ by a Burgers circuit according to the FS/RH (finish-start/right hand) rule. (a) Around the dislocation core a closed Burgers circuit C is performed in clockwise direction. The start (O) and finish (x) points of the circuit are marked. (b) The circuit is transferred to the ideal crystal. The Burgers vector connects the finish point and the start point of the Burgers circuit.

² The definition of the Burgers vector depends on the sense of the dislocation line. The sense of the Burgers circuit is that of a right handed screw. If the positive sense of the dislocation is into the paper the Burgers circuit is performed in clockwise direction (Hirth and Lothe 1982).

Dislocations in quasicrystals

The construction of a dislocation in a quasicrystal cannot be performed in physical space. Due to the lack of translational symmetry, such a procedure would unavoidably lead to a planar rather than a linear defect (Bohsung and Trebin 1989). The construction of dislocations has to be performed in the hyperlattice (Kleman 1988). For the construction of an edge dislocation in an icosahedral quasicrystal, for example, a five-dimensional hyperlattice half-plane is removed (or inserted) followed by elastic relaxation of the hyperlattice around the edge of the remaining hyperspace half-plane (Yang *et al.* 1998). The corresponding displacement field around the dislocation core defines a higher-dimensional Burgers vector $\vec{B} = \vec{b}_{\parallel} + \vec{b}_{\perp}$ as

$$\vec{B} = \oint_C d\vec{U}, \quad (1.5)$$

where C is a closed circuit around the dislocation core. Within the subspaces we find

$$\vec{b}_{\parallel} = \oint_C d\vec{u}_{\parallel} \quad \text{and} \quad \vec{b}_{\perp} = \oint_C d\vec{u}_{\perp}, \quad (1.6)$$

where $\vec{b}_{\parallel}$ and $\vec{b}_{\perp}$ denote the parallel and perpendicular Burgers-vector components, respectively. The parallel component describes the physical-space displacement field of the dislocation and is equivalent to the Burgers vector of a dislocation in an ordinary crystal. The perpendicular component describes the phason displacement field, i.e. the density of phasons associated with the dislocation.

The displacement of a two parts of a quasicrystalline structure along a plane always leads to the introduction of a fault. Due to the lack of translational symmetry the parts of the quasicrystalline structure can not be displaced in a way that a structure commensurate to the original structure is attained. Therefore, when a dislocation moves through a quasicrystalline structure it leaves a planar fault, a phason wall, in its wake (Socolar *et al.* 1986, Bohsung and Trebin 1989, Mikulla *et al.* 1995).

First, the phason defect is localized to the plane of dislocation motion. However, at elevated temperatures, the phason defects can by atomic jumps (phason jumps) move into the bulk and reduce the high density of phason faults at the plane of dislocation motion (Feuerbacher *et al.* 2003c). The accumulation of phason strain by plastic deformation has been studied by Franz *et al.* (1999). In that work the deviation vectors of diffraction spots from their ideal positions were measured and related to the amount of phason strain (cf. Bankel and Heiney 1986, Horn *et al.* 1986). It was found that the amount of phason strain increases with plastic deformation.

1.3 Plasticity of quasicrystals

Fundamentals of crystal plasticity

Plastic deformation of many materials takes place by dislocation glide, where net planes of the material are displaced by basic lattice vectors. Dislocations move along a glide plane, which usually corresponds to a low indexed crystallographic plane. Figure 1.10 shows the geometry of glide plane, glide direction and the direction of the applied stress (here: compression direction). The geometry of the glide system determines the Schmid factor

$$m_s = \cos \phi \cos \lambda, \quad (1.7)$$

where ϕ and λ denote the angles between compression direction and glide plane normal and compression direction and glide direction, respectively.

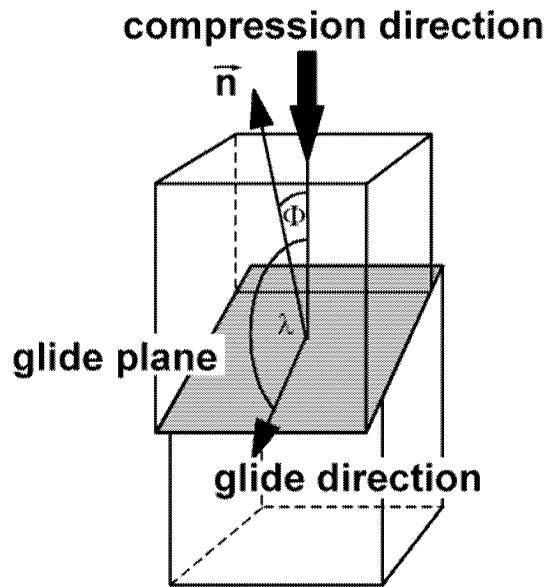


Figure 1.10: Definition of the Schmid factor. ϕ and λ denote the angles between compression direction and glide plane normal $\vec{n}$ and compression direction and glide direction, respectively.

A stress σ which is applied to the sample in compression direction causes a shear stress τ on the glide plane of

$$\tau = m_s \sigma. \quad (1.8)$$

The motion of a dislocation possessing a Burgers vector modulus b over a distance x leads to a macroscopic strain

$$\varepsilon_{plast} = m_s \rho b x, \quad (1.9)$$

where ρ is the dislocation density. The time derivation of Equation (1.9) yields the Orowan equation (cf. Evans and Rawlings 1969)

$$\dot{\varepsilon}_{plast} = m_s \rho b v, \quad (1.10)$$

where v is the dislocation velocity and $\dot{\epsilon}_{plast}$ is the plastic strain rate. The Orowan equation relates the microscopic parameters ρ , b and v and the macroscopic parameter $\dot{\epsilon}_{plast}$.

Oppositional to the shear stress τ the stress τ_i is acting on a moving dislocation. This stress originates from long-range stress fields of other dislocations and counteracts the movement of a dislocation. The effective stress acting on a moving dislocation τ_{eff} is then the shear stress τ reduced by τ_i ,

$$\tau_{eff} = \tau - |\tau_i|. \quad (1.11)$$

The dislocation velocity v , in general terms, is limited by energetical obstacles to be overcome during dislocation movement. The stress on the dislocation originating from this friction process is τ_f . If $\tau_{eff} > \tau_f$, the dislocation is continuously overcoming the obstacles. If $\tau_{eff} < \tau_f$ at an obstacle, the dislocation motion is halted since the effective stress is not high enough to overcome the obstacle. Figure 1.11 shows a schematic picture of a dislocation which is in a position x_1 at an energetic obstacle. Due to thermal fluctuations there is a non-zero probability to overcome the obstacle. The energy barrier which has to be overcome by thermal fluctuations is given by

$$\Delta G = \int_{x_1}^{x_2} (\tau_f - \tau_{eff}) l b dx, \quad (1.12)$$

where ΔG is the Gibbs free energy and l the length of the dislocation line at the obstacle. The probability of thermal activation to overcome the obstacle is

$$P = \exp \frac{-\Delta G}{kT}, \quad (1.13)$$

where k is the Boltzmann's constant and T is the absolute temperature³. The total free energy to overcome the obstacle is $\Delta F = \Delta G + \Delta W$. The first component is the Gibbs free energy of thermal activation ΔG and the work-term ΔW which is the work supplied by the effective stress (Figure 1.11)

$$\Delta W = \int_{x_1}^{x_2} \tau_{eff} l b dx. \quad (1.14)$$

If the thermal activation is the rate-controlling process, the dislocation velocity is $v = v_0 \Delta x P$, where v_0 is an attempt frequency. Hence we obtain with Equation (1.10)

$$\dot{\epsilon}_{plast} = \dot{\epsilon}_0 \exp \frac{-\Delta G}{kT}, \quad (1.15)$$

with $\dot{\epsilon}_0 = \rho b \Delta x v_0$.

³ In the present work the Kelvin and °Celcius temperature scale, following the conventions in the corresponding literature, are used parallelly. The absolute temperature is denoted T , the temperature on the °C scale is denoted T' .

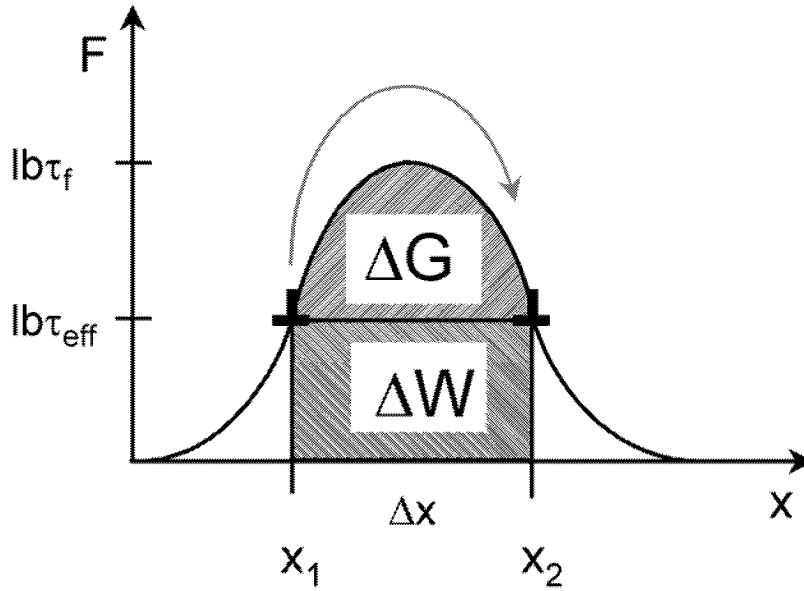


Figure 1.11: Schematic of a dislocation which is in a stable position x_1 at an energetic obstacle. The effective stress τ_{eff} is smaller than the stress τ_f to overcome the obstacle. The energy barrier ΔG is overcome by thermal activation.

The Gibbs free energy is a thermodynamic variable of state which depends on the temperature and the stress. The differential is $d(\Delta G) = -\Delta S dT - V^* d\tau$ with the definitions

$$\Delta S \equiv - \left. \frac{\partial(\Delta G)}{\partial T} \right|_{\tau^*} \quad (1.16)$$

and

$$V^* \equiv - \left. \frac{\partial(\Delta G)}{\partial \tau^*} \right|_T. \quad (1.17)$$

ΔS is the activation entropy. V^* is called the activation volume and can be written as

$$V^* = lb\Delta x = b\Delta A \quad (1.18)$$

The activation area ΔA can be interpreted as the area that is passed by a dislocation line during the thermally activated overcoming of an obstacle. This is illustrated in Figure 1.12. At first the dislocation (solid line) is in a stable position at the cluster obstacle. The dislocation is pinned at two positions indicated by P. The shear stress on the dislocation line τ_{eff} is not high enough to overcome the obstacle. The broken line represents the dislocation line after the obstacle has been overcome. The area between both lines is the activation area ΔA .

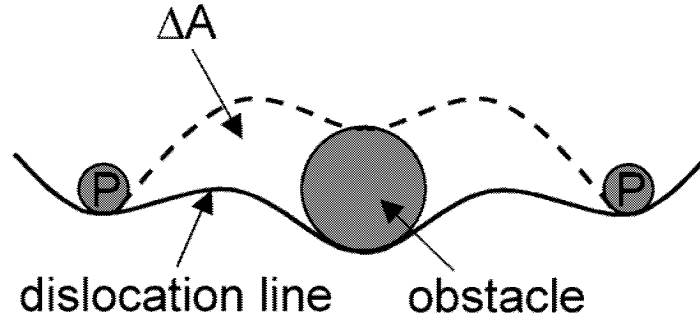


Figure 1.12: Dislocation line at an obstacle. The dislocation is pinned at the positions indicated P. The broken line represents the dislocation line after the obstacle has been overcome by thermal activation. The area between both lines is the activation area ΔA .

The activation volume is an important thermodynamic activation parameter. The experimental determination is possible according to

$$V = - \left. \frac{\partial(\Delta G)}{\partial \tau_{eff}} \right|_T = \frac{kT}{m_s} \left. \frac{\partial(\ln \dot{\epsilon}_{plast})}{\partial \sigma} \right|_T. \quad (1.19)$$

This Equation contains the experimental parameters $\dot{\epsilon}_{plast}$, the plastic strain rate, and σ the applied stress (Evans und Rawlings 1969). The comparison of the experimental activation volume V with the average Burgers vector modulus permits inference on the mode of plastic deformation. For the case of a diffusion-controlled mode of plastic deformation the experimental activation volume is expected to amount to about $V \approx |\vec{b}|^3$ (Krausz and Eyring 1975). If dislocation motion is controlled by the thermally activated overcoming of obstacles the experimental activation volume is of approximately the same size as the obstacle volume. However, a direct comparison of the experimental activation volume V and the activation volume for the overcoming of an individual obstacle is difficult. The correlation between experimental activation volume and obstacle volume is discussed in more detail in the next subsection.

The experimental determination of thermodynamic activation parameters is performed by incremental tests during plastic deformation:

- **Stress-relaxation experiments**

In a stress-relaxation experiment the deformation machine is suddenly halted during plastic deformation. The control mode is switched from a constant-strain-rate experiment to constant-strain control. The stress is measured as a function of time. During a stress-relaxation experiment the total strain of the sample remains constant, hence the total strain rate is given by $\dot{\epsilon} = \dot{\epsilon}_{plast} + \dot{\epsilon}_{elast} = 0$. Elastic strain of the sample is transferred to plastic strain, i.e. $\dot{\epsilon}_{plast} = -\dot{\epsilon}_{elast}$. The elastic strain is due to Hooke's law $\epsilon_{elast} \propto \sigma$. Hence during a stress relaxation experiment it is $\dot{\epsilon}_{plast} \propto -\dot{\sigma}$. This yields with Equation (1.19) a relation for the experimental determination of the activation volume

$$V = \frac{kT}{m_s} \left. \frac{\partial(\ln \dot{\sigma})}{\partial \sigma} \right|_T. \quad (1.20)$$

- **Strain-rate changes**

If the strain rate is rapidly changed during a deformation experiment by a small amount $\Delta\dot{\epsilon}$ the flow stress changes by $\Delta\sigma$. By means of a strain-rate change the activation volume can be determined using Equation (1.19) and the approximation

$$\frac{\Delta \ln \dot{\epsilon}}{\Delta \sigma} \approx \left. \frac{\partial \ln \dot{\epsilon}_{plast}}{\partial \sigma} \right|_T. \quad (1.21)$$

- **Temperature changes**

The Gibbs free energy of activation is not directly accessible in deformation experiments. However, the activation enthalpy ΔH can be determined via (Evans and Rawlings 1969)

$$\Delta H = \Delta G + T\Delta S = -kT^2 \left. \frac{\partial \ln \dot{\epsilon}_{plast}}{\partial \sigma} \right|_T \left. \frac{\partial \sigma}{\partial T} \right|_{\dot{\epsilon}_{plast}}. \quad (1.22)$$

A temperature change is used to determine the temperature dependence of the stress $\Delta\sigma/\Delta T$. The sample is unloaded and the temperature is changed by an amount ΔT . After thermal equilibrium is attained in the deformation machine the sample is reloaded. The temperature dependence of the stress $\Delta\sigma/\Delta T$ together with the result of the stress relaxation experiments (Equation 1.20 and 1.19) yields the activation enthalpy ΔH .

The plasticity of quasicrystals: Survey of previous work

The theory of crystal plasticity can be applied to quasicrystals with minor alterations. Similarities and differences between the plasticity of crystals and quasicrystals are discussed in the forthcoming section.

For the past 10 years the plasticity of icosahedral Al-Pd-Mn has been the subject of several investigations. Icosahedral Al-Pd-Mn, as all quasicrystals, is brittle at low temperatures. At about 690 °C the ductile range sets in at a strain rate of 10^{-5} s^{-1} . This temperature corresponds to a homologous temperature $T_h = T / T_m$, i.e. the absolute temperature scaled by the absolute melting temperature T_m , of about 0.82. In 1993 Wollgarten and coworkers have shown that plastic deformation in icosahedral Al-Pd-Mn quasicrystals is mediated by a dislocation mechanism (Wollgarten *et al.* 1993). The high-temperature macroscopic deformation behaviour and the thermodynamic activation parameters were studied by Feuerbacher *et al.* (1995).

The most significant feature of quasicrystal plasticity is the absence of work hardening at high strains. Figure 1.13 shows a typical stress-strain curve (solid line) of icosahedral Al-Pd-Mn deformed at a constant strain rate of 10^{-5} s^{-1} at 730 °C. A typical stress-strain curve of a crystalline material is shown as dashed line. At the beginning of the deformation experiment the stress increases very rapidly with increasing strain (1). In this regime the deformation is elastic. The slope of the curve in (1) corresponds to the elastic modulus after Hooke's law. The maximum stress after loading is called the upper yield stress (2). Before the upper yield stress is reached, the slope of the curve decreases due to the onset of plastic deformation. The dislocation density increases rapidly during this stage which leads to a decrease of the dislocation velocity according to Equation (1.10), hence the stress drops. For crystalline materials the stress increases again at high strains (dashed line). Due to the

occurrence of subsequent stages of dislocation interaction processes, work hardening, i.e. an increase of flow stress with increasing strain is observed (Basinski and Basinski 1979, Sevillano *et al.* 1993). The local stress minimum (3) is referred to as the lower yield stress.

In quasicrystals a different behaviour is observed. After yielding a short regime of almost constant flow stress, i.e. steady-state flow stress, is observed. At high strains the stress decreases continuously with strain (4), i.e. work softening takes place.

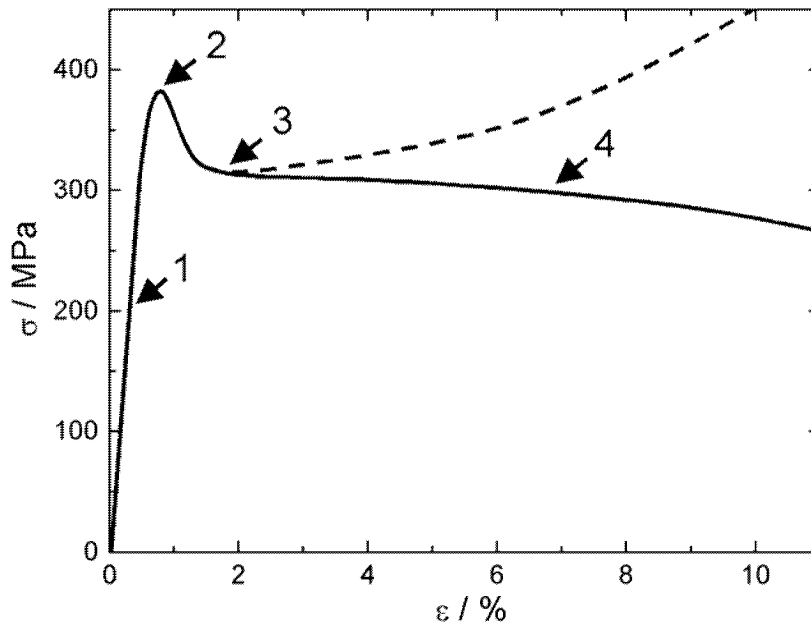


Figure 1.13: Different stages of a stress-strain curve (solid line) of icosahedral Al-Pd-Mn deformed at a constant strain rate of 10^{-5} s^{-1} at 730°C (see text). A common stress-strain curve of a crystalline material is shown as dashed line. Denoted are the elastic regime (1), the upper yield stress (2), the lower yield stress (3) and the regime of work softening (4).

Schall *et al.* (1999) determined the evolution of the dislocation density in a constant-strain-rate experiment of Al-Pd-Mn at 10^{-5} s^{-1} and 730°C . The dislocation density decreases after a maximum value of about $1.2 \times 10^{14} \text{ m}^{-2}$ at 5.6 % to about 50 % of the maximum value at 11.3 % (cf. Figure 5.6 b). Hence work softening in quasicrystals at high strains is accompanied by a decrease of the dislocation density. According to the Orowan Equation (1.10) steady-state deformation at constant plastic strain rate and Burgers-vector length is only possible at decreasing dislocation density if the dislocation velocity increases. However if the structural state of the quasicrystal is constant, an increase of the dislocation velocity is accompanied by an increase of the driving force for dislocation motion, i.e. the applied stress increases. Hence, a joint decrease of dislocation density and stress is only possible if a structural change takes place, which enhances the mobility of the dislocations.

The first qualitative description, relating the macroscopic deformation behaviour to the salient microstructural features of icosahedral quasicrystals, the cluster-friction model, was presented by Feuerbacher *et al.* (1997b). As already introduced in Chapter 1.1 the structure of icosahedral Al-Pd-Mn can be described by the quasiperiodic arrangement of Mackay-type clusters (Boudard *et al.* 1992). The clusters can be considered mechanically stable units in the

structure. This is supported by scanning-tunneling-microscopy investigations of cleavage surfaces of icosahedral Al-Pd-Mn, demonstrating the stability of the clusters (Ebert *et al.* 1996). The basic assumption of the cluster-friction model is that the Mackay-type clusters act as rate-controlling obstacles in dislocation motion. During their movement, dislocations have to overcome the clusters either by cutting or by circumventing. In either case, the ordered structure of the quasicrystal is destroyed locally, which leads to the decrease of the density of rate-controlling obstacles in the course of plastic deformation. The decrease of obstacles, which limit the dislocation velocity, weakens the structure. Dislocation motion becomes easier in the sense that the dislocation velocities increase at constant flow stress.

Figure 1.14 shows schematically the overcoming of cluster-like obstacles by a dislocation. The centres of clusters are indicated as full circles (●), the location of atoms forming the clusters is indicated as stars (*) (Boudard *et al.* 1992).

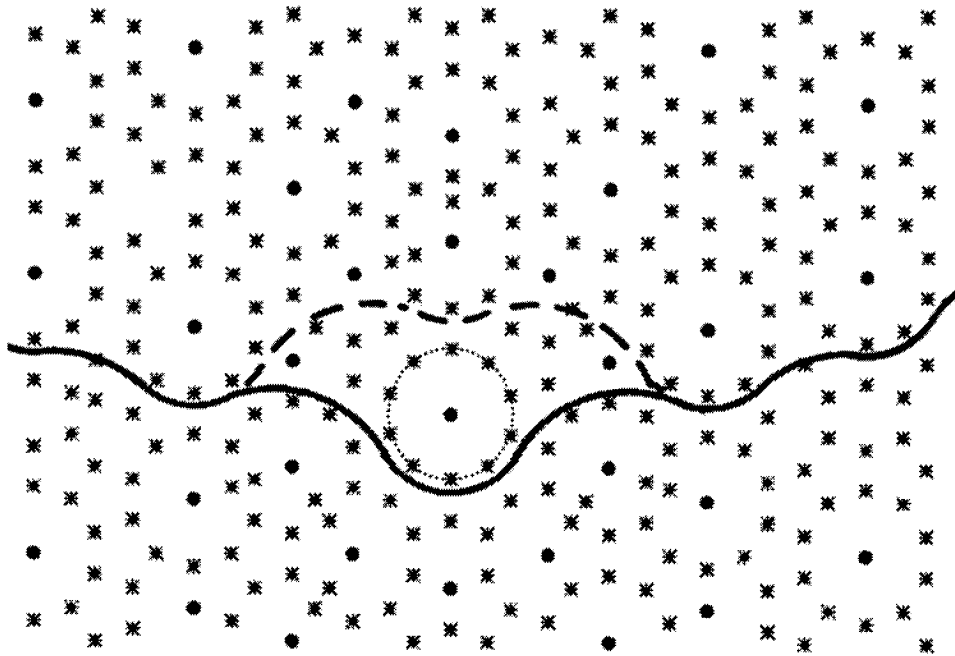


Figure 1.14: Schematic of a dislocation (line) overcoming a cluster-like obstacle (dotted circle). The centres of clusters are indicated as full circles (●), the location of atoms forming the clusters is indicated as stars (*) (Boudard *et al.* 1992).

At first the dislocation is at a stable position at the cluster obstacle (dotted circle). The shear stress on the dislocation line τ_{eff} is not high enough to overcome the obstacle. The local stress on the dislocation line is reflected by its local curvature. If the curvature radius of the dislocation line is small the local stress is high. The dislocation passes the obstacle by thermal activation. Subsequently the dislocation moves due to the applied stress τ_{eff} to the next stable position (uppermost broken line).

However, a direct comparison of the experimental activation volume V and the activation volume for the overcoming of an individual obstacle according to Figure 1.12 is not straightforwardly possible. A discrepancy between experimental and predicted activation parameters as present in the cluster-friction model (Feuerbacher *et al.* 1997b), is eliminated by the more elaborated description by Messerschmidt *et al.* (1999). These authors formulated a quantitative model of dislocation motion in quasicrystals in terms of a Labusch-Schwartz

theory of solution hardening in crystals. In this theory the extended obstacle nature and the high density of the rate-controlling obstacles in icosahedral quasicrystals is accounted for. The ratio of experimental activation volume and size of the cluster obstacles is dependent on parameters as the stress and the density and height of the energetic obstacles. If, for example, the effective stress on the dislocation line is low and hence the curvature of the dislocation line is low and the obstacle density is high, obstacles are not overcome individually by thermal activation. A number of obstacles is overcome simultaneously in one activation step.

In 2001 an empirical quantitative model formulation of the macroscopic plastic deformation behaviour was presented by Feuerbacher *et al.* (2001a). The quantitative model is introduced in detail in Chapter 5 of the present work.

The models of quasicrystal plasticity by Feuerbacher *et al.* (1997b), Messerschmidt *et al.* (1999) and Feuerbacher *et al.* (2001a) are mainly based on plastic deformation experiments on icosahedral Al-Pd-Mn quasicrystals. In order to make sure that these models describe the plastic properties of the *class* of icosahedral quasicrystals rather than these of a particular phase, the investigation of other icosahedral quasicrystals is required. To compare the plastic properties of icosahedral Al-Pd-Mn with those of other icosahedral quasicrystals, quasicrystals of the Zn-Mg-RE system are of particular interest: Firstly their structure is different as discussed in Chapter 1.1. Icosahedral Al-Pd-Mn belongs to the group of Mackay-type quasicrystals whereas Zn-Mg-RE belongs to the group of Bergman-type quasicrystals.

Different mechanical properties between Mackay and Bergman-type icosahedral quasicrystals are expected, which has already been shown by the comparison of materials parameters. For example the Youngs modulus of icosahedral quasicrystals of the Bergman-type, e.g. $E = 62$ GPa for Zn-Mg-Y (Edagawa *et al.* 1997) and $E = 81$ GPa for Al-Li-Cu (Bhaduri *et al.* 1987), is smaller than the Youngs modulus of quasicrystals of the Mackay-type, e.g. $E = 182$ GPa for Al-Pd-Mn (Tanaka *et al.* 1996) and $E = 172$ GPa for Al-Cu-Fe (Vanderwal *et al.* 1992). Furthermore the micro-hardness (Vickers) of quasicrystals of the Bergman-type, e.g. $H_V = 4.3$ GPa for Zn-Mg-Y (Edagawa *et al.* 1997) and $H_V = 3.8$ GPa for Al-Li-Cu (Bhaduri *et al.* 1987), is smaller than the micro-hardness of quasicrystals of the Mackay-type, e.g. $H_V = 9.3$ GPa for Al-Pd-Mn (Takeuchi *et al.* 1991) and $H_V = 9.8$ GPa for Al-Cu-Fe (Köster *et al.* 1993).

Up to now, plastic deformation experiments on icosahedral Zn-Mg-RE (RE = Y, Gd) were only performed on coarse-grained material containing unidentified additional foreign phases (Takeuchi *et al.* 1998). The experiments described in the present study were performed on single-quasicrystalline samples containing solely the icosahedral phase. Hence, the results presented can be interpreted as the intrinsic plastic properties of this material.

1.4 Single-quasicrystal growth

Icosahedral Al-Pd-Mn

The growth of large high-quality single quasicrystals of icosahedral Al-Pd-Mn is well established. The growth is usually performed using the Czochralski-technique. Pre-alloying of the starting materials in the composition Al: 72.1 %, Pd: 20.7 %, and Mn: 7.2 % is performed by inductive levitation melting under an argon atmosphere.

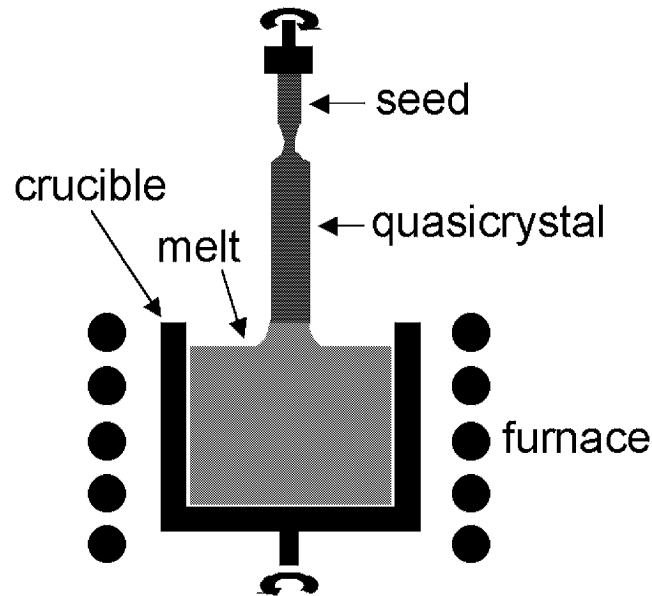


Figure 1.15: Schematic of the Czochralski apparatus used for the growth of icosahedral Al-Pd-Mn quasicrystals.

Figure 1.15 shows a sketch of the central part of the Czochralski apparatus used. The melt is heated via an inductive furnace. During the growth the quasicrystal and the crucible counter-rotate with a speed of 15 rotations per minute and the quasicrystal is pulled out of the crucible, containing the melt, at a speed of about 10 mm/h. The growth of Al-Pd-Mn is initiated by seeding with an oriented quasicrystal, hence applying the Czochralski technique an oriented single crystal of controlled size can be grown. A detailed description of the growth procedure is given by Tamura *et al.* (1996) and Feuerbacher *et al.* (2003) The material used for the present work was subjected to a detailed characterization procedure. It was characterized metallographically, by transmission electron microscopy (TEM) and scanning electron microscopy, and was demonstrated to be a single grain quasicrystal of the icosahedral phase.

Icosahedral Zn-Mg-Dy

Icosahedral Zn-Mg-Dy quasicrystals were grown first using the flux-growth technique by Canfield and Fisk (1992), and Fisher *et al.* (1998). According to Fisher and coworkers the starting materials are sealed in a molybdenum crucible under vacuum conditions in the proportions Zn: 46 %, Mg: 51 %, and Dy: 3 %. The molybdenum crucible is sealed in a quartz tube in order to protect it against oxidation. The tube is placed in a chamber furnace and heated up to a temperature of 700 °C, which is distinctly higher than the melting point (600 °C) of the alloy, in order to homogenize the melt. After a few hours a cooling sequence is started according to the following scheme: cooling down to 650 °C at 5 °/h and to 480 °C at

1. Quasicrystals

1.7 °/h. At 480 °C the excess liquid is decanted. The original crystal growth procedure by Fisher and coworkers was modified for the present work in some aspects in order to increase the size and quality of the single quasicrystals:

- A water-cooled platinum-tip, which was placed close to the bottom of the crucible and acting as a cold finger was used during crystal growth. With this local cooling, preferential grain nucleation at the centre of the crucible bottom could be achieved. The number of grains is lowered and the size of the quasicrystals is increased. Figure 1.16 shows the position of the additional cold finger during the quasicrystal growth.
- A slow cooling sequence according to the following scheme was used: cooling down to 650 °C at 5 °/h, to 575 °C at 1 °/h, and to 480 °C at 0.6 °/h. At 480 °C the excess liquid is decanted using a self-constructed sling. The decrease of the cooling rate promotes the increase of the quasicrystal size and structural perfection of the quasicrystals.
- Using a molybdenum crucible the quasicrystals rigidly stick to the crucible walls which makes it difficult to remove them from the crucible without breaking them. The Zn-Mg-Dy quasicrystals show cracks after growth, which is due to different thermal expansion coefficients of the quasicrystals and the crucible material. An image of Zn-Mg-Dy quasicrystals grown directly in a molybdenum crucible is shown in Figure 1.17 a. A number of cracks can be observed as black lines, which limit the size of the single-quasicrystalline grains available. By introducing an additional alumina crucible within the molybdenum crucible, sticking to the surface could be effectively suppressed. Figure 1.16 shows a sketch of the final crucible arrangement applied.

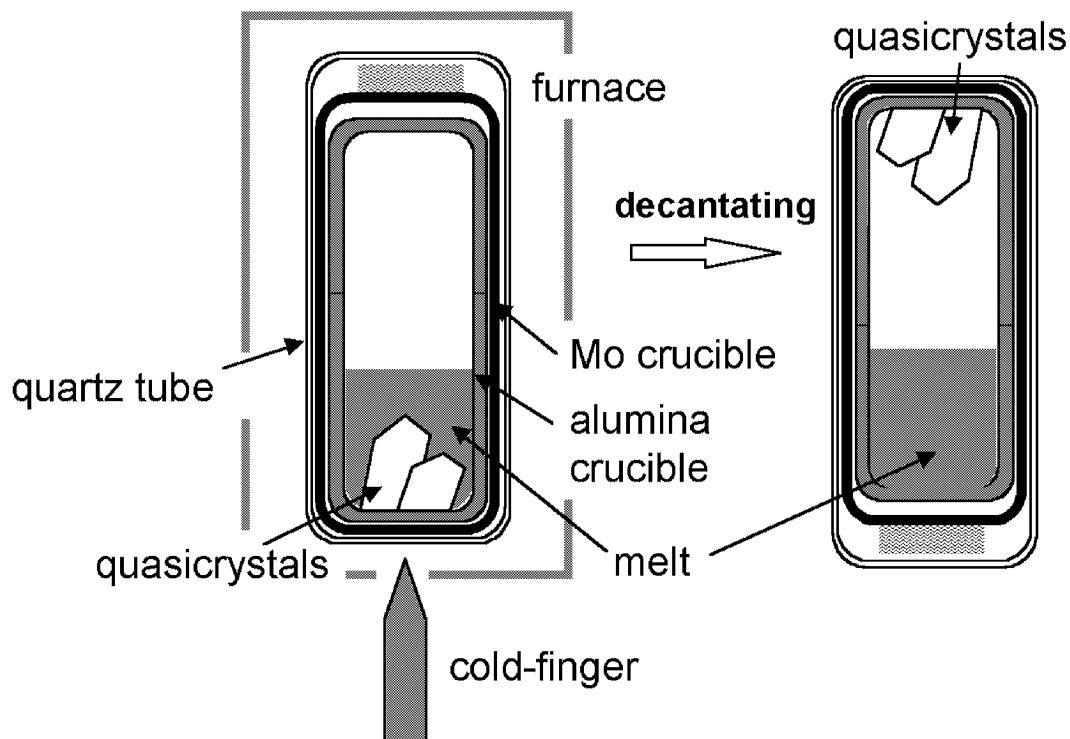


Figure 1.16: Schematic of the flux-growth technique used for the growth of Zn-Mg-Dy quasicrystals.

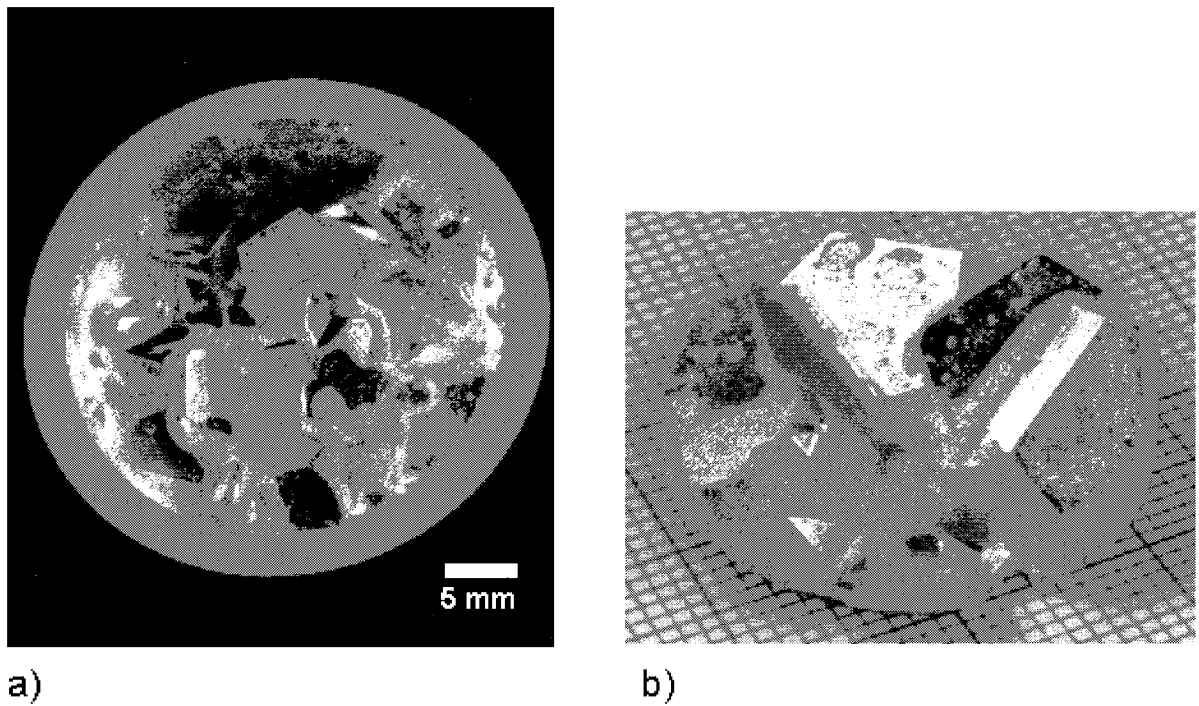


Figure 1.17: Zn-Mg-Dy quasicrystals grown with the flux-growth technique. Quasicrystals were grown directly in the molybdenum crucible (a) and via the improved procedure using an additional alumina crucible (b) (the background shows a millimetre-grid).

Figure 1.17 b shows a quasicrystal ingot that was grown via the improved procedure. The ingot could easily be taken out of the crucible and exhibits no cracks. Furthermore, the grain size was increased due to the application of the cold finger. Following this procedure the production of single quasicrystals of dodecahedral faceted morphology of up to 15 mm in diameter was enabled. The material grown was characterized metallographically and by TEM. Optical and scanning electron microscopy revealed the absence of secondary phases. The composition of the quasicrystal was determined as Zn: 62.6 %, Mg: 28.3 %, Dy: 9.1 % by means of inductively coupled plasma optical emission spectroscopy. In Figure 1.18 fundamental as well as superlattice reflections of the face-centred icosahedral phase are shown in an electron diffraction pattern along a twofold axis of the quasicrystal structure (cf. Figure 1.4). The electron diffraction patterns obtained in the transmission electron microscope show sharp spots properly aligned along the systematic rows, indicating a high structural perfection of the quasicrystals.

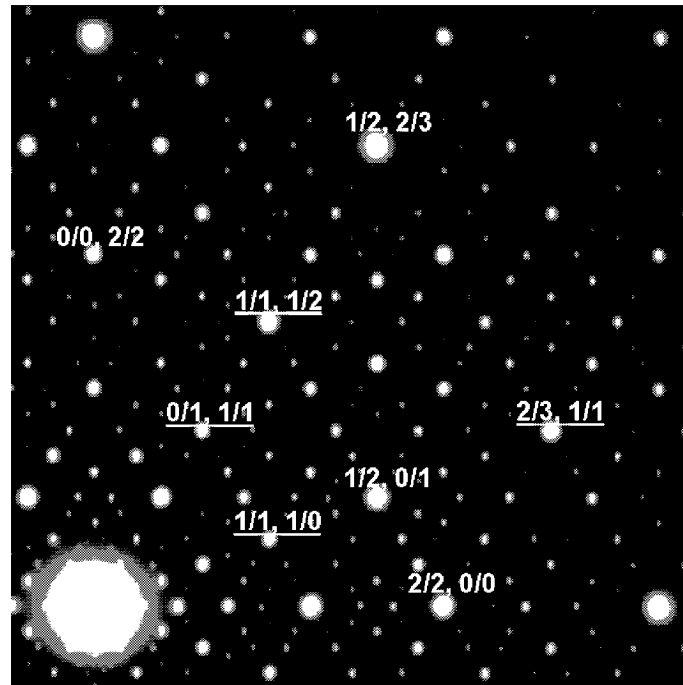


Figure 1.18: Electron diffraction pattern of a Zn-Mg-Dy quasicrystal along the twofold axis $[0/0, 0/0, 0/2]$. Diffraction spots are denoted $h/h', k/k'$. Superstructure spots are underlined.

2. Plasticity of Zn-Mg-Dy quasicrystals

2.1 Experimental procedure

For deformation experiments rectangular samples of about $3.2 \times 1.3 \times 1.3 \text{ mm}^3$ were cut by a high-precision wire saw. The long axis, along the compression direction, was oriented parallel to a twofold direction. The surfaces were carefully ground and polished in order to prevent crack formation due to surface roughness. Mechanical testing was carried out in air at temperatures between 490 and 530 °C corresponding to $T_h = 0.87$ and 0.92. A Zwick Z050 testing machine under closed loop control at constant strain rate of 10^{-6} s^{-1} and 10^{-5} s^{-1} was used to perform the plastic deformation tests (Appendix B). Thermodynamic activation parameters were determined by additional incremental tests as stress-relaxation experiments, strain-rate changes and temperature changes.

The microstructural investigations on Zn-Mg-Dy quasicrystals were performed on material subjected to different treatments. Four types of samples were investigated: (A) as-grown material, (B) heat-treated material annealed at temperatures equal to the deformation temperatures 500 and 510 °C and subsequently quenched in water, (C) material deformed up to a plastic strain of 0.2 % corresponding to the upper yield point, (D) material deformed up to a plastic strain of 1.6 % corresponding to the steady-state regime in the stress-strain curve. After plastic deformation type (C) and (D) material was rapidly unloaded and quenched in water to preserve the structural state during the deformation experiment as closely as possible. Specimens for TEM investigations were produced by standard techniques, i.e. subsequent slicing, grinding, polishing and argon-ion milling.

The microstructural investigations were carried out in JEOL 4000FX and 2000EX transmission electron microscopes operated at 200 kV. Dislocation were imaged using two-beam bright-field conditions (Appendix C). The dislocation density was determined from about ten bright-field micrographs taken at different positions of every specimen by counting the intersections of dislocations with the specimen surfaces. The dislocation density was then calculated according to

$$\rho = \frac{N}{A}, \quad (2.1)$$

where N is the number of intersections of dislocation lines with both surfaces of the specimen and A is the area of the sample region on the micrograph (Ham and Sharpe, 1961).

2.2 Results

Macroscopic plastic deformation behaviour

Figure 2.1 shows stress-strain curves for the icosahedral Zn-Mg-Dy single quasicrystals at a temperature of 500 °C and strain rates of 10^{-5} s^{-1} and 10^{-6} s^{-1} . After the upper yield point both curves exhibit a pronounced yield drop down about 60 % of the upper yield stress. At 10^{-5} s^{-1} an upper yield point of 510 MPa occurs at 1.2 % strain, followed by a yield drop down to 300 MPa. Then, up to 7.5 % strain a steady state range is found showing a constant flow-stress level of 300 MPa. The curve corresponding to the deformation at 10^{-6} s^{-1} , shows a lower

upper yield stress of 280 MPa at 1.15 % and a yield drop down to 180 MPa at 2.2 %. The vertical stress drops labelled “R” in the curves are imposed stress-relaxation tests. The interpolated courses of the stress-strain curves are plotted in the Figure by dotted lines.

Deformation tests at lower temperatures of 400 and 450 °C and a strain rate of 10^{-6} s^{-1} show brittle behaviour, i.e. fracture of the specimens is found at negligible plastic strain. Successful deformation tests were carried out in the temperature range between 490 and 530 °C at strain rates of 10^{-5} s^{-1} and 10^{-6} s^{-1} . Figure 2.2 shows the upper-yield stresses and the steady-state flow stresses determined. A monotonous decrease of the upper yield stress and the steady-state flow stress with increasing temperatures is found.

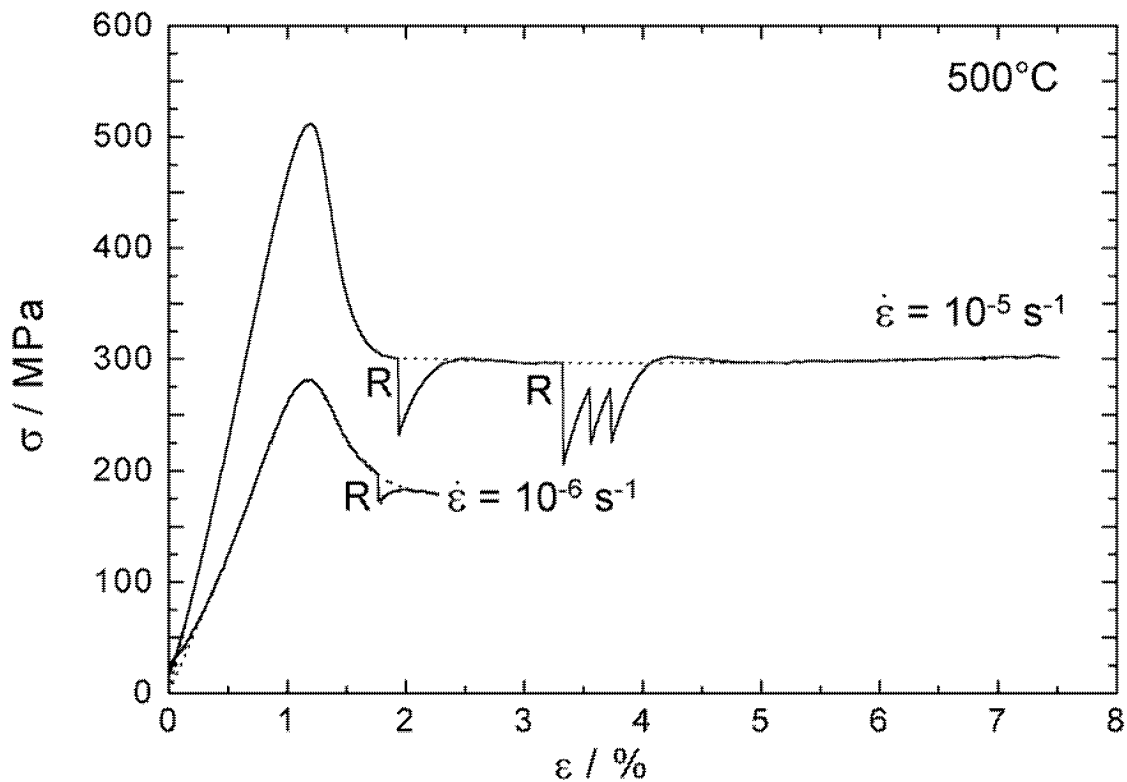


Figure 2.1: Stress-strain curves of Zn-Mg-Dy at 500 °C and strain rates of 10^{-5} and 10^{-6} s^{-1} . Vertical stress drops labelled „R“ in the curves arise from imposed stress-relaxation tests. The interpolated courses of the stress-strain curves are plotted by broken lines.

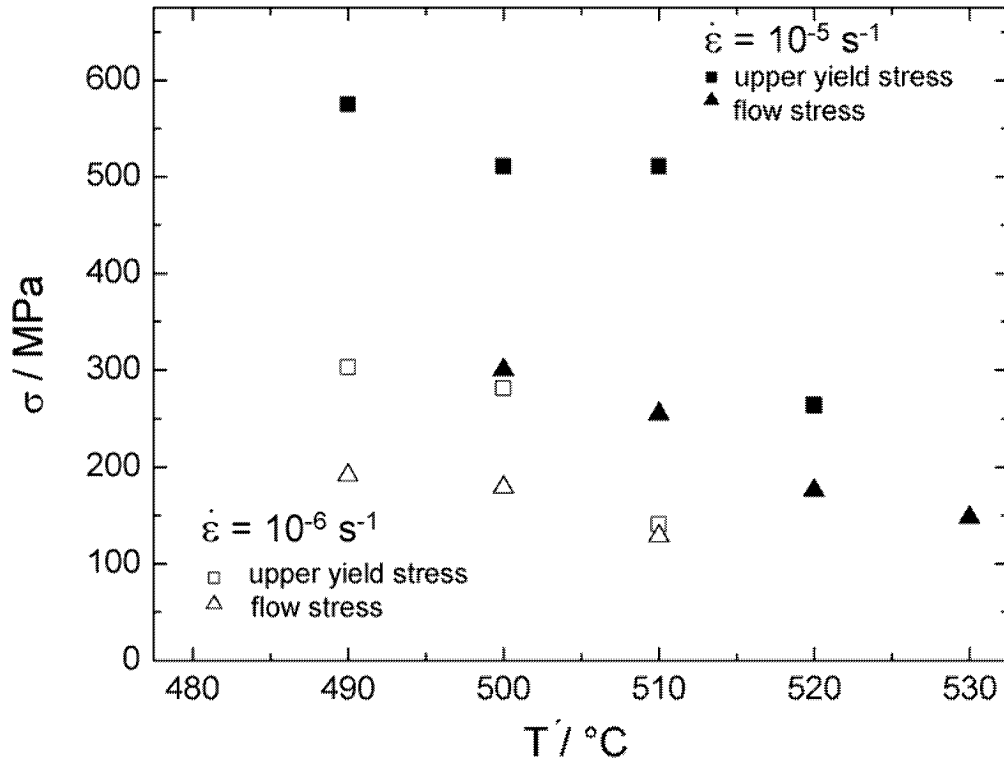


Figure 2.2: Upper yield stresses and steady-state flow stresses of Zn-Mg-Dy at $\dot{\epsilon} = 10^{-5} \text{ s}^{-1}$ and $\dot{\epsilon} = 10^{-6} \text{ s}^{-1}$ for different deformation temperatures.

Figure 2.3 shows a compilation of stress-strain curves at three different temperatures and a strain rate of 10^{-5} s^{-1} . Stress-relaxation tests, temperature changes and strain-rate changes are labelled „R“, „TC“, and „SRC“, respectively. All the curves have a number of features in common. They show a very pronounced yield drop and after yielding they reach a steady-state range showing no further changes of the stress-strain behaviour up to the highest strains of the experiments. Throughout the steady-state regime the curves show an almost constant flow stress. The lowermost curve, obtained at 520 °C, shows the typical course of a testing sequence: At a strain of 3 % a stress relaxation was carried out, after which the sample was unloaded. The temperature was increased by 10 ° and after an equilibration time of 30 min the sample was reloaded and the flow-stress level at the second temperature was determined. After unloading again the temperature was changed back to the initial temperature at which the rest of the curve was recorded. During the strain-rate change at about 7 % the strain rate was subsequently changed to $1.2 \times 10^{-5} \text{ s}^{-1}$, $0.8 \times 10^{-5} \text{ s}^{-1}$ and back to $1 \times 10^{-5} \text{ s}^{-1}$. The resulting changes of the flow stress were determined. The uppermost curve of Figure 2.3 (500 °C) was previously shown in Figure 2.1. The grey curve (510 °C) shows a yielding behaviour which exactly corresponds to that at 500 °C. In the course of this deformation test an SRC (subsequently to $1.2 \times 10^{-5} \text{ s}^{-1}$, $0.8 \times 10^{-5} \text{ s}^{-1}$ and back to $1 \times 10^{-5} \text{ s}^{-1}$) at a strain of about 3.5 % and a temperature change down to 500 °C were performed. Note that the flow stress after the temperature change exactly corresponds to that of the curve recorded at 500 °C.

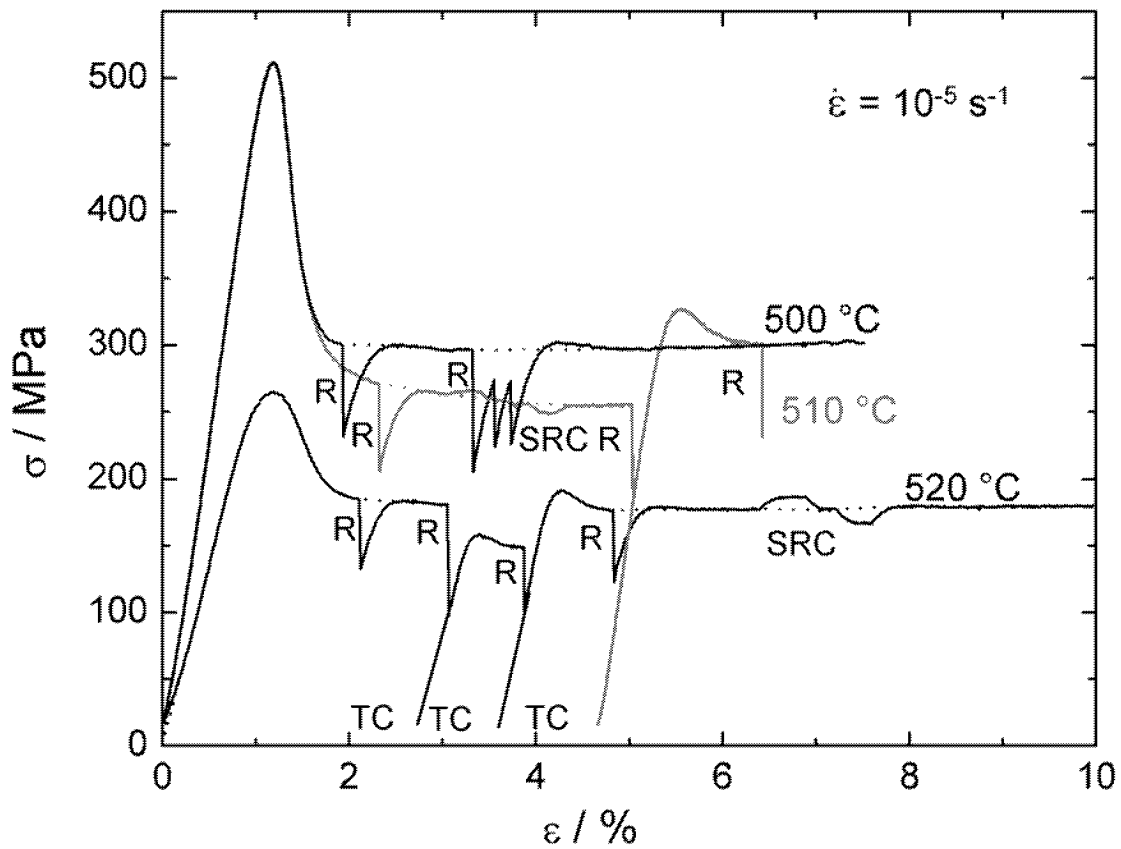


Figure 2.3: Stress-strain curves at different temperatures and a strain rate of $\dot{\epsilon} = 10^{-5} \text{ s}^{-1}$. Stress-relaxation experiments “R”, strain-rate changes “SRC” and temperature changes “TC” were performed. The interpolated courses of the stress-strain curves are plotted by broken lines.

The activation volume was evaluated from stress-relaxation experiments (Figure 2.4, full squares and circles) and strain-rate changes (Figure 2.4, open squares) according to Equations (1.20) and (1.21). The Schmid factor was chosen as $m_s = 0.5$ due to the high isotropy of the icosahedral structure. Activation volumes between 0.61 nm^3 at 145 MPa and 0.28 nm^3 at 300 MPa were determined. The data points evaluated from stress-relaxation experiments at 10^{-5} s^{-1} and 10^{-6} s^{-1} and from strain-rate changes follow one universal curve. The activation volume shows a hyperbolic stress dependence (solid line in Figure 2.4).

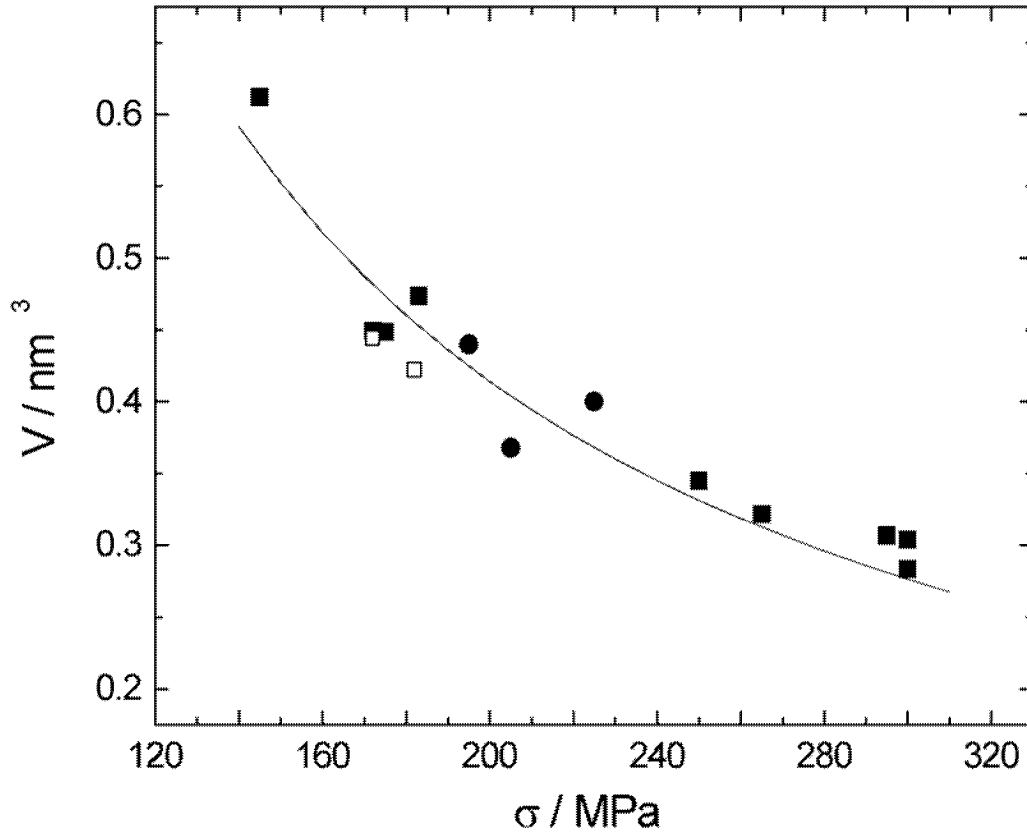


Figure 2.4: Activation volume evaluated from stress-relaxation experiments at $\dot{\epsilon} = 10^{-5} \text{ s}^{-1}$ (full squares) and $\dot{\epsilon} = 10^{-6} \text{ s}^{-1}$ (full circles) and from strain-rate changes (open squares). The hyperbolic stress dependence is shown by the solid line.

The temperature changes of 10° resulted in stress differences of 30 MPa at $T = 530^\circ\text{C}$ and 46 MPa at $T = 510^\circ\text{C}$. The corresponding values of the activation enthalpy ΔH calculated according to Equation (1.22) amount to 3.5 eV at 505°C and 3.9 eV at 525°C . Neglecting internal stresses, the work term ΔW can be calculated according to $\Delta W = m_s \sigma V$. Using the experimental activation volume the work term amounts 0.26 eV. This value is almost temperature independent in the range between 490 and 530°C .

Microstructural analysis

A microstructural analysis of Zn-Mg-Dy quasicrystals by means of TEM revealed the presence of dislocations, which were characterized by Bragg-contrast extinction experiments. The dislocation densities in the as-grown (A) and in the heat-treated (B) sample were determined as $6 \times 10^6 \text{ cm}^{-2}$ and $5 \times 10^7 \text{ cm}^{-2}$, respectively. In the deformed samples distinctly higher dislocation densities of $2.2 \times 10^8 \text{ cm}^{-2}$ and $5.6 \times 10^9 \text{ cm}^{-2}$ at strains of 0.2 (C) and 1.6 % (D) were found, respectively.

In deformed samples (C, D) and in heat-treated samples (B) microstructural analysis reveals the presence of defects showing a band-like image contrast. A bright-field Bragg-contrast image of such defects is shown in Figure 2.5.

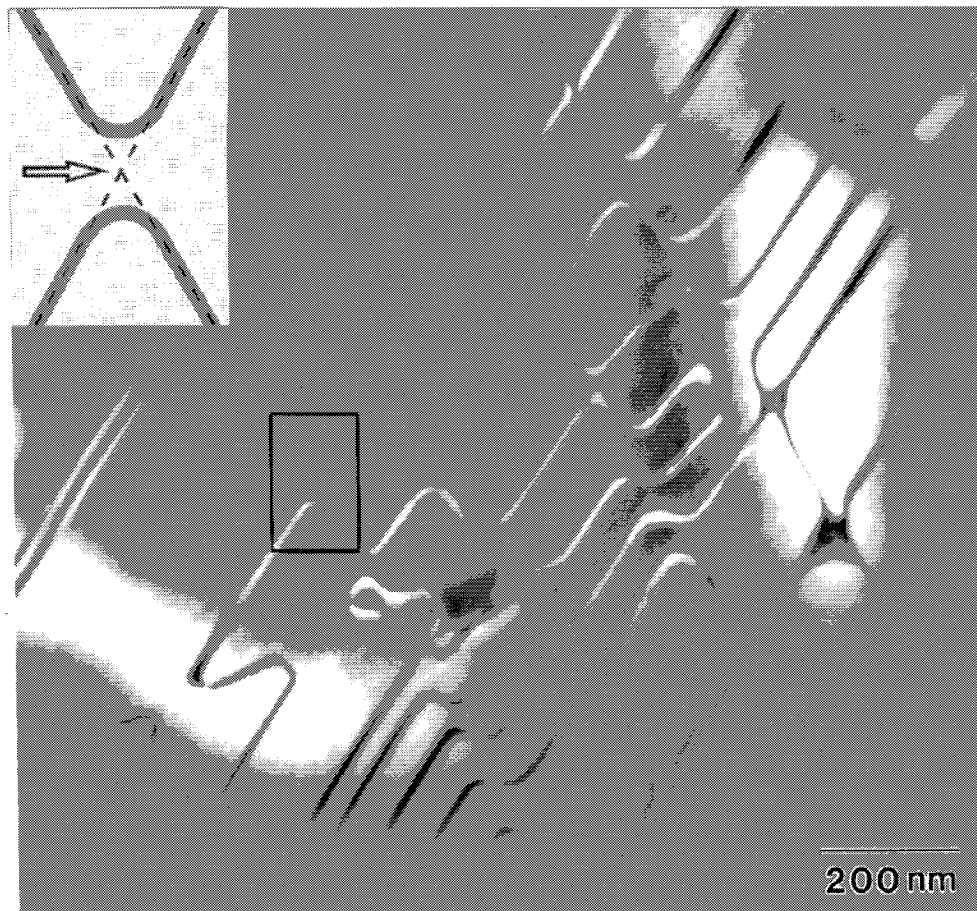


Figure 2.5: Bright-field image of planar defects in Zn-Mg-Dy quasicrystals. The inset shows a schematic of the boxed region.

The inset shows a schematic of the boxed region. Specimen-tilting experiments in the transmission electron microscope, leading to changing widths of the defect contrast, clearly show that the defects are planar. The Figure shows long and straight segments of planar defects connected by regions of strong curvature. Numerous not directly connected straight segments are, however, found to be lined up perfectly and show equal widths, indicating that these segments are apparently localized in the same plane (dashed lines in inset). At the crossings of such planes, i.e. between face-to-face oriented strongly curved regions (arrow in inset), the same contrast as in the image background is observed. Figure 2.6 shows a bright-field Bragg-contrast composite image of planar defects. Here, the defects can be continued over the strongly curved regions to straight lines of up to 5 μm length.



Figure 2.6: Bright-field transmission electron micrograph composite showing planar defects in a Zn-Mg-Dy quasicrystal.

Figure 2.7 shows a Bragg-contrast image of a heat-treated sample (B). The planar defects can be recognized as bands of uniform bright contrast against the darker background. Parts of the planar-defect contrast, showing different widths resulting from different plane orientations, are marked by thick arrows. On this micrograph dislocations can be observed (thin arrows), which show dark line contrast against the background. The planar defects are terminated by the dislocations. In the central part of the Figure, a formation similar to that shown in the inset of Figure 2.5 is seen.

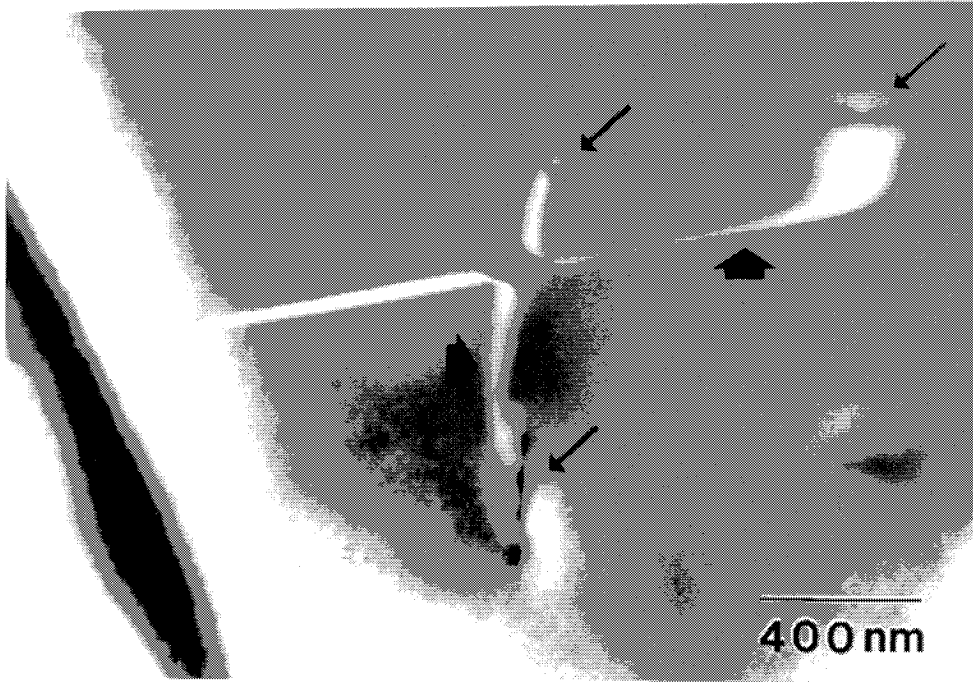


Figure 2.7: Bright-field transmission electron micrograph showing planar defects (thick arrows) terminated by dislocations (thin arrows) in a Zn-Mg-Dy quasicrystal.

Figure 2.8 shows a series of dark-field Bragg-contrast images obtained close to a twofold $[0/0\ 0/0\ 0/2]$ zone axis. In the bottom right part of the Figure, the corresponding diffraction pattern is presented. The reflections $\vec{g}_{5/1}$ to $\vec{g}_{5/5}$ used for imaging under two-beam conditions are marked with arrowheads. The indexing of the corresponding diffraction vectors according to the system of Cahn *et al.* (1986) (Equation 1.2) is given in Table 2.1.

	$h/h', k/k', l/l'$	Type	Planar defects visible
$\vec{g}_{5/1}$	(0/1, 1/1, 0/0)	s	yes
$\vec{g}_{5/2}$	(1/1, 1/2, 0/0)	s	yes
$\vec{g}_{5/3}$	(1/2, 2/3, 0/0)	f	no
$\vec{g}_{5/4}$	(2/3, 3/5, 0/0)	s	yes
$\vec{g}_{5/5}$	(2/4, 4/6, 0/0)	f	no

Table 2.1: Indices of the $\vec{g}$ -vectors used for imaging in Fig. 2.8. The spots are subdivided into fundamental spots (f) and superstructure spots (s).

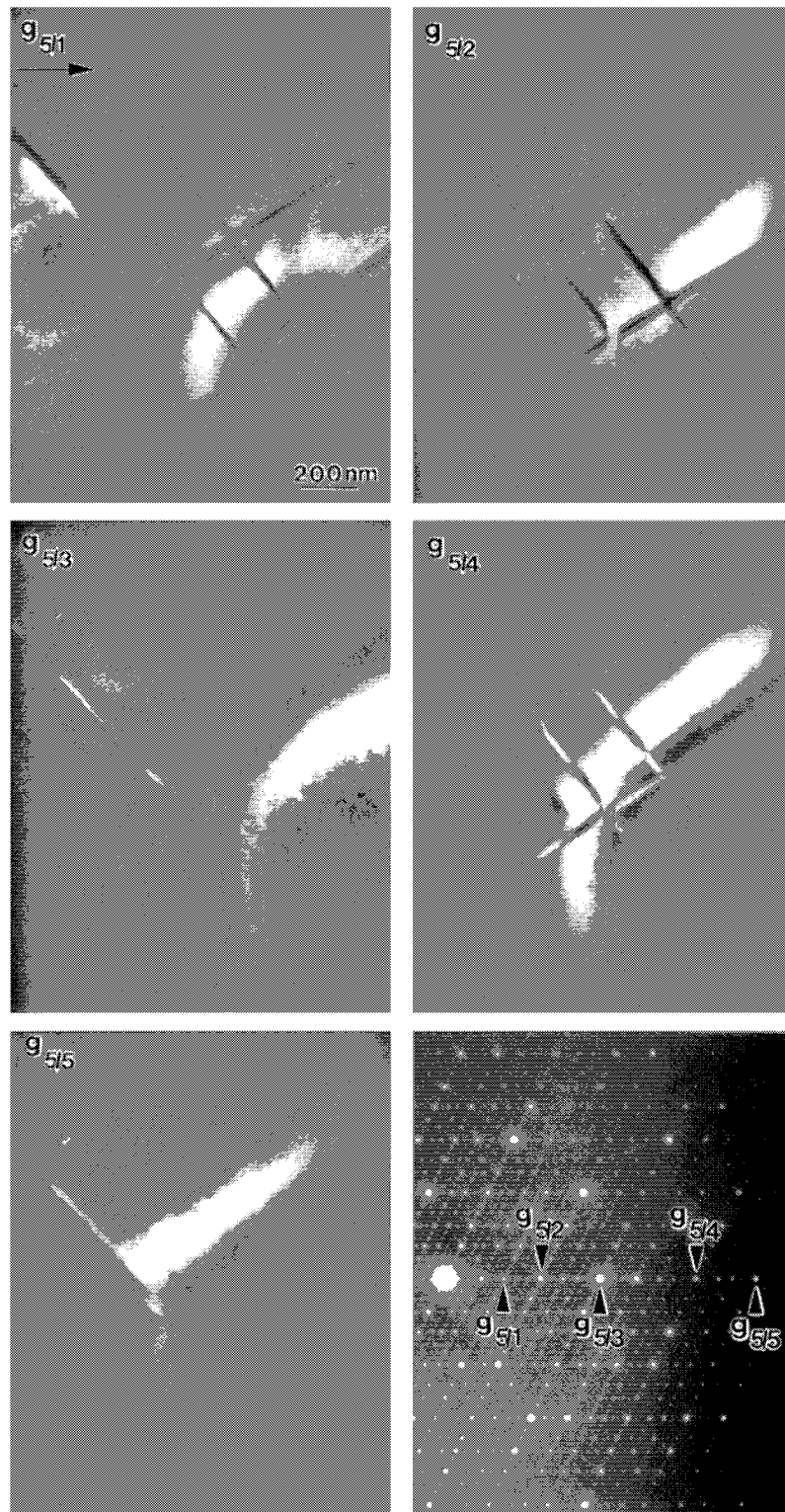


Figure 2.8: Dark-field images, using $\vec{g}_{5/1}$ to $\vec{g}_{5/5}$ for imaging. In the bottom right section the twofold diffraction pattern is shown, with arrowheads marking the corresponding reflections (indices in Tab. 2.1).

If the superstructure reflections $\vec{g}_{5/1}$, $\vec{g}_{5/2}$ and $\vec{g}_{5/4}$ are used for imaging under two-beam conditions, the planar defects are in contrast, whereas if the fundamental reflections $\vec{g}_{5/3}$ and $\vec{g}_{5/5}$ are used they are out of contrast, and only a weak residual contrast can be observed. The same conditions are found using other reflections for imaging, e.g. those in threefold or other fivefold systematic rows. Generally, if superstructure reflections are used for imaging, the planar defects are in contrast, whereas, if fundamental spots are used, the planar defects are out of contrast.

The density of planar defects depends on the treatment of the sample. While in samples (A) no planar defects could be detected, in the heat-treated sample (B) 20 % of the dislocations present in the material are connected to planar defects. Their density increases further with increasing plastic strain. In sample (C), which was deformed up to the upper yield point, 52 % of the dislocations are connected to planar defects. In sample (D), deformed up to the steady-state regime, the planar-defect density is extremely high. Since the number of defect-plane crossings is accordingly large, all segments show a strong curvature. This leads to a rather complex defect structure as shown in Figure 2.9. Here, the density of planar defects is too high to assign dislocations to the planar defects.

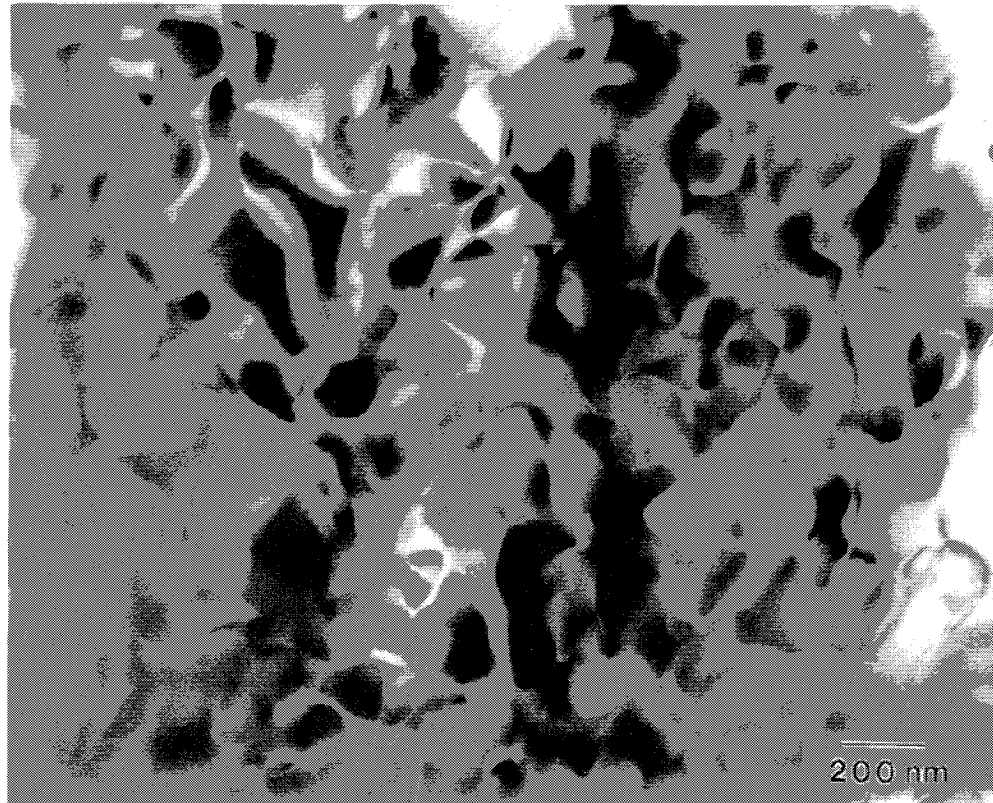


Figure 2.9: Bright-field image of a sample (D) deformed at 500 °C up to 1.6 % of plastic strain. A high density of planar defects is visible.

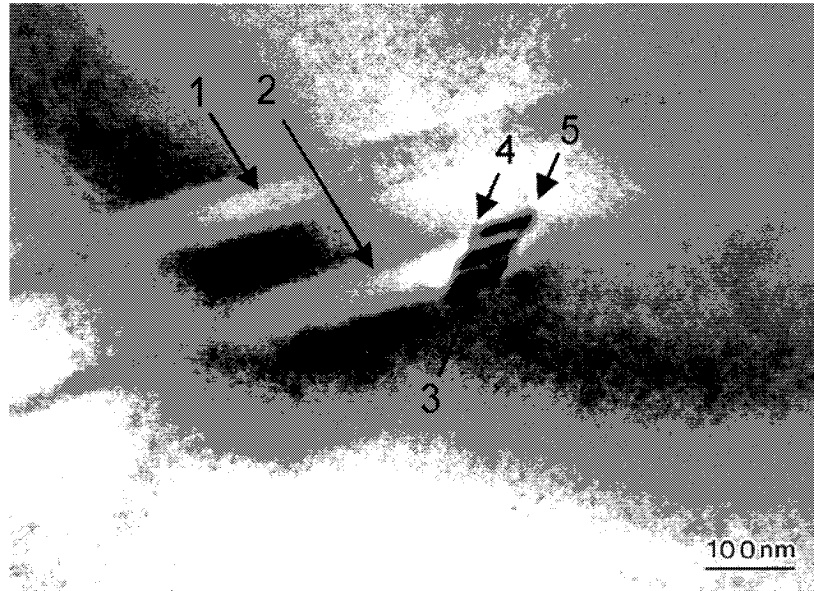


Figure 2.10: Bright-field image of planar defects showing an almost uniform image contrast (1, 2) and a planar defect (3) showing a fringe contrast between two dislocations (4, 5).

Another type of planar defects showing different imaging behaviour was found at a low density. Figure 2.10 shows two planar defects which exhibit an almost uniform image contrast over their width (arrows 1, 2) and another planar defect (arrow 3), which shows a fringe contrast. This planar defect can also be imaged using two-beam Bragg-contrast conditions with fundamental reflections contrary to the planar defects described before. The planar defect (arrow 3) is terminated by dislocations (arrow 4, 5).

Figure 2.11 a shows a two-beam dark-field micrograph using a superstructure reflection for imaging of a sample which was deformed at 510 °C to 0.2 % strain and subsequently cooled under load to a temperature of 460 °C. Dislocations can be observed (thin arrows) which trail planar defects with uniform strong contrast (thick arrow). The same sample region is imaged in Figure 2.11 b under two-beam dark-field conditions using a fundamental spot. The dislocations are visible. A fringe-like image contrast of a planar defect can be observed (thick arrow). Directly at the dislocation (thin arrow) the image contrast is strong, but it fades out with increasing distance from the dislocation.

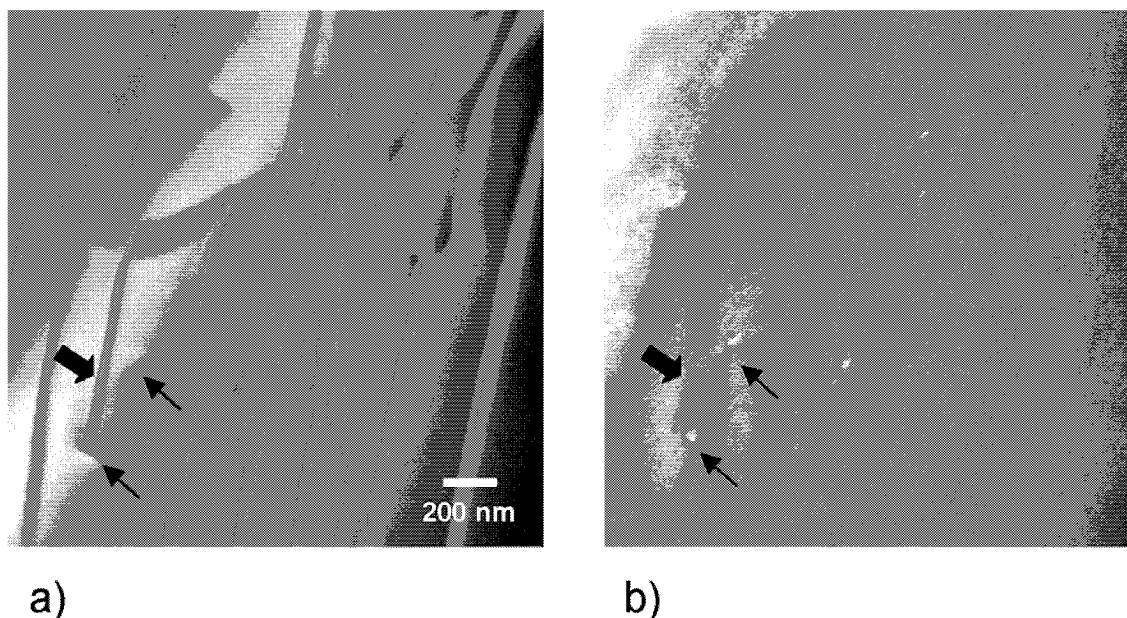


Figure 2.11: Two-beam dark-field micrograph using (a) a superstructure spot and (b) a fundamental spot of a sample which was deformed at 510 °C to 0.2 % strain and subsequently cooled under load to a temperature of 460 °C. Dislocations (thin arrows) and the location of planar defects are indicated.

2.3 Discussion

Plastic deformation experiments were performed on Zn-Mg-Dy icosahedral single quasicrystals at temperatures between 490 °C and 530 °C and strain rates of 10^{-5} and 10^{-6} s $^{-1}$. The stress-strain curves were recorded and the thermodynamic activation parameters of the deformation process were determined by performing stress-relaxation tests, strain-rate changes and temperature changes. A microstructural investigation by means of TEM was performed on plastically deformed and undeformed material. Planar defects and dislocations were observed and characterized.

The observation of an increase in dislocation density by three orders of magnitude during plastic deformation provides direct evidence that the plastic deformation process is mediated by a dislocation mechanism. A closer inspection of the experimental dislocation-density evolution will be given in Chapter 4. The material was shown to remain single quasicrystalline during deformation and the inspection of electron diffraction patterns of plastically deformed material reveal that no phase transition takes place.

Macroscopic plastic deformation behaviour

Plastic deformation of the specimens was at strain rates of 10^{-6} and 10^{-5} s $^{-1}$ possible at temperatures of 490 °C and higher. At lower temperatures brittle fracture of the samples occurs. Hence, a brittle to ductile transition exists, located between 450 and 490 °C for the range of strain rates applied in the present experiments. At elevated temperatures, i.e. in the ductile regime, the stress-strain curves show an extraordinarily strong yield drop after the upper yield stress. Stress drops of about 40 % of the maximum stress are observed, which is significantly more than for the case of icosahedral Al-Pd-Mn, for which yield drops of 10 to 15 % of the maximum stress were found (Schall *et al.* 1999). At higher strains, after the yield

drop, the stress strain curves show an almost constant flow stress level, which can be referred to as steady-state flow stress. In this deformation stage, which extends up to the highest strains of about 8 % of the present experiments, neither a significant hardening nor softening behaviour is found.

In this respect, the behaviour of icosahedral Zn-Mg-Dy differs from that of other quasicrystalline materials. All icosahedral quasicrystals on which deformation experiments have been performed to date show a softening behaviour at high strains, i.e. the flow stress continuously decreases with increasing strain. This has e.g. been observed for polycrystalline Al-Cu-Fe (Bresson and Gratias, 1993) and for several other polycrystalline alloys (Kang and Dubois, 1992), and also for single-quasicrystalline Al-Pd-Mn (Wollgarten *et al.* 1993, Feuerbacher *et al.* 1997).

For a comparison of the steady-state flow stress with that of icosahedral Al-Pd-Mn the homologous temperature T_h is considered. According to a differential temperature analysis, T_m amounts to 873 K ($T'_m = 600$ °C) for the present alloy composition, i.e. experiments were conducted in the homologous temperature range from 0.87 to 0.92. At $T_h = 0.89$ a flow stress of 300 MPa was observed. In icosahedral Al-Pd-Mn a flow stress of 320 MPa was observed at the homologous temperature 0.88 (Schall *et al.* 1999). Thus, the flow stresses of these alloys are very similar. However, at the same temperatures the upper yield stresses in Zn-Mg-Dy and Al-Pd-Mn amount to 510 MPa and 400 MPa, respectively. This large difference is due to the extraordinarily large yield drop effect in icosahedral Zn-Mg-Dy.

The activation volumes observed range from 0.61 to 0.28 nm³ depending on the applied stress. The absolute values of the activation volume as well as its stress dependence are very close to the values found for icosahedral Al-Pd-Mn (Feuerbacher *et al.* 1997). This can be taken as an indication that the plastic deformation mechanisms of these alloys are similar. The rate-controlling mechanism has been ascribed to the interaction of dislocations with elementary clusters (Feuerbacher *et al.* 1997b).

The comparison between activation enthalpy and work term shows that the latter value is much smaller. Hence, it can be concluded that dislocation movement is thermally activated. The activation enthalpy of 3.5 to 3.9 eV is smaller than the values of about 6.5 eV and 5 eV at 750 °C found by Feuerbacher *et al.* (1995), and Geyer *et al.* (2000) respectively.

Plastic deformation experiments on icosahedral Zn-Mg-RE (RE = Gd, Y) were conducted by Takeuchi *et al.* (1998) on coarse-grained material containing a second, unknown phase. These experiments were performed between 150 and 400 °C, i.e. under experimental conditions where no plastic deformation was achieved using single-quasicrystalline, single-phase samples in the present work. Takeuchi *et al.* (1998) found an activation volume smaller than 1 nm² at high stresses increasing to very large values of about 18 nm² as the stress approaches zero. They evaluated a total activation enthalpy of 1.9 eV. These values do not correspond well to the present results. However, this is most probably due to the different experimental conditions and the different compositions and qualities of the samples.

Microstructural analysis

The microstructural investigation by means of TEM on deformed and undeformed material revealed the existence of planar defects. Contrast-extinction studies of these defects were performed under various two-beam imaging conditions. It was shown that these defects are in contrast if superstructure reflections of the face-centred hyperlattice are used for imaging, and that their contrast is extinct if fundamental reflections are used. An antiphase boundary in an ordered quasicrystal is a planar defect possessing a translation vector $\vec{T} =$

$a_0[1, 0, 0, 0, 0, 0] = a_0[1/0, 0/1, 0/0]$ or a symmetric equivalent vector, i.e. leading to a hyperlattice shift of half a unit cell (Ebalard and Spaepen 1989, Devaud-Rzepski *et al.* 1989). The contrast is extinct if $\vec{G}\vec{T} = n$, where $\vec{G}$ is a six-dimensional reciprocal vector and n is an integer number (cf. Devaud-Rzepski *et al.* 1989). Hence, if $\vec{G}$ is any reciprocal vector ($h/h', k/k', l/l'$) the contrast is extinct if $h + k' = 2n$. According to Table 1.1 ($h + k'$) is even if $\vec{G}$ corresponds to a reciprocal lattice vector of the simple-cubic direct lattice, i.e. $\vec{G}$ corresponds to a fundamental reflection of the face-centred icosahedral structure (cf. Figure 1.4 a). On the other hand ($h + k'$) is odd if $\vec{G}$ corresponds to a superstructure reflection. This gives clear evidence that the planar defects imaged in the preset work are antiphase boundaries of the face-centred icosahedral structure.

Antiphase boundaries in icosahedral quasicrystals were first observed by Devaud-Rzepski *et al.* (1989) in icosahedral Al-Cu-Fe, a phase which also possesses a face-centred hyperlattice (Ebalard and Spaepen 1989). In their paper, Devaud-Rzepski *et al.* report on the formation of antiphase boundaries in rapidly solidified icosahedral Al-Cu-Fe quasicrystals, whereas the slowly cooled alloy was reported to possess a single-domain structure. This corresponds to the results of the present work, where antiphase boundaries were found in the heat-treated and quenched samples of type (B) but not in the slowly cooled samples (A).

Besides the increasing density of dislocations as a result of plastic deformation, the density of antiphase boundaries is also observed to increase strongly with increasing plastic strain. A detailed investigation on the evolution of the density of antiphase boundaries is presented in Chapter 4. Furthermore, higher percentages of dislocations are attached to antiphase boundaries in deformed samples (C) than in undeformed samples (B). These facts strongly indicate that the antiphase boundaries are introduced into the structure by moving dislocations during plastic deformation. In terms of the six-dimensional hyperlattice, this observation can be understood as a result of the movement of hyperlattice partials, the Burgers vectors of which do not correspond to a translation vector of the six-dimensional lattice. In the highly ordered face-centred hyperlattice, dislocations with Burgers vectors corresponding to translation vectors of the six-dimensional lattice would be hyperlattice superdislocations, the projection of which into physical space leads to energetically unfavourably large Burgers-vector magnitudes (Appendix D). Splitting into hyperlattice partials, a mechanism to be seen in analogy to superpartial splitting in ordered FCC-alloys, leads to dislocations with energetically more favourable shorter Burgers vectors, which, however, causes the formation of antiphase boundaries. Figure 2.12 illustrates a superdislocation and split superpartials in a two-dimensional ordered structure (cf. Hirth and Lothe 1982). The unit cell of the structure which consists of two types of atoms (filled and open circles) is indicated as dotted square. In Figure 2.12 a a superdislocation is introduced into the structure. The Burgers vector modulus of the superdislocation corresponds to the lattice parameter of the structure. Figure 2.12 b shows two superpartial dislocations which are connected by an antiphase boundary (dashed line). The Burgers vector modulus of a superpartial dislocation is equal to half the lattice parameter of the structure.

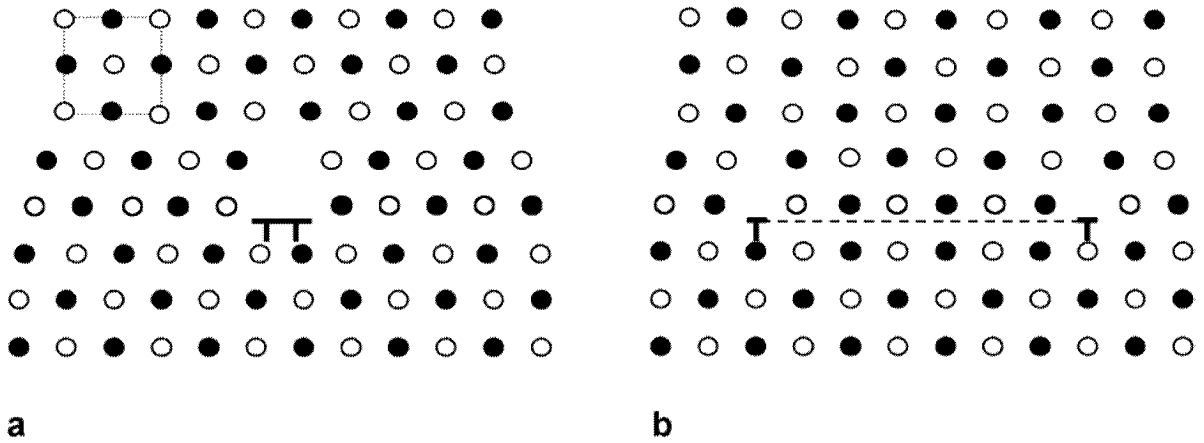


Figure 2.12: (a) Superdislocation and (b) two superpartial dislocations in an ordered two-dimensional structure. The unit cell of the structure is indicated as dotted square. The superpartial dislocations are connected by an antiphase boundary (dashed line).

In an ordered face-centred icosahedral structure, there are only two types of domains and one type of antiphase boundary (Ebalard and Spaepen 1989) and therefore stable networks of antiphase boundaries do not exist. It can be shown that crossings of antiphase boundaries lead to their annihilation at the line of intersection (Hirth and Lothe 1982). This is illustrated schematically in Figure 2.13 for a two-dimensional ordered structure.

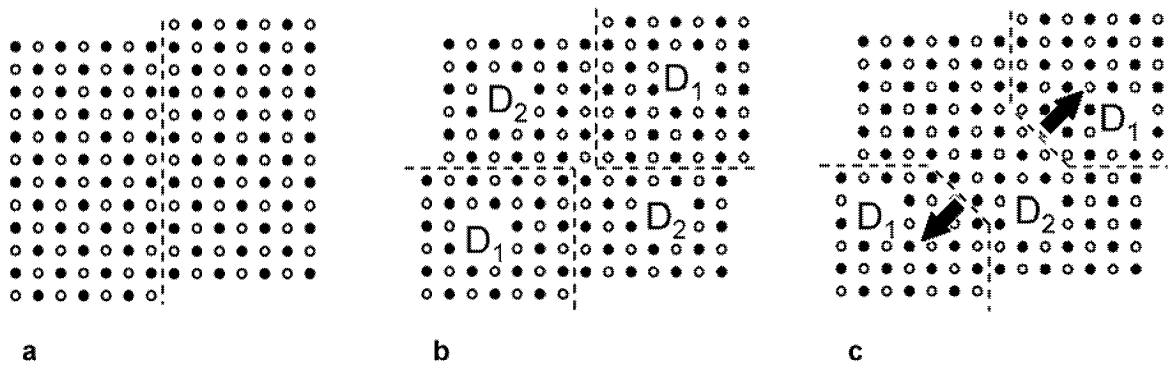


Figure 2.13: (a) Schematic of a two-dimensional ordered lattice, including a vertically aligned antiphase boundary (dashed line). After introducing an additional horizontal antiphase boundary (b), the lattice is separated into two types of domains (denoted as D_1 and D_2). Movement of the antiphase boundaries in the direction of the arrows (c) leads to a reduction of the total energy.

Figure 2.13 a shows an antiphase boundary (dashed line) that was created by a superpartial dislocation which has moved vertically through the ordered structure. In Figure 2.13 b the structure was horizontally crossed by a second superpartial dislocation creating another antiphase boundary in horizontal orientation. At the crossing point of the antiphase boundaries, the original structure is recovered, leading to the presence of three domains of the two types D_1 and D_2 . An antiphase boundary is associated with an interfacial energy (cf. Hirth and Lothe 1982). In order to decrease the energy, the fault area is reduced by diffusive

rearrangement of atoms, leading to a situation as shown in Figure 2.13 c. The further increase of the radius of the curved segments, i.e. further movement of the antiphase boundaries in the direction of the arrows in Figure 2.13 c, leads to proceeding reduction of the total energy. Therefore, the arrangement of antiphase boundaries is not stable. The experimentally observed arrangements of antiphase boundaries at the crossings of planes of dislocation motion as shown in Figures 2.5, 2.6, and 2.7 correspond to the situation shown in Figure 2.13 c. This scenario of the formation of the antiphase boundary crossing arrangement observed is supported by the additional study of a sample heated for 2 h at 500 °C, which, in contrast to samples of type (B), was not rapidly quenched but slowly cooled at a rate of 300 °C h⁻¹. The microstructural investigation of these samples (Fig. 2.14) shows that the shape of the antiphase boundaries is less straight compared with those in quenched samples (Figs. 2.5, 2.6, and 2.7). Figure 2.14 shows two crossings of antiphase boundaries (see schematic in inset). In contrast to the rapidly quenched material (B), the distance from the antiphase boundaries to the intersecting lines of the glide planes is much higher. Due to the slower cooling rate, the material is subjected to high temperatures for a longer time. This leads to a further progression of the antiphase boundary arrangement towards a state of lower total energy. The diffusion controlled mechanism of domain ripening is known as Ostwald ripening (Lifshitz and Slyozhov 1961, Wagner 1961).

Besides the antiphase boundaries another type of planar defects was found at a low density (Figure 2.10), which shows a strong fringe contrast and can be imaged using fundamental spots. Due to the imaging condition this kind of planar defect can be referred to as stacking fault (SF) (Williams and Carter 1996). The image contrast of the SF is terminated by dislocations on both sides of the defect. However, in samples cooled under load a weak fringe-like image contrast of a planar defect was imaged using a fundamental spot (Figure 2.11 b), which is only terminated at one side by a dislocation. With increasing distance from the dislocation the image contrast of the planar defect fades out. In Zn-Mg-Dy samples that were unloaded at high temperature and quenched, these faults were not observed.

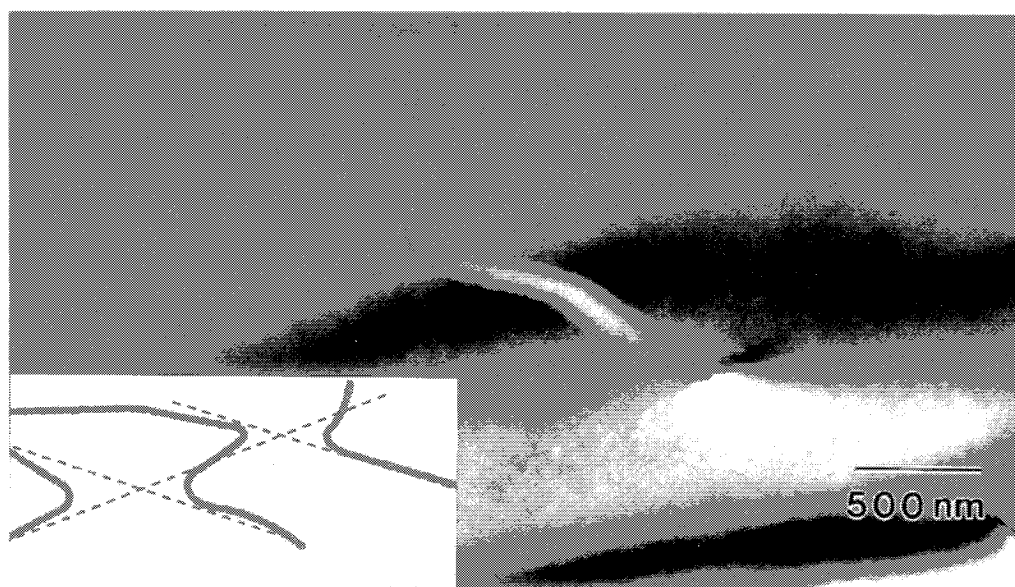


Figure 2.14: Bright-field image of a heat-treated and slowly cooled sample. The antiphase boundaries are less straight due to longer subjection to higher temperatures. The dashed lines in the inset show the plane of motion of the dislocations.

In in-situ straining experiments in a transmission electron microscope by Feuerbacher *et al.* (2003c) moving dislocations were observed in Al-Pd-Mn, which trail planar defects possessing a fringe-like contrast. The image contrast disappears shortly after the dislocation has passed. In samples rapidly cooled in the microscope, image contrast showing similar behaviour is observed, i.e. fringe-like contrast of a planar defect which fades out with increasing distance from the dislocation. Feuerbacher *et al.* interpreted their observation in terms of the creation of a phason fault by a moving dislocation, which subsequently dissolves rapidly by the diffusion of phasons into the surrounding material. The observations in the present work is interpreted analogously. This interpretation is supported by the fact, that this kind of planar faults was only observed in material deformed at low temperatures. In material that was deformed and unloaded at high temperatures, diffusion leads to rapid dissolution of the phason defect so that these defects cannot be observed experimentally.

3. Lattice fringe analysis of planar defects

Antiphase boundaries of the face-centred icosahedral structure were identified in Zn-Mg-Dy samples subjected to heat treatments and/or plastic deformations. Besides the antiphase boundaries another type of planar defects was found at a low density, which was referred to as stacking fault. In the following Chapter both kinds of planar defects are studied by means of lattice-fringe images obtained by TEM (Appendix C).

3.1 Experimental procedure

For the study of antiphase boundaries and stacking faults in Zn-Mg-Dy, experimental conditions for the specimen preparation have to be selected carefully. In heat-treated and quenched samples the densities of antiphase boundaries are moderate, so that a single antiphase boundary can be analysed conveniently. They were frequently found to be straightly lined up perpendicular to fivefold planes (Fig. 3.1).

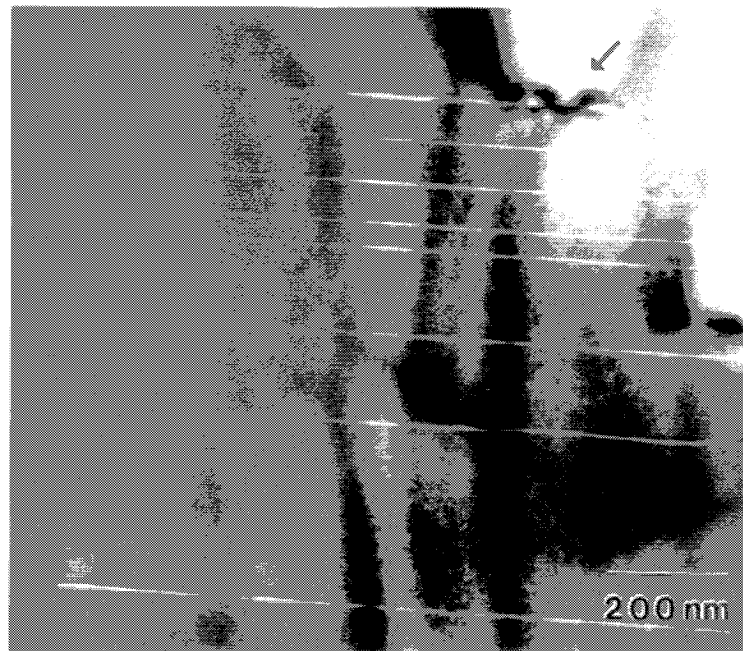


Figure 3.1: Bright-field image of antiphase boundaries arranged parallel to a fivefold plane, viewed in an edge-on orientation. A dislocation terminating a planar defect is marked by an arrow.

The investigation of a single antiphase boundary in a deformed sample is difficult due to the high density of antiphase boundaries and their strong curvature (Figure 2.9 and Heggen *et al.* 2001). Therefore the heat-treated and quenched samples are most suitable for a lattice fringe analysis of a single antiphase boundary in edge-on orientation. The sample used for imaging of the antiphase boundary in the present study was heat-treated for 7 h at 510 °C and subsequently quenched in water.

Stacking faults were exclusively observed in plastically deformed samples. In samples rapidly unloaded and quenched after a deformation test, these defects are present at a very low density. The extension of a stacking fault between two dislocations is of the order of

100 nm (cf. Figure 2.10). The sample for the study of stacking faults was treated by subsequent deformation to the upper-yield stress, cooling under load from 510 °C to 450 °C, rapid unloading and quenching. In this sample the density and the average length of stacking faults is higher than in the conventionally deformed samples.

Both samples, the heat-treated and quenched sample and the sample which was cooled under load, were prepared for TEM by slicing, grinding, polishing and argon-ion milling. The lattice fringe analysis was carried out in a JEOL 4000EX transmission electron microscope operated at 400 kV. The lattice-fringe analysis was performed using the software Digital Micrograph by Gatan Inc. In a first step the digitised experimental images were numerically Fourier transformed (Appendix E) and the corresponding power spectrum was displayed (cf. Fig. 3.2 b). A circular aperture was set to a choice of Fourier components and the corresponding part of the complex spectrum was back transformed.

3.2 Results

Figure 3.2 a shows a lattice-fringe image of an antiphase boundary in a Zn-Mg-Dy quasicrystal. The specimen is oriented with a twofold axis along the electron beam. The plane normal of the antiphase boundary is parallel to a fivefold direction and perpendicular to the direction of the electron beam. The location of the antiphase boundary is indicated by arrowheads. Viewed under a grazing angle along the direction indicated by an arrow the lattice-plane shifts induced by the antiphase boundary are clearly visible. The power spectrum of Figure 3.2 a is given in Figure 3.2 b. The Fourier components that were used for the inverse transformation are labelled and their indexing is given in Table 3.1. Reciprocal lattice vectors corresponding to reflections of systematic rows parallel to twofold-, threefold-, and fivefold-directions are distinguished by the first index of the reciprocal lattice vectors (e.g. $\vec{g}_{2/x}$, $\vec{g}_{3/x}$, and $\vec{g}_{5/x}$). Note that the reciprocal lattice vectors $\vec{g}_{2/1}$, $\vec{g}_{3/2}$, and $\vec{g}_{5/3}$ refer to fundamental and $\vec{g}_{3/1}$, $\vec{g}_{5/1}$, $\vec{g}_{5/2}$ to superlattice reflections of the face-centred hyperlattice of the quasicrystal.

The corresponding inverse Fourier transforms are shown in Figure 3.3, the labels correspond to those in Figure 3.2 b. The images of Figure 3.3 show only the enlarged central part of the inverse-Fourier-transformed images. It is clearly visible that the lattice fringes show no shifts using the fundamental spots whereas using the superstructure spots a shift of π is visible at the location of the antiphase boundary, i.e. the fringes on either side of the antiphase boundary are shifted exactly by half a period of the fringe pattern. The results are compiled in Table 3.1. The results of additional lattice-fringe analyses not shown in Figure 3.3 are given in brackets.

Figure 3.4 a shows a lattice-fringe picture of a stacking fault. As in Figure 3.2 a the TEM-specimen is oriented along a twofold axis and the plane normal of the stacking fault is parallel to a fivefold direction and perpendicular to the incident electron beam. The corresponding power spectrum is given in Figure 3.4 b. The Fourier components that were used for the inverse transformation are labelled and their indexing is given in Table 3.1. The inverse Fourier transforms are presented in Figure 3.5. Using $\vec{g}_{2/4}$ the lattice fringe image is not shifted. A weak distortion is noticeable using $\vec{g}_{2/3}$, while using $\vec{g}_{2/2}$, $\vec{g}_{5/1}$, $\vec{g}_{5/2}$, and $\vec{g}_{5/3}$ lattice fringe shifts at the location of the stacking fault are clearly visible.

Label	$h/h', k/k', l/l'$	Type	Shifts of fringes at an antiphase boundary	Shifts of fringes at a stacking fault
$\vec{g}_{2/1}$	(2/2, 0/0, 0/0)	f	no	
$\vec{g}_{2/2}$	(0/0, 2/2, 0/0)	f	(no)	yes
$\vec{g}_{2/3}$	(0/0, 2/4, 0/0)	f	(no)	yes
$\vec{g}_{2/4}$	(2/0, 0/0, 0/0)	f	(no)	no
$\vec{g}_{3/1}$	($\bar{1}/\bar{1}$, 1/0, 0/0)	s	yes	
$\vec{g}_{3/2}$	($\bar{1}/\bar{2}$, 0/1, 0/0)	f	no	
$\vec{g}_{5/1}$	(0/1, 1/1, 0/0)	s	yes	yes
$\vec{g}_{5/2}$	(1/1, 1/2, 0/0)	s	yes	yes
$\vec{g}_{5/3}$	(1/2, 2/3, 0/0)	f	no	yes

Table 3.1: Results of the inverse Fourier transformation analysis. f: fundamental reflection, s: super-structure reflection. The results of additional lattice-fringe analyses not shown in Figure 3.3 are given in brackets.

3.3 Discussion

The Fourier-filtered images of an antiphase boundary (Fig. 3.3) clearly show a shift of the lattice fringes if Fourier components corresponding to superstructure spots are used for the back transformation, while if Fourier components corresponding to fundamental spots are used the fringes show no shifts. Using Fourier components corresponding to superstructure spots a fringe shift of half the fringe periodicity is observed. These observations are characteristic for antiphase boundaries in an ordered face-centred lattice possessing no additional lattice distortion (cf. Williams and Carter 1996). The antiphase boundary shows no noticeable thickness, i.e. no extension along its normal direction. A layer of disordered material at the interface of two domains (cf. Leroux *et al.* 1990) is not recognizable. Furthermore, the antiphase boundary appears perfect in the sense that there is no additional lattice shift in the fundamental lattice, as is has been observed for antiphase boundaries in some materials e.g. in Ga-As (Rasmussen *et al.* 1991).

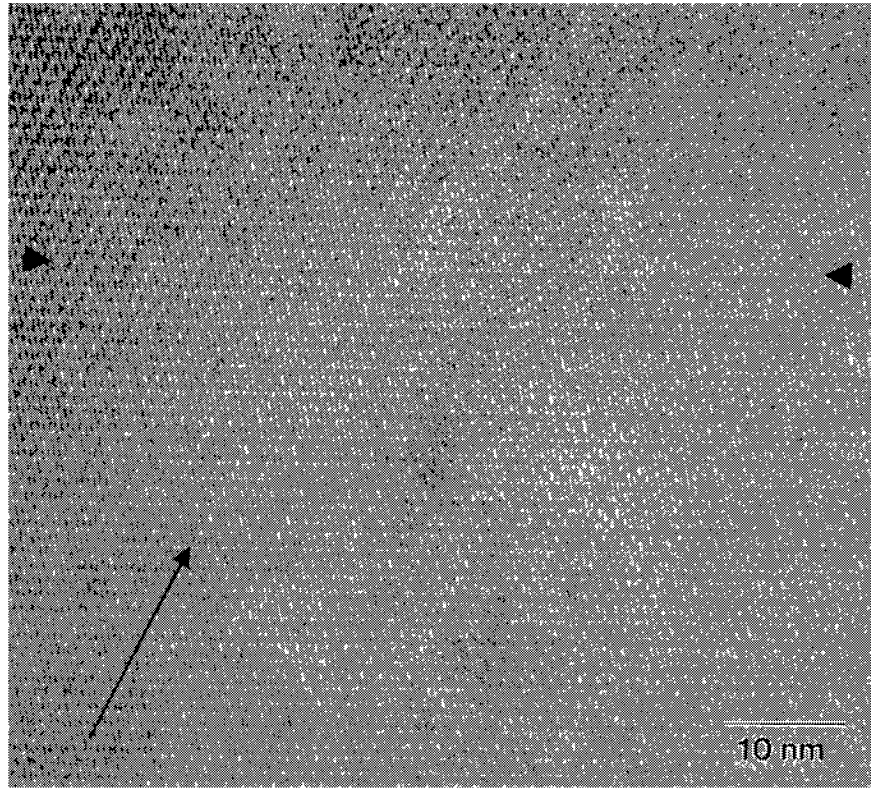
Contrary to the antiphase boundary the inverse-Fourier-transformed images of the stacking fault (Figure 3.5) show lattice-fringe shifts using Fourier components corresponding to fundamental spots as well. These observations clearly indicate that two different kinds of planar faults are found in Zn-Mg-Dy quasicrystals. Besides antiphase boundaries that possess a π -shift of the superlattice planes, stacking faults were found that create shifts of various amounts in the fundamental lattice.

In plastically deformed icosahedral Al-Pd-Mn quasicrystals stacking faults were characterized by Wang *et al.* (1998). The displacement-fields of the stacking faults were

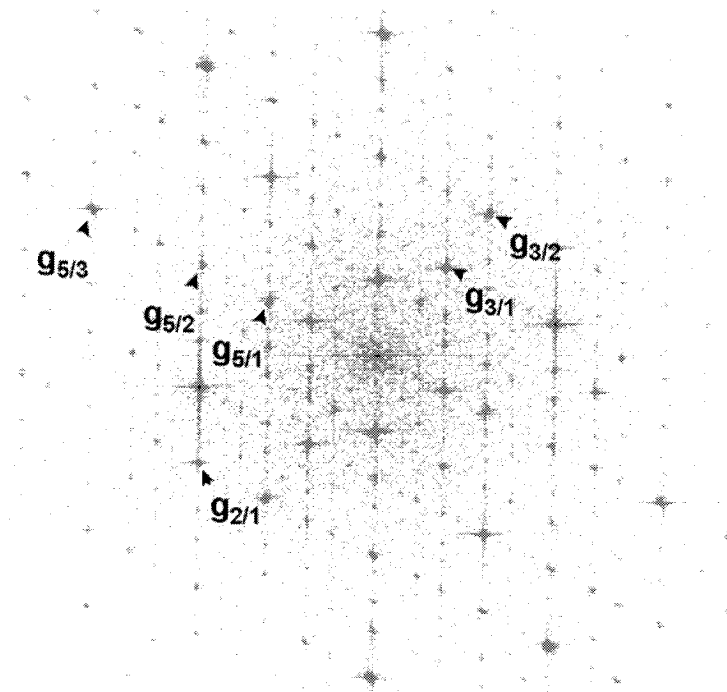
3. Lattice fringe analysis of planar defects

determined to be parallel to their plane normals. In contrast to the present investigation, where only fivefold planar-defect normals were observed, Wang *et al.* observed twofold plane normals as well. A lattice-fringe analysis revealed that these defects were not conventional planar faults. The stacking faults were found to be broadened, forming wavyly bounded stacking fault platelets of 2.5 to 10 nm thickness. This observation was interpreted in terms of moving dislocations in quasicrystalline materials leaving phason-type stacking faults behind which broaden and then disappear owing to intense diffusion at high temperatures. In the present investigation these features were not found for the antiphase boundaries and the stacking faults investigated in icosahedral Zn-Mg-Dy. All defects investigated were found to be very straight and their thickness was determined to be below 1.5 nm.

The results of the lattice fringe investigations confirm the results of the bright-field TEM investigations presented in Chapter 2 about the occurrence of antiphase boundaries and stacking faults in icosahedral Zn-Mg-Dy quasicrystals. Particularly, antiphase boundaries show no additional lattice shift in the fundamental lattice.



a)



b)

Figure 3.2: (a) Lattice fringe image of an antiphase boundary (location is indicated by arrowheads). The antiphase boundary can be recognized viewing under a grazing angle along the direction indicated by an arrow. (b) Corresponding Fourier transform. The indexing is given in Table 3.1.

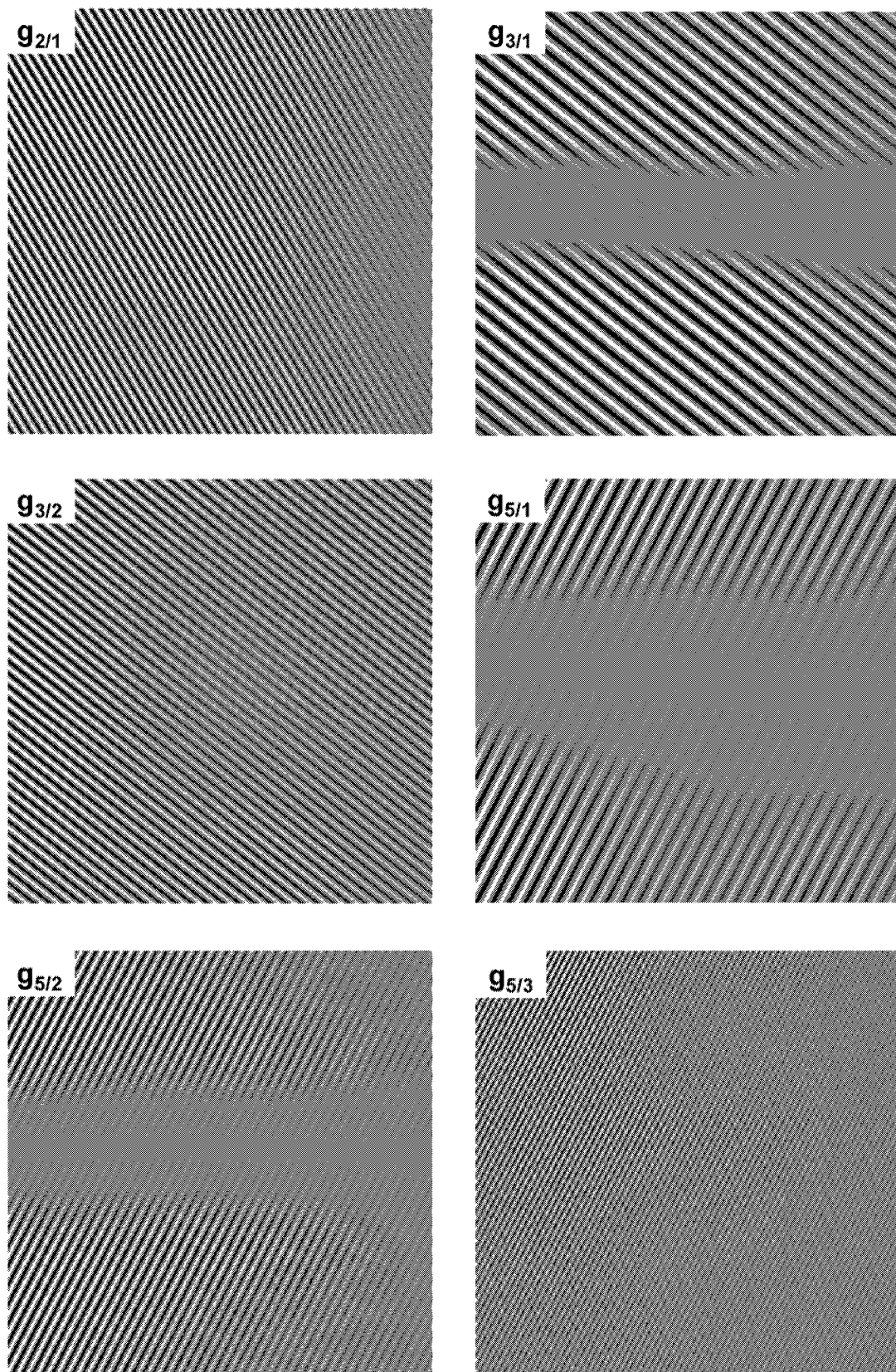
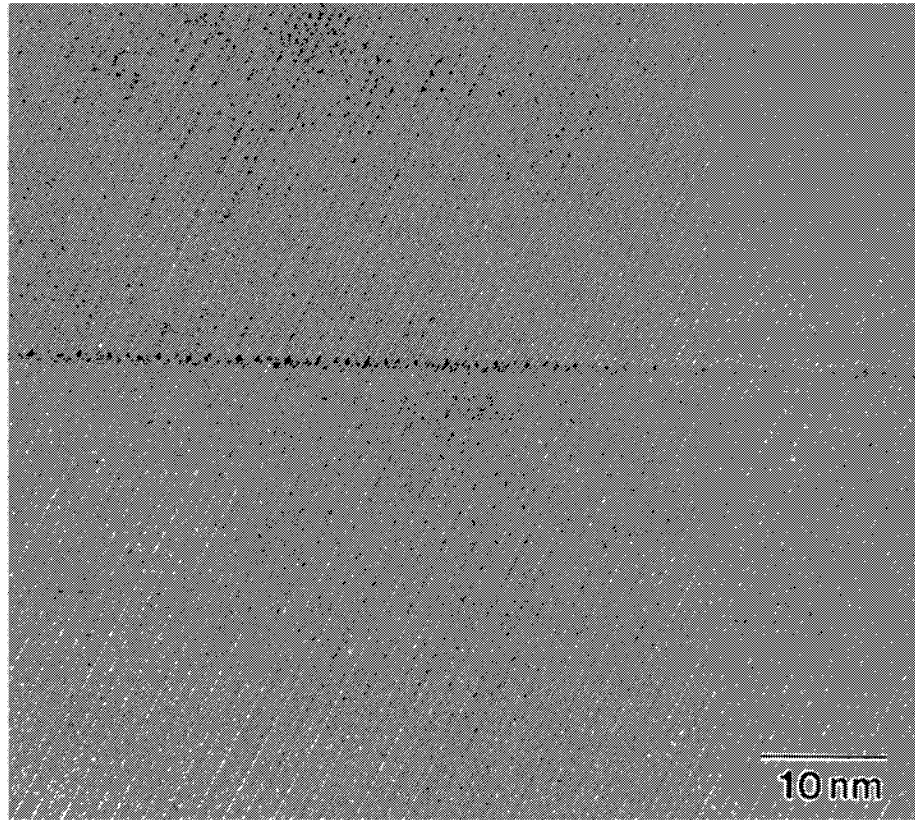
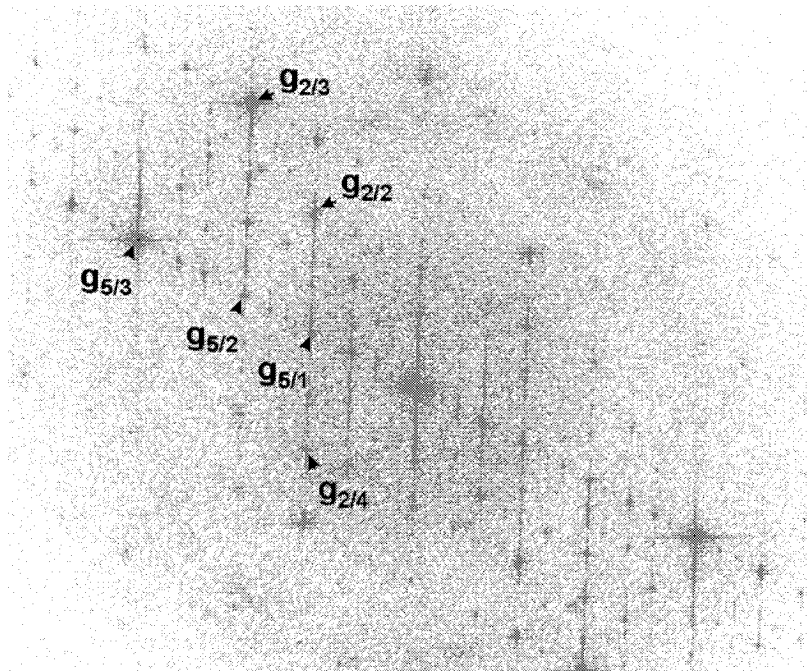


Figure 3.3: Inverse Fourier transforms of Figure 3.2 a containing an antiphase boundary. The labels correspond to the indexing in Figure 3.2 b.



a)



b)

Figure 3.4: (a) Lattice fringe image of a stacking fault. (b) Corresponding Fourier transform. The indexing is given in Table 3.1.

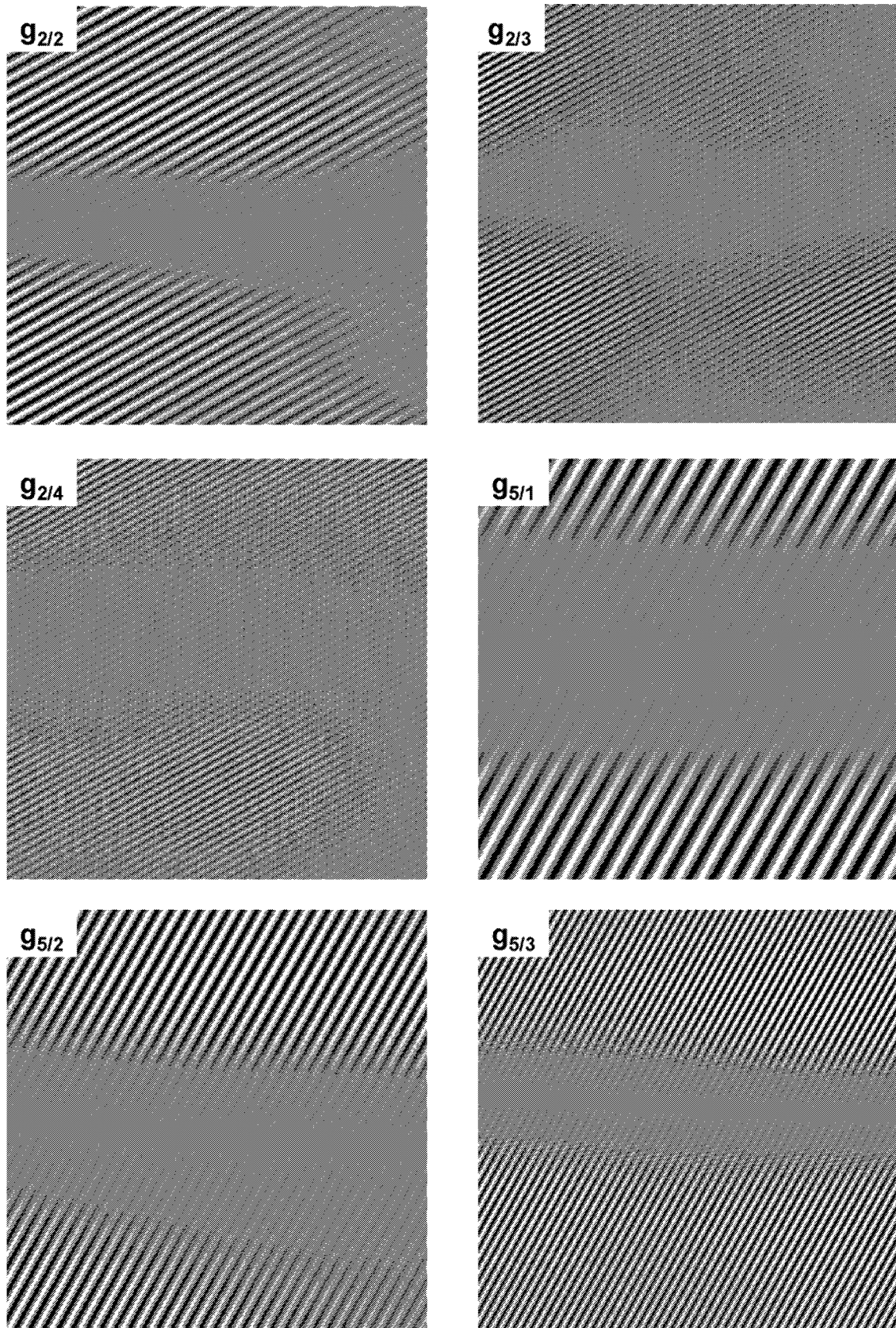


Figure 3.5: Inverse Fourier transforms of Figure 3.4 a containing a stacking fault.

4. Analysis of dislocation motion

Antiphase boundaries in Zn-Mg-Dy quasicrystals were shown to be generated during plastic deformation by the motion of dislocations. Hence, the observation of antiphase boundaries allows the direct identification of the planes of dislocation motion. Together with the determination of the Burgers vector of the dislocation, the unambiguous determination of the mode of dislocation motion (glide vs. climb) is possible. A detailed microstructural investigation of antiphase boundaries and the dislocations attached to them is described in this Chapter.

4.1 Experimental procedure

Zn-Mg-Dy samples were plastically deformed as described in Chapter 2. The samples used for dislocation- and antiphase boundary-density determination (Figure 4.1 a, b) were unloaded at a specified amount of plastic strain and subsequently quenched on a cold metal plate to conserve the microstructural state which is present in the material during plastic deformation. For a detailed microstructural analysis of planes of antiphase boundaries and Burgers vectors of dislocations, additional samples cooled under load from 520 to 450 °C and subsequently quenched on a cold metal plate were prepared. Subsequently, the samples were prepared for TEM. The dislocation density was determined by counting the number of intersections of dislocations with the specimen surfaces on bright-field images and calculated according to Equation (2.1). The density of antiphase boundaries was determined by counting the number of intersections of antiphase boundaries with a given line pattern (Underwood, 1970). The density is given by

$$\rho_{APB} = \frac{P}{L}. \quad (4.1)$$

P represents the number of intersections and L is the total length of line elements of the line pattern. For the present investigation a line pattern consisting of concentric circles was used in order to get direction-independent results.

4.2 Results

Five samples were deformed at a constant strain rate of 10^{-5} s^{-1} and at a temperature of 520 °C to different amounts of plastic strain ε_{plast} . In Figure 4.1 a, the dislocation density of the five samples is plotted against plastic strain. Up to $\varepsilon_{plast} = 4 \%$ the dislocation density strongly increases with plastic strain. At $\varepsilon_{plast} = 8.5 \%$ it drops to about 60 % of the maximum value. Figure 4.1 b shows the density of the antiphase boundaries as a function of ε_{plast} . Here a maximum value of about 10^5 cm^{-1} is reached at a plastic strain of 1.06 %. At $\varepsilon_{plast} = 8.5 \%$ the density of the antiphase boundaries drops to about 75 % of the maximum value. Since the density of antiphase boundaries is already high at low plastic strains, the microstructural analysis of the plane directions and the Burgers-vector directions of dislocations attached to the antiphase boundaries was limited to samples deformed up to plastic strains of 0.13 % and 0.21 %.

In Figure 4.2 a, the orientation of the plane normals of the antiphase boundaries with respect to the compression direction is presented in the upper left part of a stereographic

4. Analysis of dislocation motion

projection of the icosahedral point group. The twofold compression direction is indicated (C) and a 45° -cone around the compression direction is plotted as a broken line. The number of symmetrically equivalent plane normals observed is denoted in the corresponding symbol of the quasicrystallographic direction.

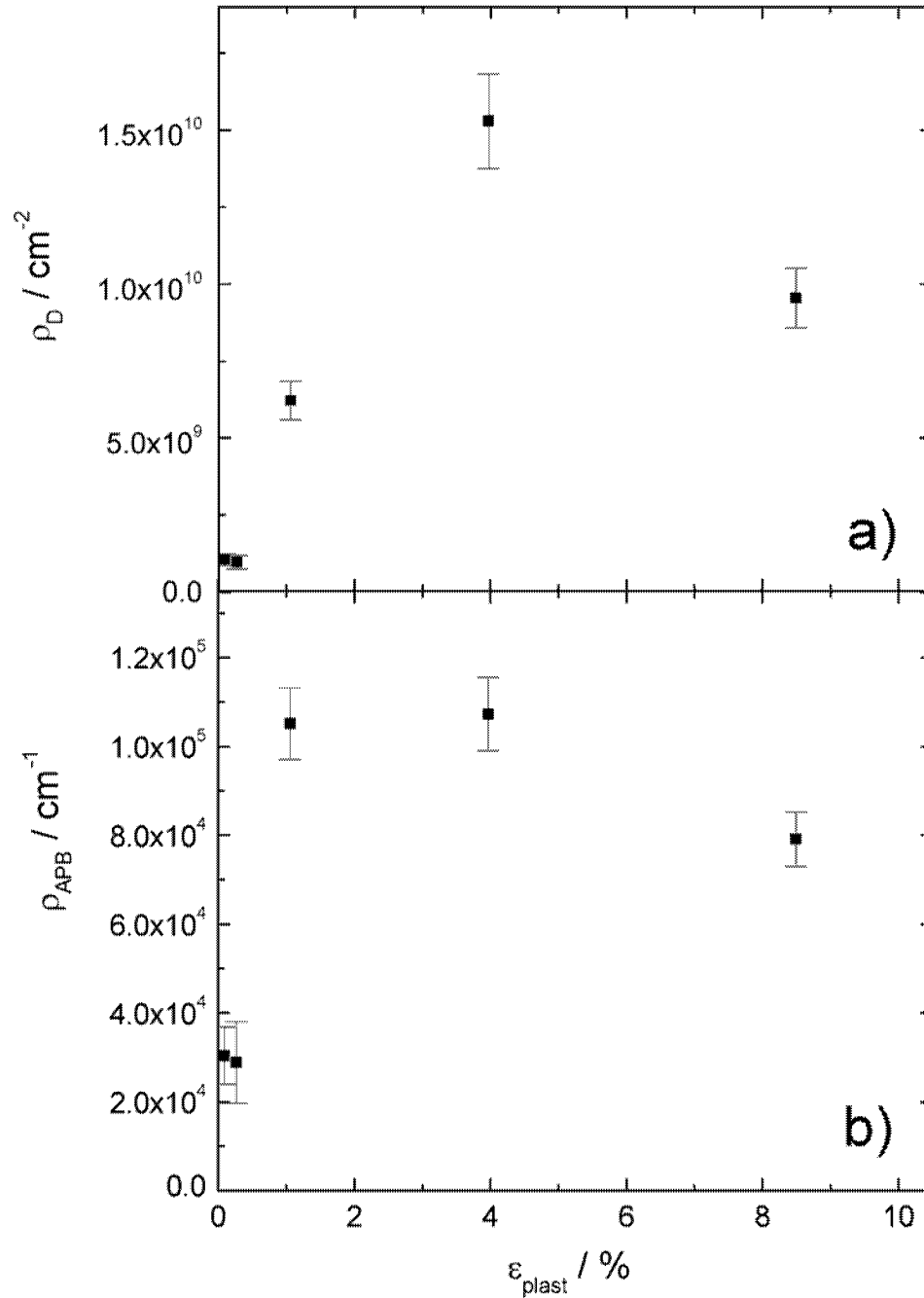


Figure 4.1: Five samples were deformed at $\dot{\epsilon} = 10^{-5} \text{ s}^{-1}$ and $T' = 520^\circ \text{C}$ to different amount of plastic strain ϵ_{plast} . (a) The dislocation density ρ_D and (b) the density of antiphase boundaries ρ_{APB} are plotted against plastic strain.

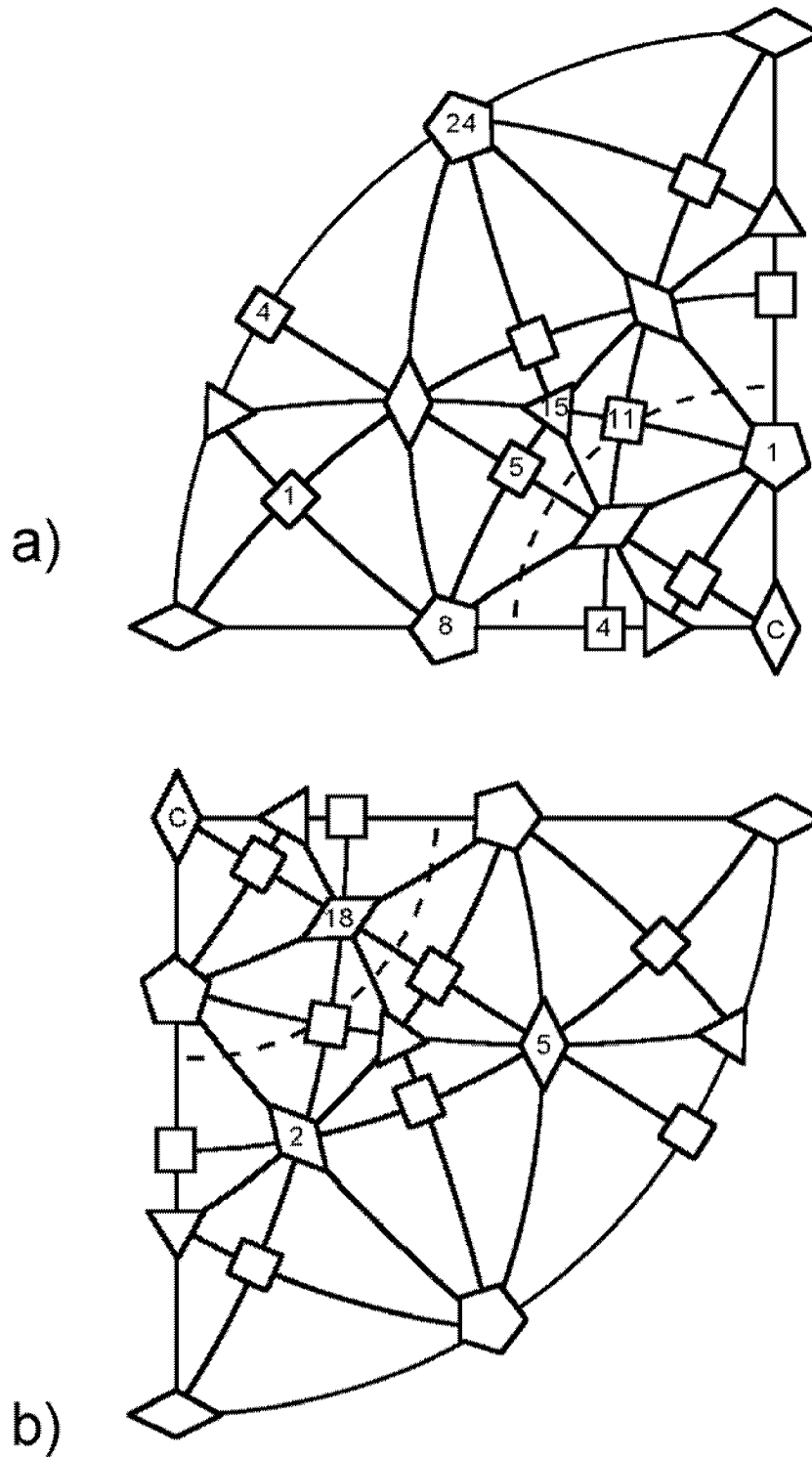


Figure 4.2: The orientation of (a) plane normals of antiphase boundaries and of (b) Burgers-vector directions of dislocations, attached to the antiphase boundaries are presented. The numbers indicate the frequency of appearance of different directions. The compression direction is denoted (C). The dotted line indicates a 45°-cone around the compression direction. The total number of plane normals and Burgers vector directions determined is 73 and 25, respectively.

4. Analysis of dislocation motion

In Figure 4.2 b, the orientation of symmetrically equivalent Burgers-vector directions of dislocations attached to the antiphase boundaries is presented in a stereographic projection of the icosahedral point group. In Table 4.1 the frequency of occurrence is compiled for the different symmetry directions of the antiphase boundaries in deformed samples (cf. Figure 4.2 a) and in heat-treated samples (Heggen *et al.* 2001). The high proportion of fivefold planes in the heat-treated samples and the fact that twofold planes were not found in both kinds of samples are remarkable.

Symmetry of plane	deformed samples (total number of planes determined: 73)	heat-treated samples (total number of planes determined: 58)
fivefold	45 %	90 %
threefold	21 %	10 %
twofold	0 %	0 %
pseudo twofold	34 %	0 %

Table 4.1: Frequency of occurrence of plane symmetries of antiphase boundaries in heat-treated and deformed samples.

The frequency of occurrence of angles between the plane normals of the antiphase boundaries and the compression direction are shown in Figure 4.3 a. The majority of the antiphase boundaries are inclined at angles between 30 and 60° with respect to the compression direction, but also a large number of antiphase boundaries at angles of 90°, i.e. aligned parallel to the compression direction, are found. Figure 4.3 b shows the distribution of angles between the plane normals of antiphase boundaries and the directions of Burgers vectors of the dislocations attached to the antiphase boundaries. A value of 90° is most frequently found, i.e. most of the dislocations possess Burgers vectors lying in the fault plane of the antiphase boundary. Figure 4.3 c shows the frequency of occurrence of angles between the dislocation lines and the Burgers vectors. Here, an angle of 60° is most frequently found, but also pure edge (90°) and pure screw (0°) orientations were observed.

In samples that were cooled under load after compression stacking faults were found. The Burgers vector of the dislocations attached to the stacking faults and the displacement vector of the fault planes were determined by contrast-extinction experiments for 15 cases. These directions were all found to be parallel to the plane normals of the stacking faults, which were all lying in fivefold planes.

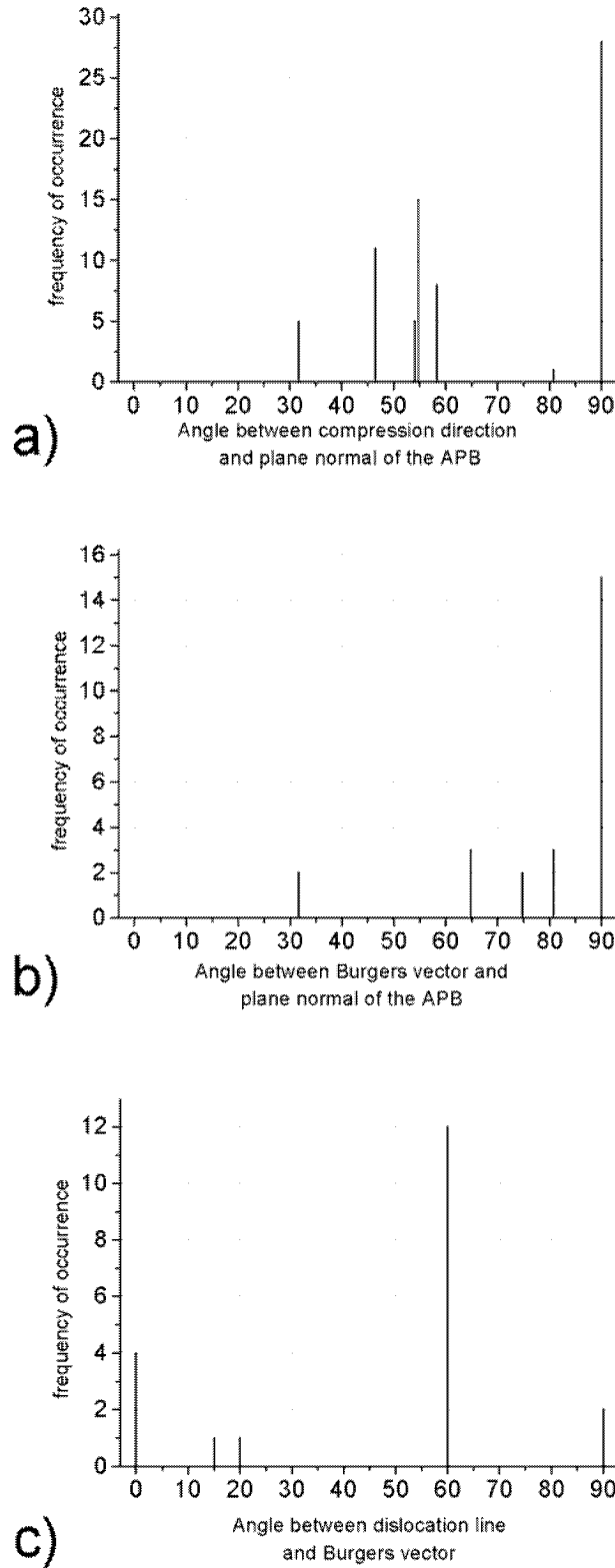


Figure 4.3: Frequency of occurrence of (a) angles between the compression direction and the plane normals of the antiphase boundaries, (b) angles between the plane normals of antiphase boundaries and the direction of the Burgers vector of the dislocation attached to the antiphase boundaries and (c) angles between the dislocation lines and the Burgers-vector directions.

4.3 Discussion

Up to now the direct determination of the planes of dislocation motion in plastically deformed icosahedral quasicrystals has not been possible. However, the appearance of antiphase boundaries in Zn-Mg-Dy provides a deeper insight into the microstructural processes of dislocation motion in single quasicrystals: Since the antiphase boundaries directly visualize the planes of dislocation motion, together with the determination of line and Burgers-vector directions of the attached dislocations, the unambiguous determination of the mode of dislocation motion (glide or climb) and the type of dislocation (edge- and/or screw components) is possible.

The dislocation density increases strongly with the onset of plastic deformation and reaches a maximum value at 4 % of plastic strain and decreases subsequently. At 8.5 % of plastic strain the dislocation density has dropped to 62 % of the maximum value. A similar dislocation-density evolution was observed for icosahedral Al-Pd-Mn (Schall *et al.* 1999). The decrease of the dislocation density can be attributed to recovery processes and is a feature of the plasticity of icosahedral Al-Pd-Mn quasicrystals which is described in the constitutive model for quasicrystal plasticity by Feuerbacher *et al.* (2001a). In this sense, the comparable evolution of the dislocation density of icosahedral Zn-Mg-Dy and Al-Pd-Mn furnishes evidence of the similarity of the plastic deformation mechanisms in both materials. A more detailed discussion of quasicrystal plasticity on the basis of the constitutive model approach is given in Chapter 5.

The density of the antiphase boundaries strongly increases with the onset of plastic deformation and reaches a maximum at about 1 % of plastic strain. At this strain, a high density of antiphase boundaries is visible (cf. Figure 2.9). However, a stable network of antiphase boundaries cannot exist in a two-domain face-centred-icosahedral structure, since crossings of antiphase boundaries lead to their annihilation at the line of intersection (cf. Chapter 2.3, Ebalard and Spaepen 1989, Heggen *et al.* 2001). Therefore the competing processes of diffusional domain ripening and the formation of new antiphase boundaries by moving partial dislocations leads to a saturation of the antiphase boundary density in the constant-strain-rate experiment. At higher strain the density of antiphase boundaries decreases slightly according to the decrease of the dislocation density.

The determination of line directions and Burgers vectors of dislocations show that most dislocations are of mixed type (Figure 4.3 c). An angle of 60° between line direction and Burgers vector direction, corresponding to the angle between twofold directions, is most frequently found. It was shown that in the deformed samples investigated, the plane normals of the antiphase boundary and the Burgers vector of the bounding dislocations in most cases make an angle of 90°. Thus, pure glide is the main mode of dislocation motion. However, smaller angles were also detected showing that climb processes do take place as well. In undeformed and heat-treated samples antiphase boundaries possessing particularly small angles of 20.9° and 31.7° between the plane normals and the Burgers vector of the bounding dislocations were found (Heggen *et al.* 2001).

In the heat-treated samples 90 % of the antiphase boundaries are aligned along closely packed fivefold planes, while in the deformed samples, as a result of the external uniaxial stress, the motion of partial dislocations takes also place on threefold and pseudo twofold planes inclined by angles between 30° and 60° with respect to the compression direction. In some cases, antiphase boundaries inclined by angles close to 45° to the compression direction but not being parallel to low indexed planes were found. Thus, the maximization of the resolved shear stress rather than the retention of a low-index plane is the deciding parameter for the choice of the plane of dislocation motion.

On the other hand a large proportion of antiphase boundaries with fivefold plane normals aligned parallel to the compression direction (Figure 4.3 a) has been detected in deformed material. Furthermore stacking faults with parallel displacement fields, i.e. Burgers-vector directions of the bounding dislocations, and plane normals, pointing along a fivefold direction perpendicular to the twofold compression direction were detected. Dislocation motion on these planes during deformation necessarily takes place by pure climb. Thus, in addition to the primary deformation mechanism of dislocation glide on planes of high resolved shear stress, processes possessing climb components as well as pure climb take place. These observations correspond to those of earlier studies by Wang *et al.* (1998) and Caillard *et al.* (2000) on icosahedral Al-Pd-Mn in which dislocation-induced planar faults and their strain-field direction or the Burgers-vector direction of their bounding dislocations were analysed by TEM. The observations in these studies were also interpreted in favour of the occurrence of pure climb in quasicrystals. However, in the present study glide is shown to be the predominant mode of dislocation motion.

5. Plastic deformation experiments on icosahedral

Al-Pd-Mn quasicrystals

5.1 Introduction

The first qualitative description of the plasticity of icosahedral quasicrystals, the cluster-friction model, was presented by Feuerbacher *et al.* in 1997b. The basic assumption of the cluster-friction model is that the Mackay-type clusters act as rate-controlling obstacles in dislocation motion. The ordered structure of the quasicrystal, and hence the density of clusters, is destroyed locally during dislocation motion, which leads to the decrease of the density of rate-controlling obstacles in the course of plastic deformation. The decrease of obstacles, which limit the dislocation velocity, weakens the structure and leads to work softening in a constant strain rate experiment.

In 2001 an empirical quantitative model formulation of the macroscopic plastic deformation behaviour was presented by Feuerbacher *et al.* (2001a). In this work, the degree of order in the quasicrystal structure was expressed introducing an order parameter λ in a heuristic way. Different contributions like topological or chemical order are not distinguished. The evolution of the order parameter λ and the dislocation density ρ in a constant-strain-rate experiment is described in terms of constitutive equations. Stress-strain curves and dislocation-density evolutions calculated correspondingly were compared with experimental data of Al-Pd-Mn at 10^{-5} s^{-1} and 730 °C. The experimental stress-strain curve and the dislocation-density evolution for a constant-strain-rate experiment was successfully described using the constitutive model.

In the present work the investigation of the plastic deformation behaviour is extended to a wide range of strain rates, covering four orders of magnitude. The strain-rate dependence is investigated at two different temperatures and additional experiments to very high plastic strains were carried out. The aim is the description of the features of quasicrystal plasticity in a wide range of experimental parameters in the comprehensive framework of the constitutive model.

Constitutive Equations

In the following section the basic aspects of the constitutive-equation approach are described. In this model the evolution of two microstructural parameters, the dislocation density ρ and the order parameter λ are the decisive parameters describing the stress-strain behaviour. The description of the order using the parameter λ is general: A value of $\lambda = 1$ represents a perfect ordered structure, lower values between 1 and 0 represent increasingly disordered states. Looking at the evolution of λ , it is supposed that the decrease of order $d\lambda^-$ is proportional the plastic-strain increase $d\varepsilon_{plast}$. The proportionality factor between the decrease of order $d\lambda^-$ and the strain increment $d\varepsilon_{plast}$ is the characteristic strain ε_0 .

Furthermore the decrease of order $d\lambda^-$ associated with the plastic-strain increase $d\varepsilon_{plast}$ is proportional to the current degree of order λ , hence $d\lambda^-(\varepsilon_{plast}) = -\lambda \frac{d\varepsilon_{plast}}{\varepsilon_0}$.

Since deformation experiments on Al-Pd-Mn quasicrystals are performed at high temperatures, diffusional processes, leading to a partial restoring of order, have to be accounted for. It is assumed that the increase $d\lambda$ with time is proportional to $(1-\lambda)$, the measure of order destroyed. Accordingly the evolution of the order parameter λ is described by an Ansatz

$$d\lambda(\varepsilon_{plast}) = -\lambda \frac{d\varepsilon_{plast}}{\varepsilon_0} + (1-\lambda) \frac{dt}{\tau_0}, \quad (5.1)$$

where τ_0 the characteristic time for the reordering process. The process of reordering is temperature-activated, thus the characteristic rate of reordering $1/\tau_0$ is dependent on temperature (Feuerbacher *et al.* 2001a). The characteristic strain can be considered as temperature-independent. Equation (5.1) can be solved analytically for the case of constant plastic strain rate. In the limit of large plastic strain the order parameter λ approaches the finite value λ_∞ . At increasing temperatures the contribution of reordering gets more dominant, thus λ_∞ tends to unity. The contribution of disordering gets dominant at high plastic strain rates, thus λ_∞ tends to zero. The macroscopic plastic strain rate $\dot{\varepsilon}_{plast}$ is given by the Orowan relation

$$\dot{\varepsilon}_{plast} = m_s \rho b v, \quad (5.2)$$

where m_s is the average Schmidt factor, ρ is the dislocation density and b the magnitude of the dislocation Burgers vector. The dependence of the dislocation velocity on the applied stress is described by the empirical law

$$v = B \left(\frac{\sigma}{\hat{\sigma}} \right)^m, \quad (5.3)$$

where B and m are temperature-dependent parameters and $\hat{\sigma}$ is an internal variable that can be regarded as a "reference stress" (Kocks 1976). If the structure is constant $v \propto \sigma^m$ holds. The reference stress $\hat{\sigma}$, which is equal to the stress σ at the dislocation velocity $v = B$, represents the current microstructural state of the material. The reference stress $\hat{\sigma}$ consists of different stress contributions

$$\hat{\sigma} = \sigma_0 + \alpha \mu b \sqrt{\rho(\varepsilon)} + \Delta \sigma \lambda(\varepsilon), \quad (5.4)$$

where the first term σ_0 is a constant background friction stress. The second term stands for the stress contribution determined by dislocation-dislocation interactions (Taylor hardening), and is proportional to the square root of the strain-dependent dislocation density. The parameter α is a numerical constant of the order of unity and μ is the shear modulus. The first two contributions are frequently used for the description of crystal plasticity for the case of a coarse-grained material with dislocation-dislocation interactions as the principal hardening mechanism (Mecking *et al.* 1981, Estrin 1996). The third term on the right-hand side of Equation (5.4) represents the quasicrystal-specific stress contribution. The quantity $\Delta \sigma$ stands for the flow-stress contribution originating from the destruction of order, e.g. the generation

of phason defects, by the movement of dislocations in the quasicrystalline material. This stress contribution is weighted by the strain-dependent order parameter λ .

The total strain $\varepsilon = \varepsilon_{plast} + \varepsilon_{elast}$ is the sum of the plastic strain ε_{plast} and the elastic strain $\varepsilon_{elast} = \sigma / E$, where E denotes the elastic constant. Combining these Equations with Equation (5.2) and (5.3) yields

$$\frac{d\sigma}{d\varepsilon} = E \left(1 - \frac{m_s \rho b B (\sigma / \hat{\sigma})^m}{\dot{\varepsilon}} \right). \quad (5.5)$$

The evolution of the dislocation density ρ is described according to an Equation originally given by Kocks (1976)

$$\frac{d\rho}{d\varepsilon_{plast}} = \frac{M}{b} \sqrt{\rho} - \frac{Y}{b} \rho. \quad (5.6)$$

The first term on the right-hand side corresponds to the athermal storage of dislocations and involves a parameter M . The second term, entering with a negative sign, describes the annihilation of dislocations by dynamic recovery, i.e. the annihilation of moving dislocations during plastic deformation. The annihilation parameter Y is related to the characteristic annihilation distance for e.g. a cross-slip mechanism. In the work of Feuerbacher *et al.* (2001a), the strain dependence of Y was taken into account by setting:

$$Y = \frac{Y_0}{1 + (\Delta\sigma / \sigma_0) \lambda}, \quad (5.7)$$

where Y_0 is a constant. In the present work, the static recovery of dislocations was accounted for by the relation

$$\frac{d\rho}{dt} = -A\rho^2, \quad (5.8)$$

where A denotes a static recovery parameter. Static recovery is dislocation-dislocation annihilation which takes place without the application of an external stress. The dislocations move due to internal stress fields and dislocation-dislocation interaction. Equation (5.8) was used by Schall *et al.* (1999) for the description of dislocation recovery in static annealing experiments. In the primary description of the constitutive model static recovery was accounted for (Feuerbacher *et al.* 2000). However, in the work published by Feuerbacher *et al.* (2001a) static recovery according to Equation (5.8) was not taken into account.

5.2 Experimental procedure

Deformation samples were cut from Al-Pd-Mn single quasicrystals, grown by the Czochralski method. The size of a deformation sample is approximately $2 \times 2 \times 5 \text{ mm}^3$; the long direction is oriented along a twofold direction. The surfaces were carefully ground in order to avoid crack formation. The mechanical testing was performed in a modified ZWICK Z050 high-temperature testing machine. The samples are uniaxially deformed in compression along the long specimen axis at constant temperature and strain rate. The experimental setup of the deformation machine is described in Appendix B.

The stress and strain values given in this work are so-called “true” quantities, which are related to the actual state of the sample during deformation and not on the initial state. Upon plastic straining the cross section of a deformation sample changes at constant volume of the sample. For homogeneous deformation the true stress is then given by $\sigma = L/A_c$ where L is the load and A_c is the current cross section of the sample. The true stress can be expressed by the strain at constant volume (cf. Poirier, 1985)

$$\sigma = \sigma_{tech}(1 - \varepsilon_{tech}), \quad (5.9)$$

where the technical stress $\sigma_{tech} = L/A_0$ is given by the load L and the initial specimen cross section A_0 . With the technical strain $\varepsilon_{tech} = \Delta l/l_0$ defined by the change of the length Δl and the original sample length l_0 , the true strain can be expressed as (cf. Poirier, 1985)

$$\varepsilon = \ln\left(\frac{1}{1 - \varepsilon_{tech}}\right). \quad (5.10)$$

In the present work true-stress vs. true-strain curves are referred to as stress-strain curves since graphs showing technical stresses or technical strains are not presented. Plastic deformation experiments at constant strain rate are usually closed loop controlled to a constant technical strain rate $\dot{\varepsilon}_{tech} = \frac{1}{l_0} \frac{dl}{dt}$. This value relates the length change of the sample

with time $\frac{dl}{dt}$ to its initial length l_0 . The true strain rate $\dot{\varepsilon}_{true} = \frac{1}{l} \frac{dl}{dt}$ is related to the current length of the sample l . Hence, the true strain can be written in terms of the technical strain as

$$\dot{\varepsilon}_{true} = \frac{\dot{\varepsilon}_{tech}}{1 - \varepsilon_{tech}}. \quad (5.11)$$

In this work plastic deformation tests were performed with constant technical strain rate in a regime up to 12 % of plastic strain. At high strains the difference between $\dot{\varepsilon}_{true}$ and $\dot{\varepsilon}_{tech}$ becomes significant. Plastic deformation experiments up to higher amounts of strain were therefore performed under constant-true-strain-rate conditions and are referred accordingly.

After mechanical testing, the deformations were terminated by rapid unloading and quenching of the samples on a cold metal plate. The procedure between unloading and quenching of the sample to room temperature usually takes about 10 s. The microstructure of the deformed materials was studied by means of TEM. Specimens for TEM investigation are produced following standard preparation procedures such as slicing, mechanical grinding and polishing followed by argon-ion milling on a liquid nitrogen-cooled stage. The microstructural analyses were carried out using JEOL 4000FX and 2000EX transmission electron microscopes. The dislocation density was determined by counting the number of intersections of dislocations with the specimen surfaces on bright-field images (Appendix C). The dislocation density was calculated according to Equation (2.1).

5.3 Results

Figure 5.1 shows four stress-strain curves that were taken at a deformation temperature of 730 °C at different constant strain rates. During the experiments at 10^{-5} and 10^{-6} s $^{-1}$ additional stress-relaxation experiments and strain-rate changes were performed, which are indicated at the 10^{-5} s $^{-1}$ curve as “R” and “SRC”, respectively.

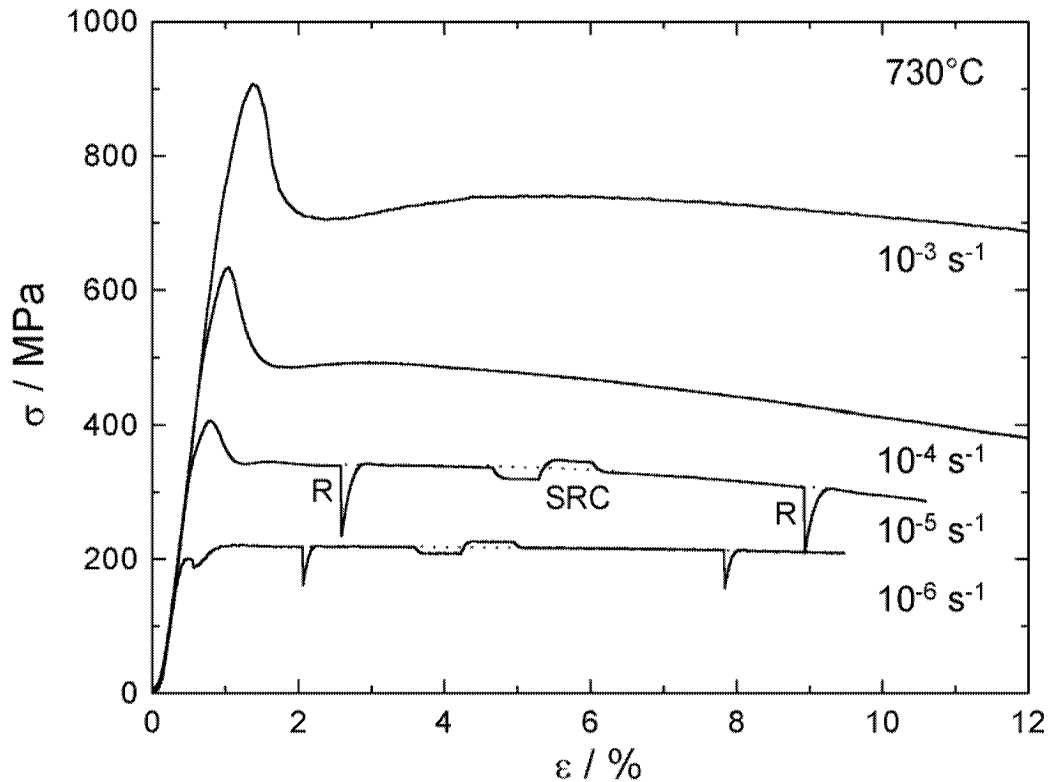


Figure 5.1: Stress-strain curves at 730 °C and strain rates between 10^{-6} and 10^{-3} s $^{-1}$. Additional stress-relaxation experiments and strain-rate changes are labelled as “R” and “SRC”, respectively. The course of the stress-strain curve without additional experiment is indicated as dotted line.

The course of the stress-strain curve performed without additional experiment is indicated as dotted line. The curve at 10^{-3} s $^{-1}$ exhibits an upper yield stress of 907 MPa after elastic loading. Subsequently, the stress drops to a lower yield stress of 705 MPa at 2.4 % strain and increases again to develop a second stress maximum of 740 MPa at 5.4 % strain. At higher strain the flow stress decreases continuously. The curve at 10^{-4} s $^{-1}$ shows a similar behaviour: After the lower yield stress of 485 MPa at 1.8 % strain the stress increases again and reaches a second stress maximum of 492 MPa at 3.0 %. At higher strain a pronounced softening can be found: the stress drops to 380 MPa at 12 %. At 10^{-5} s $^{-1}$ only a slight stress buckle at 1.6 % strain is observed. At higher strain the flow stress decreases continuously. The curvature of stress-strain curves is highly dependent on the sample material and may differ even between deformation samples cut from the same crystal. In most cases a continuous decrease of the

flow stress after yielding is observed at 10^{-5} s^{-1} and 730°C (cf. Feuerbacher *et al.* 1995, Schall 1999). At the lowest strain rate of 10^{-6} s^{-1} the flow stress decreases slightly from 219 MPa at 1 % to 210 MPa at 9.5 % of strain, i.e. only a slight softening can be found. In contrast to the other curves, the stress-strain curve at 10^{-6} s^{-1} shows no yielding. However, a stress-strain curve, that was taken at an even lower strain rate of $0.7 \times 10^{-6} \text{ s}^{-1}$ (Figure 5.2), shows distinct yielding behaviour, comparable to the other curves. Here, the stress remains at a constant level of $202 \pm 1 \text{ MPa}$ between 1 and 6.7 % of strain, i.e. no strain softening is found.

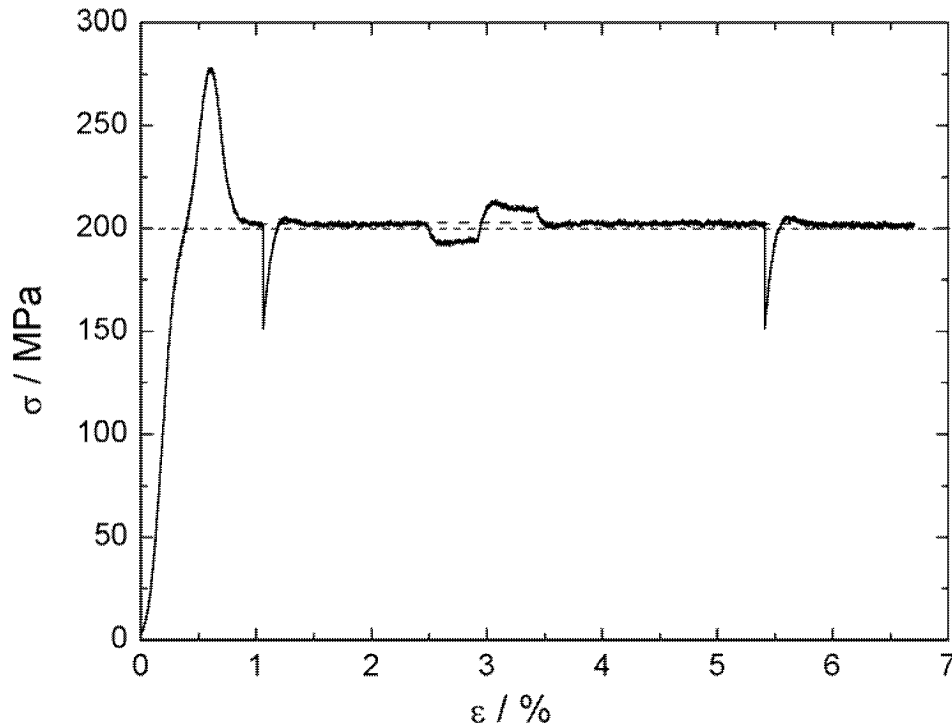


Figure 5.2: Stress-strain curve at 730°C and a strain rate of $0.7 \times 10^{-6} \text{ s}^{-1}$. The broken line indicates a constant stress level of 200 MPa.

Figure 5.3 shows stress-strain curves at a temperature of 760°C . Here, additional stress-relaxation experiments and strain-rate changes were performed at all strain rates. The curve at 10^{-3} s^{-1} shows an increase of the flow stress after the lower yield stress. In this strain region a stress-relaxation experiment was performed. After reloading a distinct yield effect can be observed, which originates from structural changes during the relaxation experiment. The course of the stress-strain curve indicates that a second stress maximum is present. However, the exact determination of its location is not possible due to the additional strain-rate changes and stress-relaxation experiments. An interpolated curve was plotted as broken line. It shows that the stress maximum is located between 3 and 4 % of strain. The stress-strain curves at 10^{-4} and 10^{-5} s^{-1} show no hardening stage after the lower yield stress; a continuous decrease of the flow stress is found after the lower yield point. At 10^{-6} s^{-1} slight yielding is observed after the onset of plastic deformation. In the strain regime between 1 and 8 % the stress decreases slightly from 142 to 133 MPa.

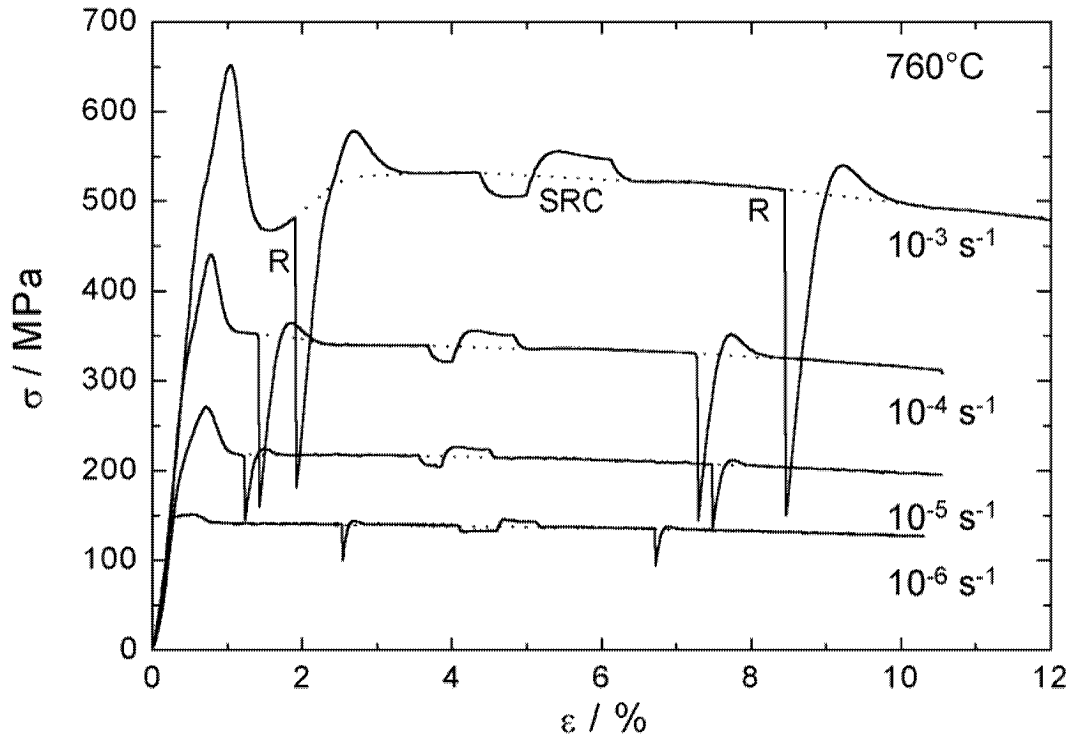


Figure 5.3: Stress-strain curves at 760 °C and strain rates between 10^{-6} and 10^{-3} s^{-1} . Stress-relaxation experiments and strain-rate changes are labelled as “R” and “SRC”, respectively.

The microstructure of the deformed samples was analysed using TEM. All deformed samples were demonstrated to be single-grain icosahedral quasicrystals after deformation. The dislocation densities were determined and they are plotted as squares in Figures 5.6 a to d and 5.7 a to d as a function of plastic strain. The data was completed with experimental data by Schall *et al.* (1999).

For the calculation of stress-strain curves, the set of differential Equations 5.1, 5.5, and 5.6 is solved numerically in terms of the total strain ε . The calculated solution $\sigma(\varepsilon)$ is directly compared with the set of experimental curves presented in Figures 5.1 and 5.2. Furthermore, the evolution of the dislocation density $\rho(\varepsilon)$ was calculated and compared with experimental dislocation densities at different strains (cf. Figures 5.6, 5.7). The curves for all strain rates were fitted using a single set of parameters for each temperature. Wherever possible, parameter values determined by independent experiments were used (cf. Table 5.1). Firstly, computed curves were fitted to the experimental data at 730 °C. Seven free parameters were varied to fit the calculated to the experimental curves. These are the stress parameters $\Delta\sigma$ and σ_0 , the parameters for destruction and restoration of order ε_0 and τ_0 , the constant B , the storage constant M and the annihilation constant Y_0 . Subsequently, at 760 °C five parameters were varied: $\Delta\sigma$, σ_0 , τ_0 , B , and Y_0 . The parameter for destruction of order ε_0 , and the storage parameter M are supposed to be temperature independent quantities, hence the corresponding parameters obtained at 730 °C were used.

5. Plastic deformation experiments on i-Al-Pd-Mn quasicrystals

Parameter	730 °C			760 °C		
	Value	free/fixed	Ref.	Value	free/fixed	Ref.
$\Delta\sigma$	130 MPa	free		85 MPa	free	
σ_0	65 MPa	free		55 MPa	free	
ε_0	0.1	free		0.1	fixed (cf. 730 °C)	
τ_0	2×10^4 s	free		10^4 s	free	
B	4.5×10^{-9} m s ⁻¹	free		9×10^{-9} m s ⁻¹	free	
M	0.38	free		0.38	fixed (cf. 730 °C)	
Y_0	7.8×10^{-9}	free		1.33×10^{-8}	free	
μ	80 GPa	fixed	Feu. '96b	70 GPa	fixed	Feu. '96b
b	1.83×10^{-10} m	fixed	Feu. '96b	1.83×10^{-10} m	fixed	Feu. '96b
ρ	2×10^{11} m ⁻²	fixed	Hegg. '00a	2×10^{11} m ⁻²	fixed	Hegg. '00a
A	4.6×10^{-18} m ² s ⁻²	fixed	Scha. '99	1.7×10^{-17} m ² s ⁻²	fixed	Scha. '99
E	80 GPa	fixed	Feu. '95	70 GPa	fixed	Feu. '95
m	4.8	fixed	Feu. '96b	4.6	fixed	Feu. '96b
n	5	fixed	Estr. '84	5	fixed	Estr. '84
m_s	0.4	fixed	Mess. '00	0.4	fixed	Mess. '00

Table 5.1: Parameters used for the computation of stress-strain curves and the evolution of the dislocation density and the order parameter. “Fixed” parameters were determined by independent experiments and “free” parameters were varied to fit the calculated to the experimental curves.

Figure 5.4 shows the simulated stress-strain curves at 730 °C for strain rates between 10^{-3} and 10^{-6} s⁻¹. At the highest strain rate of 10^{-3} s⁻¹ a pronounced hardening stage after the lower yield stress of 720 MPa at 2.3 % can be seen. A second stress maximum of 768 MPa occurs at 6.0 % of strain. At higher strains work softening takes place. The stress-strain curve at 10^{-4} s⁻¹ shows a less pronounced hardening stage after the lower yield stress. A second stress maximum is seen at 3.2 % strain. At 10^{-5} s⁻¹ work softening occurs after the yield drop. At the lowest strain rate of 10^{-6} s⁻¹ the stress decreases slightly from 177 MPa at 1 % to 167 MPa at 9.5 %. Simulated stress-strain curves at 760 °C are shown in Figure 5.5. At the highest strain rate of 10^{-3} s⁻¹ a hardening stage after the lower yield stress takes place. A second stress maximum of 532 MPa is seen at 3.6 % of strain, a lower strain value than for the corresponding computed curve at 730 °C. At 10^{-4} and 10^{-5} s⁻¹ continuous softening after the yield drop is seen. At the lowest strain rate of 10^{-6} s⁻¹ work softening takes place only directly after yielding. Between 1 and 8 % the stress decreases slightly from 122 to 119 MPa.

Figures 5.6 a to d show the simulated evolution of the dislocation densities (solid lines) and the corresponding experimental dislocation densities at certain strain values for strain rates between 10^{-6} and 10^{-3} s⁻¹. The course of the dislocation-density evolutions show similarities for all strain rates: Firstly, the dislocation density increases strongly with the onset of plastic deformation, then a maximum value is reached and at higher strains the dislocation density decreases. The substantial differences between the curves are:

- The maximum value of the dislocation density increases with increasing strain rate. At 10^{-6} s⁻¹ a maximum value of 4.3×10^{13} m⁻² is reached, at 10^{-3} s⁻¹ a maximum value of 6.1×10^{14} m⁻² is reached.

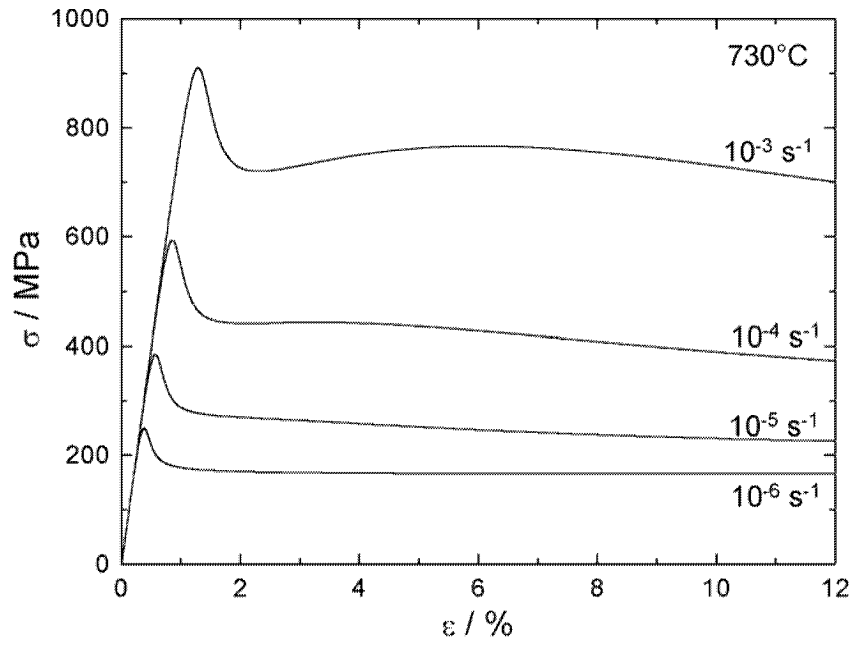


Figure 5.4: Computed stress-strain curves at 730 °C and strain rates between 10^{-3} and 10^{-6} s^{-1}

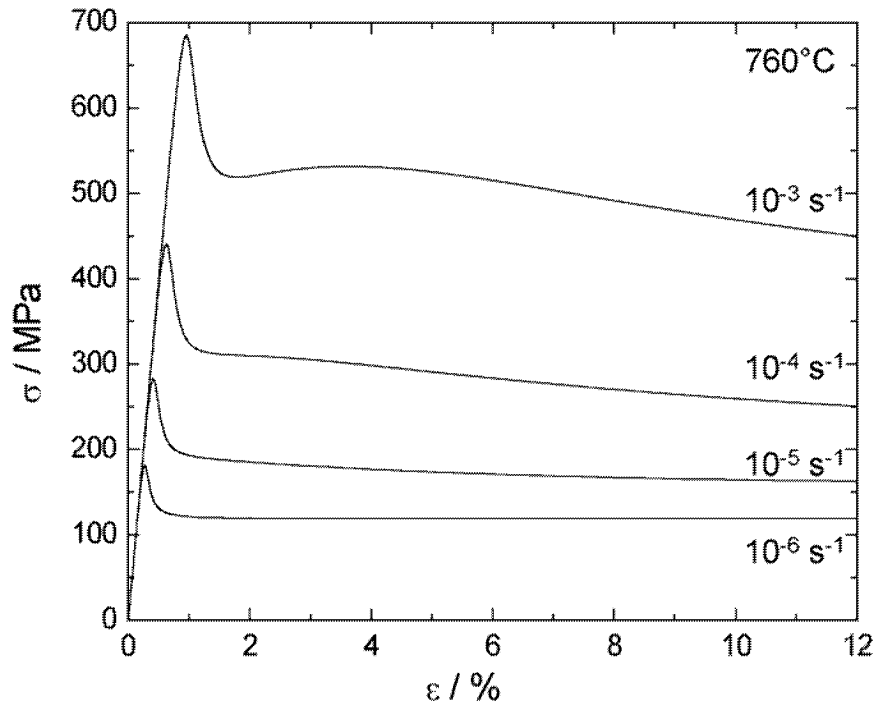


Figure 5.5: Computed stress-strain curves at 760 °C and strain rates between 10^{-3} and 10^{-6} s^{-1}

- With increasing strain rate, the point at which the maximum dislocation density is reached, shifts to higher strains. At 10^{-6} s^{-1} the maximum value is reached at 2.5 %, at 10^{-3} s^{-1} the maximum value is reached at 7.4 %.
- The decrease of the dislocation density with strain after the maximum is stronger with increasing strain rate. At 10^{-6} s^{-1} the dislocation density drops within 4 % of strain after the maximum to a dislocation density value of 96 % of the maximum value. The dislocation density is almost constant at strain values beyond 7 %. At 10^{-5} s^{-1} the dislocation density drops within 4 % of strain after the maximum to a dislocation density value of 81 % of the maximum value. Up to the value of 12 % strain no steady-state of the dislocation density is attained.

Figures 5.7 a to d shows the evolution of the dislocation density at 760 °C. The solid line represents the best fit obtained with a single set of parameters. Here, the same strain-rate dependence is found as at 730 °C, i.e. with increasing strain rate an increase of the maximum dislocation density, a shift of the dislocation-density maximum to higher strain and a stronger decrease of the dislocation density after the maximum occurs.

From the comparison of Figures 5.6 a to d and 5.7 a to d the following features can be observed as consequence of higher temperature:

- The maximum values of the dislocation density are lower at higher temperature.
- The maximum of the dislocation density shifts to lower strain at higher temperature.
- The decrease of the dislocation density after the maximum is less pronounced at higher temperature. At 10^{-6} s^{-1} and 760 °C only a very slight dislocation-density maximum is found at 1.7 % strain. Subsequently the dislocation density remains at a almost constant level.

Figures 5.8 a, b show the evolution of the order parameter at 730 and 760 °C at different strain rates. In Figure 5.8 a the order parameter drops with the onset of plastic deformation in almost the same way for the high strain rates of 10^{-3} and 10^{-4} s^{-1} ; at 12 % strain values of $\lambda = 0.33$ are reached. It can be observed that the onset of plastic deformation occurs at higher strain at 10^{-3} than at 10^{-4} s^{-1} . At 10^{-5} s^{-1} the drop of the order parameter with strain is slower; at 12 % strain a value of $\lambda = 0.45$ is reached. A different behaviour is found for the low strain rate of 10^{-6} s^{-1} . Here, a constant value of $\lambda = 0.83$ is reached after approximately 8 % of strain. It should be noted, that the order parameter reaches a steady-state value at strain rates higher than 10^{-6} s^{-1} but at strains much higher than 12 %. At 760 °C (Figure 5.8 b) a very similar evolution of the order parameter is observed at high strain rates of 10^{-3} and 10^{-4} s^{-1} compared to the corresponding curves at 730 °C. At 10^{-5} s^{-1} the order parameter at 12 % strain is equal to 0.55, which is a higher value than at 730 °C. At the lowest strain rate of 10^{-6} s^{-1} a constant value of $\lambda = 0.91$ is reached after approximately 5 % of strain. Hence a constant order parameter with a higher value is reached at lower strain than during the corresponding experiment at 730 °C.

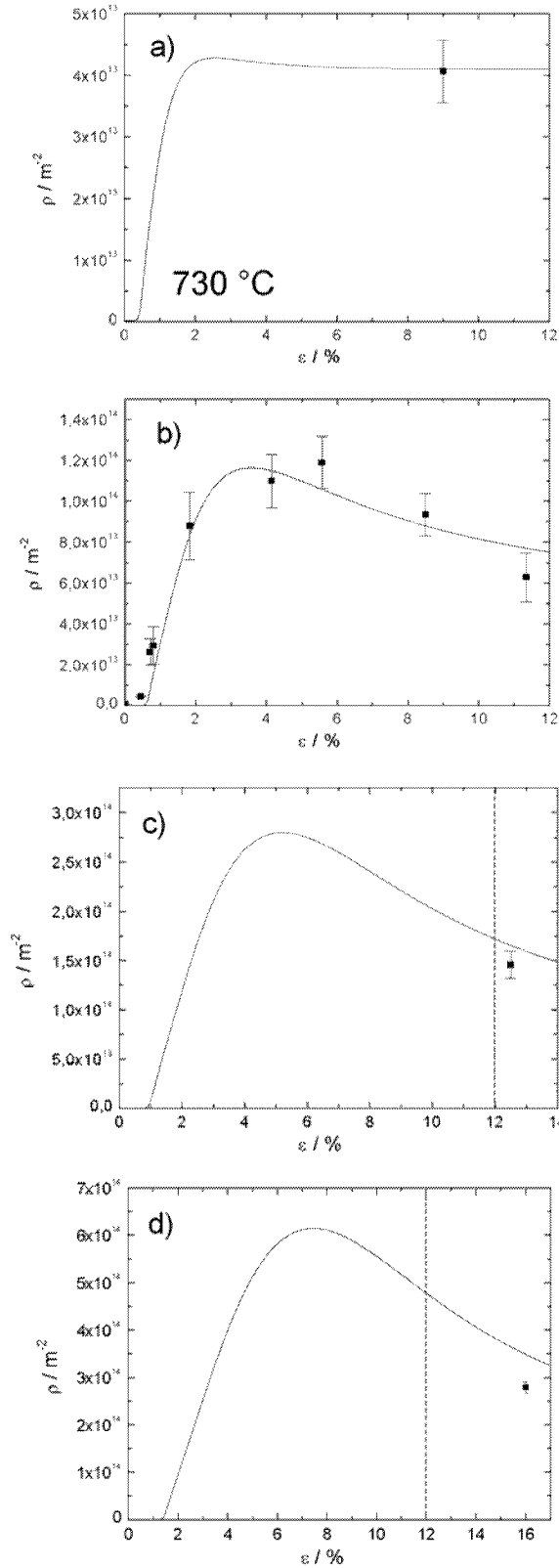


Figure 5.6: Computed evolution of the dislocation densities (solid lines) and experimental dislocation densities (squares) at 730 °C and strain rates between 10^{-3} and 10^{-6} s^{-1} . Experimental dislocation densities in Figure (b) were taken from Schall et al. (1999). Please note that different scales are used on the abscissas (the broken lines indicate 12 % strain).

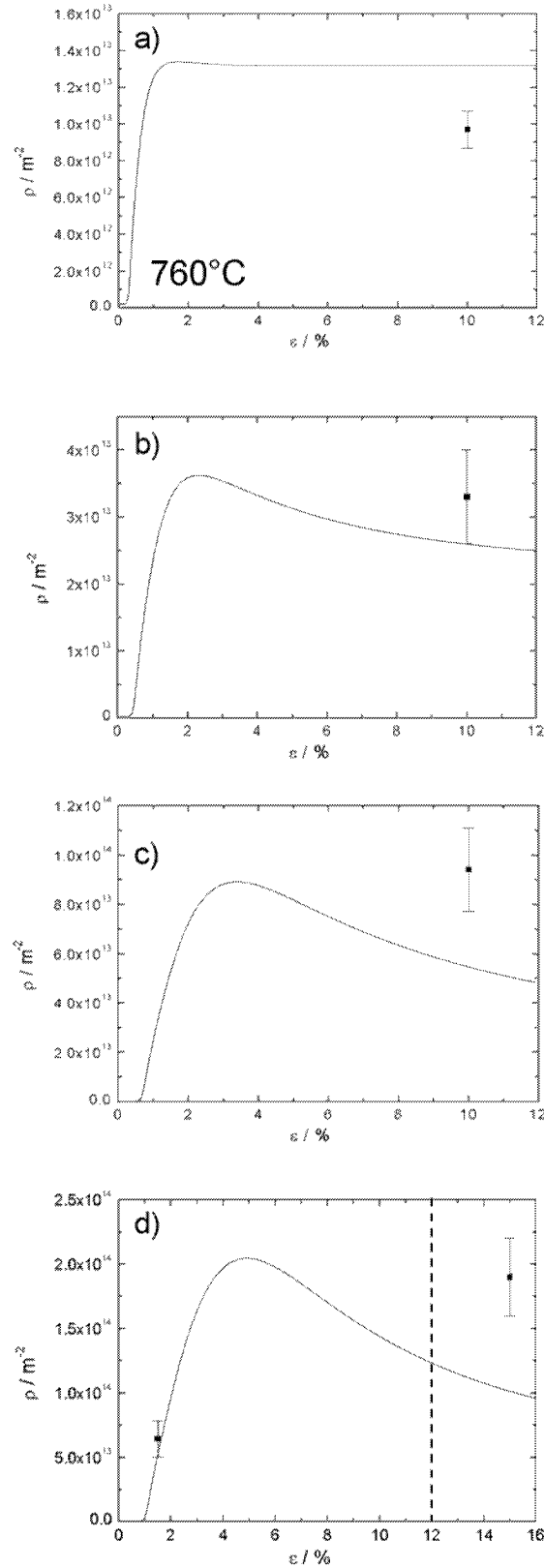


Figure 5.7: Computed evolution of the dislocation densities (solid lines) and experimental dislocation densities (squares) at 760 °C and strain rates between 10^{-3} and 10^{-6} s^{-1} . Please note that different scales are used on the abscissas (the broken line indicates 12 % strain).

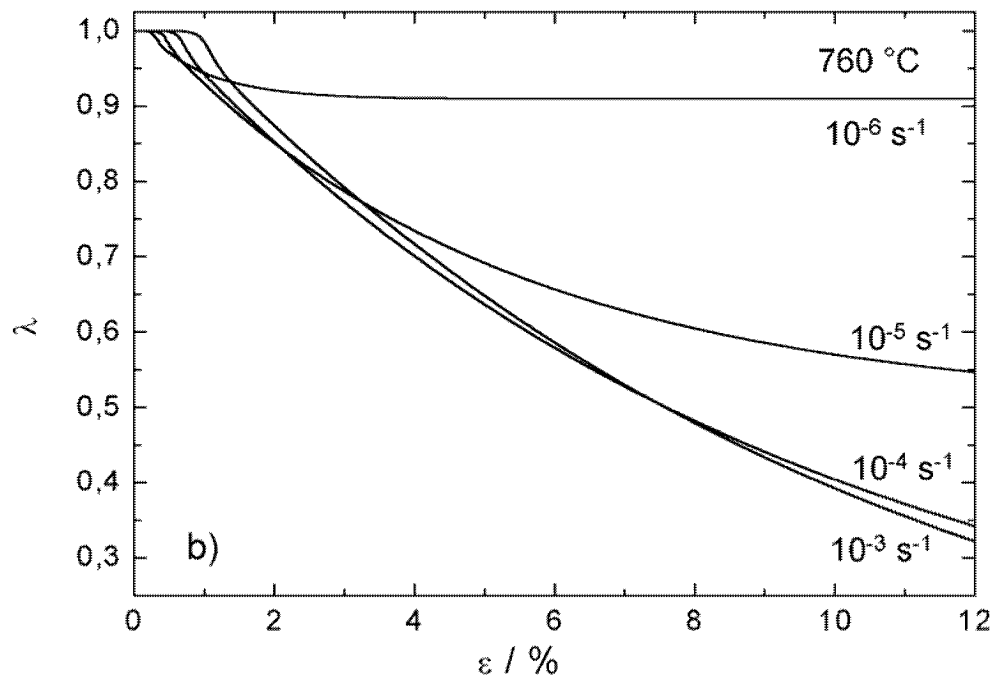
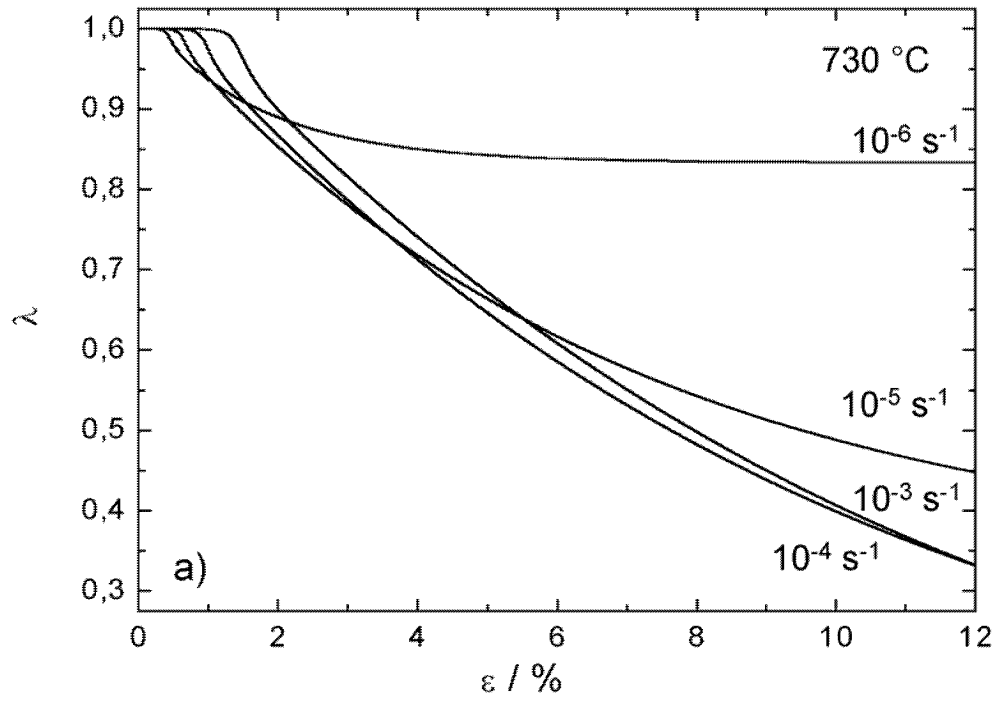


Figure 5.8: Evolution of the order parameter at strain rates between 10^{-3} and 10^{-6} s^{-1} at 730 °C (a) and at 760 °C (b).

Figure 5.9 shows a plastic deformation experiment that was performed at 760 °C up to high strains. In this experiment the deformation was closed loop controlled to a constant true strain rate of 10^{-4} s^{-1} . Figure 5.9 shows the stress-strain curve which can directly be compared at low strain with the corresponding curve in Figure 5.2. After yielding the stress firstly decreases. A maximum softening rate is reached at about 15 % of strain. Then, at a strain of about 50 % the flow stress reaches a constant value of 80 MPa, which is only one quarter of the flow stress at the lower yield point. After deformation the microstructure of the sample was analysed by means of TEM. The sample showed the occurrence of quasicrystalline grains of an average diameter of 2 μm .

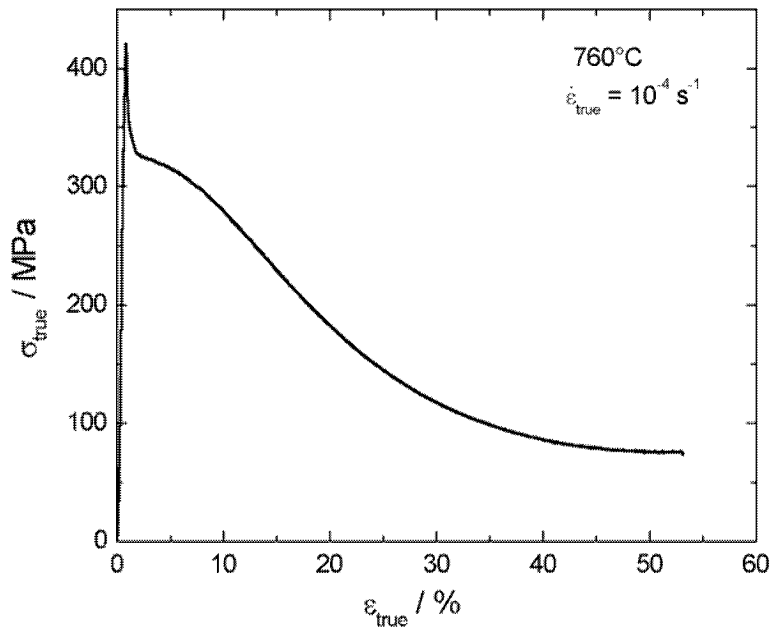


Figure 5.9: Plastic deformation experiment at 760 °C controlled to a constant true strain rate of 10^{-4} s^{-1} .

5.4 Discussion

In the present work plastic deformation experiments on icosahedral Al-Pd-Mn were extended to a wide range of strain rates. This led to the disclosure of new features of the plastic behaviour, i.e. an extended hardening stage after yielding at high strain rates and an almost constant flow stress at low strain rates. The constitutive model was successfully used to describe the plastic behaviour at different strain rates using a single set of fit parameters. Furthermore, the experiments were performed at two different temperatures. The temperature dependence of the plastic behaviour and the parameters were studied.

Stress-strain curves

At medium strain rates of 10^{-5} s^{-1} at 730°C and 10^{-4} and 10^{-5} s^{-1} at 760°C work softening after the lower yield stress is observed in experimental stress-strain curves. This observation is in accordance with previous investigations: In most of the previous works, the plastic deformation behaviour of Al-Pd-Mn has been studied at a constant strain rate of 10^{-5} s^{-1} (cf. Wollgarten *et al.* 1993, Feuerbacher *et al.* 1997, Messerschmidt *et al.* 2000, Geyer *et al.* 2000). At this strain rate the flow stress decreases continuously after the yield drop, i.e. work softening occurs (Wollgarten *et al.* 1993, Feuerbacher *et al.* 1997b). Work softening has also been observed in various other quasicrystalline materials (Bresson and Gratias 1993, Kang and Dubois 1992). Thus, the occurrence of work softening has been regarded as characteristic feature of quasicrystal plasticity. At high strain rates higher and lower than the intermediate of 10^{-5} s^{-1} , however, a different stress-strain behaviour was observed in the present experiments. At 760°C and 10^{-3} and 10^{-4} s^{-1} at 730°C work hardening was observed after the lower yield stress. After reaching a second stress maximum at 3 to 5.4 % of strain, work softening occurs at high stress. At a low strain rate of 10^{-6} s^{-1} at 730 and 760°C and $0.7 \times 10^{-6} \text{ s}^{-1}$ at 730°C the stress remains at an almost constant level at high strains; almost no work softening is found.

The stress-strain curves computed according to the constitutive model (Figures 5.4 and 5.5) perfectly reproduce all essential features of the experimental curves. Work softening at high strain is well reproduced and is accompanied by a decreasing dislocation density. Furthermore, the extent of the hardening regime, which is observed at high strain rates, as well as the almost constant flow stress at low strain rates are reproduced well. One set of parameters was used for all strain rates at one temperature. Hence, the strain-rate dependence, which was tested over four magnitudes of strain rate, is an intrinsic property the constitutive equations and is not a consequence of a choice of particular parameters values. Furthermore, the temperature dependence of the plastic behaviour can be modelled by the variation of parameters. The constitutive model is capable to predict plastic deformation behaviour in an extended range of experimental parameters, e.g. the behaviour at very high or low strain rates can be computed as well as at high strains.

The absence of pronounced yielding in both experimental stress-strain curves at 10^{-6} s^{-1} is not in accordance with the computed curves. However, in a creep curve at an even lower strain rate of $7 \times 10^{-7} \text{ s}^{-1}$ pronounced yielding was found. This demonstrates that yielding is not generally absent at low strain rates. It is assumed that the experimental observation of yielding in low strain-rate experiments is more difficult than at high strain rates. Only if the initial dislocation density is uniformly small a significant yield drop can be observed. A variation of the dislocation density has direct influence on the magnitude of the yield drop (Johnston 1962, Gillis and Gilman 1965). Since the maximum dislocation densities are small at low strain rates, these experiments are more critical with respect to a variation of the dislocation density. Dislocation-density fluctuations can be introduced by non-uniform straining of the sample at the beginning of the experiment as a consequence of deviation from exact parallel compression surfaces of the sample.

The correlations between the evolution of the microstructural parameters, i.e. the dislocation density ρ and the order parameter λ , and the stress-strain behaviour is explained in detail for the computed deformation experiment at $T' = 730^\circ\text{C}$ and a strain rates of $\dot{\varepsilon} = 10^{-3} \text{ s}^{-1}$ (cf. Figure 5.4). Figure 5.10 a shows the plastic strain rate $\dot{\varepsilon}_{\text{plast}}$ as a function of total strain ε , Figure 5.10 b shows the dislocation velocity v according to Equation (5.3), and Figure 5.10 c shows the rate of dislocation production and annihilation.

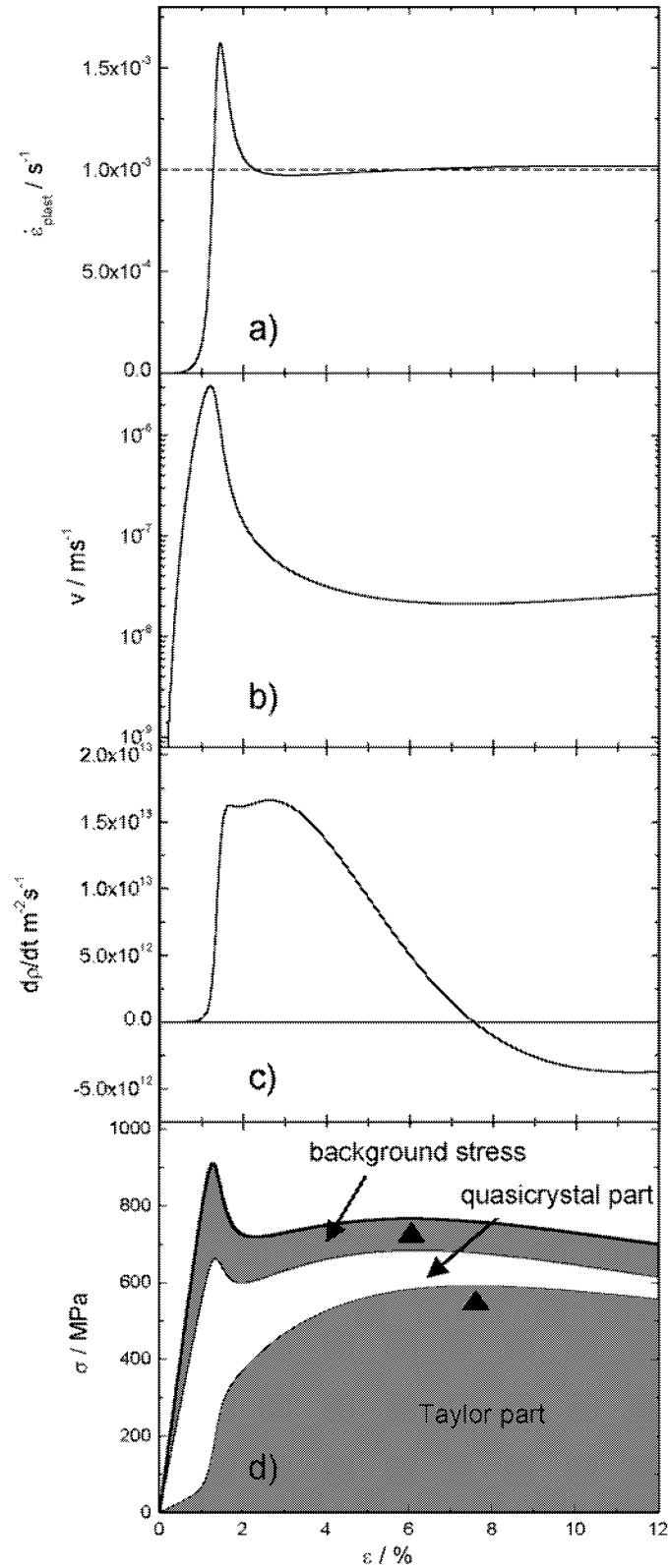


Figure 5.10: (a) plastic strain rate, (b) dislocation velocity, (c) rate of dislocation production and annihilation and (d) computed stress contributions, i.e. the Taylor part (light grey), the quasicrystal-part (white) and the background stress (dark grey), at 730°C and $\dot{\varepsilon} = 10^{-3} \text{ s}^{-1}$. The arrowheads indicate local maxima of the stress contributions.

Figure 5.10 d shows the stress contributions to the total stress according to Equations (5.3) and (5.4). The upper curve represents the total stress, the lower curve is the Taylor contribution, the difference between the lower curve and the middle curve corresponds to the quasicrystal contribution, and the difference between the middle curve and the upper curve corresponds to the background stress. The evolution of the Taylor contribution to the stress at $T' = 730\text{ }^{\circ}\text{C}$ and $\dot{\varepsilon} = 10^{-3}\text{ s}^{-1}$ in Figure 5.10 d can be compared to the dislocation-density evolution in Figure 5.6 d: At the beginning of the deformation experiment the stress increases elastically. The dislocation density is low, hence the contribution of the Taylor contribution is small. Up to the upper yield point, the dislocation velocity increases strongly with increasing stress (cf. Equation 5.3) - plastic straining of the sample is initiated. With the increase of the plastic strain rate dislocation storage according to Equation (5.6) commences. The storage of dislocations is reflected in the strong increase of the dislocation density (Figure 5.6 d) and the increase of the Taylor contribution.

The strong increase of the dislocation density (Figure 5.6 d) leads to a strong decrease of the dislocation velocity (Figure 5.10 b) according to the Orowan equation (5.2). Hence the total stress σ decreases according to Equation (5.3). Furthermore, the decrease of stress decreases the elastic-strain contribution, hence the plastic strain rate is higher than the total strain rate. After the upper yield stress at 1.28 % the maximum plastic strain rate of $1.62 \times 10^{-3}\text{ s}^{-1}$ is reached at 1.45 %. The rate of dislocation storage shows two maxima, the first one at 1.68 % corresponds to the maximum plastic strain rate and the second one at 2.64 % to the maximum dislocation density which enters Equation (5.6). The strong increase of dislocation density (cf. Figure 5.6 d) leads to an increase of dislocation interactions which is reflected in the strong increase of the Taylor contribution after yielding.

In the stress range between 2.3 and 6.0 % the stress σ increases. However, according to Equation (5.3) the reason for the stress increase is not the dislocation velocity v , since according to Figure 5.10 b, the dislocation velocity decreases in this strain regime. The stress increase is caused by a strong increase of the Taylor contribution to the reference stress $\hat{\sigma}$ in Equation (5.3). With the increase of the dislocation density the annihilation by dynamic recovery gets stronger. In a structure, which remains constant with strain, the annihilation distance for dislocation recovery remains constant, hence, a constant dislocation density at high strains would be obtained. The structure of a quasicrystal, however, is continuously disordered by the movement of dislocations. With the onset of plastic deformation, i.e. increasing plastic strain rate (Figure 5.10 a), disordering of the structure is initiated according to Equation (5.1), which can be directly observed by the sharp drop of the order parameter at 1.4 % in Figure 5.8 a, and then continues with plastic straining. At the high strain rate of $\dot{\varepsilon} = 10^{-3}\text{ s}^{-1}$ reordering, which takes place diffusively, is reflected in the decreasing slope of the λ vs. ε curve.

With decreasing order, the contribution of the quasicrystal contribution gets smaller (cf. Equation 5.4), which can be directly observed in Figure 5.10 d. The annihilation of dislocations is affected by the disordering of the structure. The order parameter λ enters the recovery parameter in Equation (5.7) and disordering supports dislocation recovery. Hence the dislocation density and the Taylor contribution of the stress decrease. From Figure 5.10 d it can be clearly seen that the stress maximum due to the Taylor contribution is at higher strains than the second stress maximum of the stress-strain curve (indicated by arrowheads). This shift of the stress maximum to lower strain is caused by the quasicrystal contribution which is decreasing continuously after yielding.

Figure 5.11 a to d shows the evolution of the stress contributions at different temperatures and strain rates. Figure 5.11 a shows again the stress contributions at $730\text{ }^{\circ}\text{C}$ and 10^{-3} s^{-1} .

Comparing this Figure to Figure 5.11 b, which shows the stress contributions at 730 °C and 10^{-5} s^{-1} , the influence of the strain rate on the stress contributions can be seen. The share of the Taylor contribution to the total stress is smaller than in Figure 5.11 a because of the lower maximum dislocation density at the lower strain rate (cf. Figures 5.6 b and d). Only a very weak maximum of the Taylor stress is observed at 3.8 % of strain, reflecting the formation of a dislocation-density maximum, which is less pronounced at lower strain rate. However, the decrease of the quasicrystal contribution impedes that the course of the total stress is affected by the Taylor-stress maximum. The superposition of all stress contributions continuously decreases after the yield drop, i.e. continuous softening takes place.

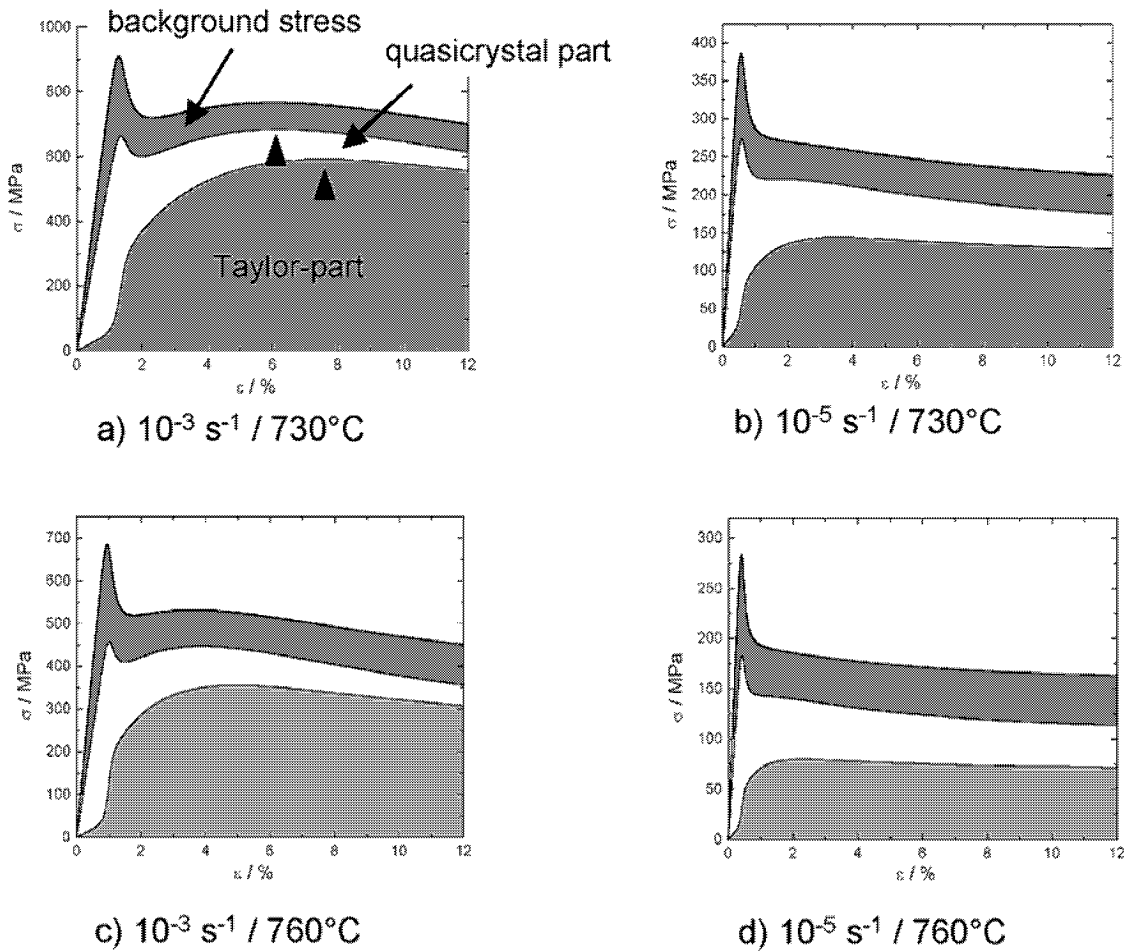


Figure 5.11: Computed stress contributions at 730 and 760 °C and 10^{-3} and 10^{-5} s^{-1} , respectively. The Taylor part (light grey), the quasicrystal-part (white) and the background stress (dark grey) are plotted. The arrowheads indicate local maxima of the stress contributions.

The effect of a temperature increase can be observed in Figures 5.11 c and d which show the stress contributions at 760 °C and at 10^{-3} and 10^{-5} s^{-1} , respectively. The share of the Taylor contribution to the total stress is smaller than in the corresponding Figures 5.11 a and b at the

lower temperature. Furthermore, the maximum is less pronounced and shifts to lower strains. Again, the behaviour of the Taylor contribution reflects the dislocation-density evolution at different strain rates and temperatures. The dislocation density and hence the contribution of the Taylor stress is smaller because dynamic recovery is stronger at higher temperatures, which is reflected in the values of Y in Table 5.1. Reordering of the structure, which takes place according to the characteristic time constant τ_0 in Table 5.1, is increased upon the increase of the temperature. The degree of order is higher in the deformation experiment at 760 °C and $\dot{\epsilon} = 10^{-6} \text{ s}^{-1}$ than at the corresponding experiment at 730 °C (cf. Figures 5.8 a and b). At high strain rates of 10^{-3} and 10^{-4} s^{-1} , pronounced effects of structural reordering are not observed, since the duration of the experiment is shorter than the timescale on which significant reordering takes place. Hence, the evolution of the order parameter is very close in Figures 5.8 a and b. However, structural reordering does affect the deformation experiment at the low strain rate of 10^{-6} s^{-1} . Here, the structure is in equilibrium and a steady-stress state is reached after approximately 8 and 5 % as shown in Figures 5.8 a and 5.9 a, respectively. This results in a very constant quasicrystal contribution of the stress and in an almost unaffected dynamic recovery parameter. Hence, the dislocation density remains on a constant level after a very weak maximum. All stress contributions remain at an almost constant level and add up to a constant flow stress.

The strong influence of dislocation recovery on the plasticity of quasicrystals was discussed by Messerschmidt *et al.* (2000). Steady-state deformation of quasicrystals is only possible if recovery compensates the strong work hardening after the onset of plastic deformation. The interaction between dislocation-density evolution and structure as well as the transient between work hardening and softening is described very comprehensively in the constitutive model. At lower temperatures dislocation recovery is slower, hence hardening occurs at higher strains (cf Figures 5.4 and 5.5). A transition to brittle behaviour can be demonstrated if the recovery parameter Y_0 is further lowered. In the computed stress-strain curves this leads to a strong amplification of hardening and the stress may exceed the fracture stress after a small amount of plastic strain. The brittle-to-ductile transition temperature at 10^{-5} s^{-1} was determined as about 635 °C (Feuerbacher 1996b). At a lower strain rate of 10^{-6} s^{-1} plastic straining is possible down to 550 °C (Messerschmidt *et al.* 1999) because recovery can still take place if slow straining is performed.

The free parameters of the constitutive model were determined by fitting the computed stress-strain curves to the experimental curves. The reliable determination of materials parameters from the fit parameters is difficult. Firstly, the variation of experimental values is considerable. Experimental stress-strain curves of Al-Pd-Mn quasicrystals, for example, show a variation of about 10 % of stress even if deformation samples are prepared from the same crystal. Furthermore, the error bars in Figures 5.6 and 5.7 show only the statistical deviation of the dislocation densities from a series of micrographs. The dislocation density in two samples, deformed under the same circumstances may vary by a factor of 2. Secondly, the precise determination of single material parameters is restricted by the high number of free parameters in the constitutive model which may be mutually dependent. However, the principal behaviour, i.e. the appearance of the additional hardening stage after the lower yield stress at high strain rates, the continuous softening after yielding at medium strain rates and the almost constant flow stress after yielding at low strain rates is a stable feature of the model for a wide range of parameter values.

The parameters τ_0 , B and Y_0 are free at both temperatures, i.e. they were determined by fitting the computed stress-strain curves to the experimental curves. The temperature dependence of B can be determined comparing the Power law (5.2) with the Arrhenius form of the kinetic Equation (cf. Kocks *et al.* 1975). With $B = B_0 \exp(-\Delta E_B/kT)$ we obtain an

activation energy $\Delta E_B = 1.5$ eV which is a reasonable value. Likewise a value for the activation energy of recovery $\Delta E_Y = 1.5$ eV was obtained from the temperature dependence of Y_0 . This value compares well to the activation energy of diffusion $Q = 1.25$ eV in Al-Pd-Mn (Galler 2003).

In a recent work by Messerschmidt *et al.* (2001) the temperature dependence of steady-state flow stress is modelled based on an evolution law of the dislocation density by considering the contribution of long-range dislocation interaction. The equations do not involve a particular quasicrystal contribution, and consequently they do not describe the softening observed at large strains. The temperature dependence of the athermal stress component, i.e. the Taylor contribution, to the total stress was calculated under steady state conditions for constant strain-rate experiments at 10^{-5} s^{-1} . The Taylor contribution to the total stress was shown to increase with decreasing temperature: At 730 and 760 °C values of 63 % and 55 % were determined. The Taylor contributions to the stress in our computations are similar, although in the present work no steady-state is attained at low strains due to the evolution of the order parameter. At a strain of 6 % the Taylor contribution to the total stress is 55 % and 43 % at 730 and 760 °C, respectively. This comparison shows, that the quota of the Taylor contributions to the stresses are similar, although a different approach was used by Messerschmidt *et al.* (2001). In this sense, the magnitude of the Taylor contributions obtained in the present work appears to be reasonable.

A careful comparison of the experimental and computed stress-strain curves reveals a difference in the shape of the curves before the upper yield stress. The computed curves in Figures 5.4 and 5.5 match very well in the elastic regime. Directly before reaching the upper yield stress, however, the curves at 10^{-4} , 10^{-5} and 10^{-6} s^{-1} deviate from the elastic curves at 10^{-3} s^{-1} which evolve to the highest stress values. The experimental stress-strain curves in Figures 5.1, 5.2 and 5.3 show a different behaviour. Here, the slope of the stress-strain curve deviates from the elastic curve much earlier. In Figure 5.2 the deviation from the slope of the elastic curve can be observed in a stress range between 175 MPa to the upper yield stress. This behaviour has been attributed to pre-yield plasticity (Bartsch *et al.* 1997), accompanied by strong work hardening. Pre-yield plasticity is the occurrence of plastic deformation before the upper yield point. It is a feature of Al-Pd-Mn quasicrystals but not a general feature of the plasticity of icosahedral quasicrystals, e.g. it has not been observed in icosahedral Zn-Mg-Dy quasicrystals (cf. Chapter 2). This phenomenon is not described by the present constitutive model.

Deformation behaviour at high strains

The plastic behaviour at high strain was studied in a constant strain rate experiment at $\dot{\epsilon} = 10^{-4} \text{ s}^{-1}$ and 760 °C (Figure 5.9). Continuous softening was found up to a constant flow stress which is attained at a high strain of 50 %. The microstructural investigation showed a decomposition of the sample into a polycrystalline structure. The influence of this effect on the plastic deformation behaviour is hard to describe quantitatively, thus no quantitative modelling of the experimental curve was attempted in order to obtain parameter values. Nevertheless, the stress-strain curve (solid line in Figure 5.12 a) and the dislocation-density and order-parameter evolution (Figures 5.12 b, c) of a deformation experiment to high strain at $\dot{\epsilon} = 10^{-4} \text{ s}^{-1}$ and 760 °C was computed using the parameters in Table 5.1. The comparison between the computed and experimental stress-strain curves reveals that the experimental curve drops down to a much lower stress level than the computed curve. The quantitative difference may be mainly attributed to the microstructural state of the deformed sample.

However, the qualitative behaviour is very similar. After extensive softening both curves reach a steady state flow stress at about 50 % of strain.

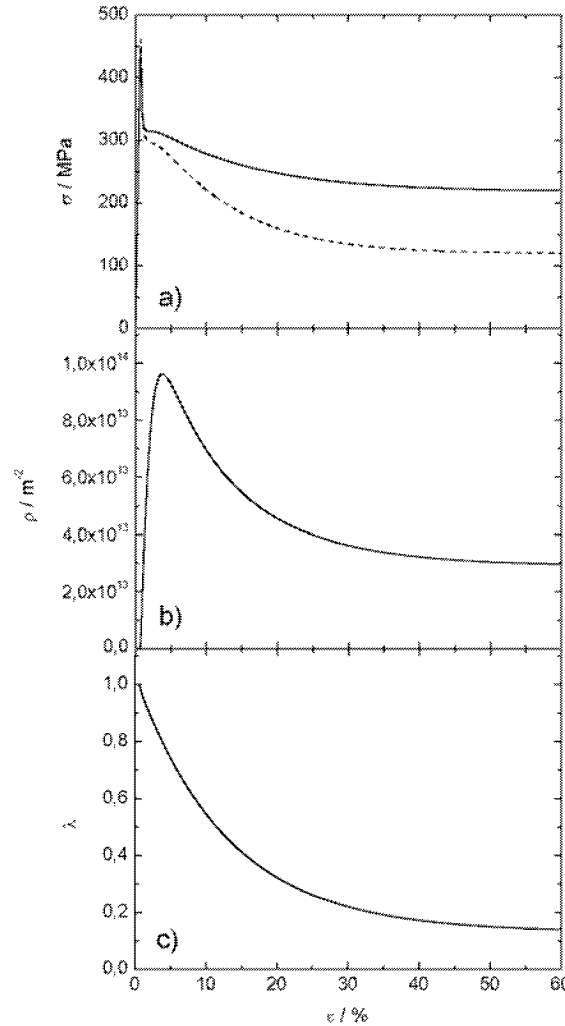


Figure 5.12: (a) Computed stress-strain curve (solid line), (b) dislocation-density evolution and (c) order-parameter evolution of a deformation experiment to high strain at $\dot{\epsilon} = 10^{-4} \text{ s}^{-1}$ and 760°C using the parameters in Table 5.1. The broken line represents a stress-strain curve computed using a modified set of parameters.

The broken curve in Figure 5.12 a represents a stress-strain curve that was computed with a slightly modified set of parameters. Explicitly, the free parameters Y_0 and $\Delta\sigma$ were increased and σ_0 was decreased. It is thus possible, with a modified set of parameters, to model the experimental curve up to high strains. However, due to the severe microstructural alterations taking place at high strains, this exceeds the scope of the model and is therefore to be considered with caution.

The interpretation of plastic deformation experiments performed to high strains remains furthermore difficult, even performed under constant-true-strain-rate conditions. Geometrical effects of sample straining, which change the length-to-diameter ratio, have to be taken into account. Figure 5.13 illustrates dislocation motion on planes inclined in a 45° angle to the compression direction, i.e. on planes possessing maximal shear stress, in samples possessing different length-to-diameter ratios. Figure 5.13 a shows a sketch of a sample with a common

length-to-diameter ratio of 5:2 corresponding to the samples used in the present work. Dislocation motion on planes inclined in a 45° angle to the compression direction is possible in the hatched sample region, i.e. in 60 % of the sample volume. If the sample is strained in compression the length-to-diameter ratio decreases (Figure 5.13 b). The contribution of the sample volume decreases, in which dislocation motion on planes inclined in a 45° angle to the compression direction can take place. This results either in a decrease of the distance between slip systems, which increases the interaction between them, or decrease the number of slip systems, which increases the strain contribution of each slip system. In both cases, this results in an increase of the flow stress in a constant-strain-rate experiment. After 46 % technical strain, i.e. 61 % true strain according to Equation (5.10), a cubic shape of the deformation sample is approached (Figure 5.13 c). Hence, the sample volume where dislocation motion on planes inclined in a 45° angle to the compression direction is essentially nil.

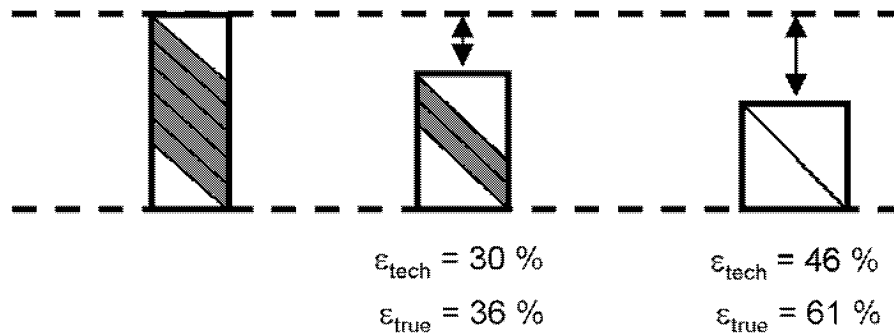


Figure 5.13: Illustration of the sample volume in which dislocation motion on planes inclined in a 45° angle to the compression direction is possible in dependence of the strain applied to the sample. The change of the length-to-diameter ratio was calculated for a three-dimensional sample.

In a work by Kabutoya *et al.* (2002) plastic deformation experiments on Al-Pd-Mn quasicrystals were performed applying a constant technical strain rate of $1.7 \times 10^{-4} \text{ s}^{-1}$. The experiments were performed up to very high true strains of about 90 %. Besides the hardening stage at the onset of plastic deformation and the softening stage after the yielding the transient to a third stage was observed between 20 and 40 % of strain. In the third stage hardening up to high strains was observed. At constant cross-head speed the true strain rate increases with increasing strain according to Equation 5.11, which leads to an increase of the flow stress. Furthermore, geometrical effects may lead to strong stress increase especially at high strain. Hence the conduction of plastic deformation experiments to very high strain may not produce meaningful results.

6. Generalizing discussion: The plasticity of icosahedral Zn-Mg-Dy and Al-Pd-Mn quasicrystals

6.1 Plastic deformation behaviour

For icosahedral Al-Pd-Mn quasicrystals, the constitutive-model approach comprehensively describes the dynamics of order and dislocation-density evolution during plastic deformation. The model successfully describes the additional hardening stage and the occurrence of a constant-flow-stress regime, which was observed for the first time in the extended strain-rate range in the present work. The constitutive-equation approach has also been applied for the description of Zn-Mg-Dy plastic deformation data by Feuerbacher (2002). Figure 6.1 shows experimental and computed stress-strain curves of a constant-strain-rate experiment at 10^{-5} s^{-1} and 520 °C. The calculated dislocation-density evolution is plotted in Figure 6.2 in comparison to experimental dislocation densities at different strain according to Figure 4.1 a.

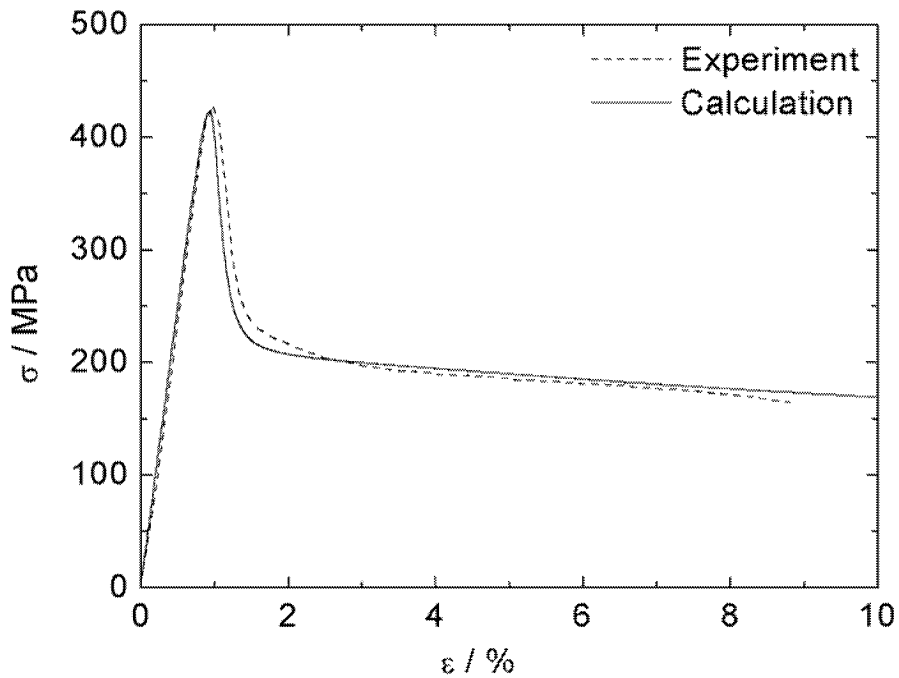


Figure 6.1: Experimental (dashed line) and calculated stress-strain curves (solid line, Feuerbacher 2002) of Zn-Mg-Dy deformed at a 520 °C and a strain rate of 10^{-5} s^{-1} .

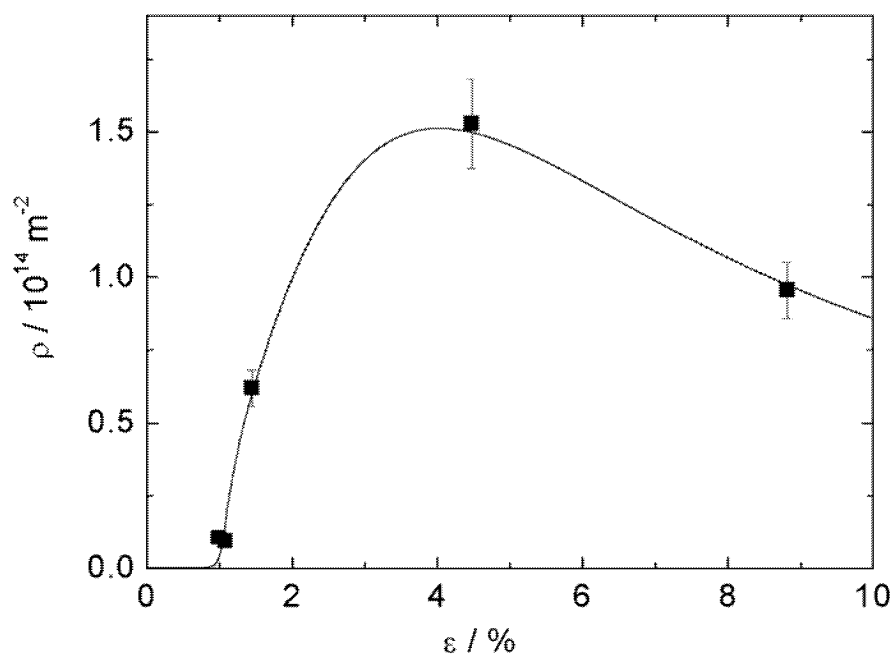


Figure 6.2: Experimental dislocation densities (squares) and calculated evolution of the dislocation density (line, Feuerbacher 2002) during a constant-strain-rate deformation of Zn-Mg-Dy at 520 °C and $\dot{\epsilon} = 10^{-5} \text{ s}^{-1}$

It can be observed that experimental data and computed curves are in good accordance. Yet, the model has not been applied to Zn-Mg-Dy plastic deformation experiments at various strain rates and temperatures, as it was done for Al-Pd-Mn in the present work. A detailed comparison of the parameters governing plastic deformation in Zn-Mg-Dy and Al-Pd-Mn is only reliable if the computations for Zn-Mg-Dy are extended to a wider range of experimental data, since the constitutive model approach involves a high number of unknown parameters in the case of Zn-Mg-Dy. However, it can be concluded that the constitutive model successfully describes the plastic deformation behaviour of Zn-Mg-Dy as well as for Al-Pd-Mn. In both materials plastic deformation depends on the interplay of dislocation storage and recovery and the strain-driven disordering and diffusion-driven reordering of the material. These processes generally lead to work softening at high strains. However, it has been shown that the dynamics of the evolution of the dislocation density and order parameter vary according to the temperature and strain rate. This leads at high strain rates and/or low temperature to an expansion of the hardening regime. At low strain rates and/or high temperatures, a structural steady state may be achieved, which leads to constant flow-stress levels.

In Zn-Mg-Dy no pronounced softening was observed during constant strain-rate experiments at 500 and 510 °C up to 7.5 and 10 % strain (cf. Figure 2.1 and 2.3). This behaviour contrasts to that of other quasicrystals at first glance (Chapter 2.3). However, it has been shown in Chapter 5.4 that the appearance of softening depends on the strain-rate and temperature range. A constant flow-stress level at low temperature, as it was observed at 500 and 510 °C, may be caused by conjoined hardening due to dislocation storage and structural softening. At 520 °C work softening after yielding occurs (Figure 6.1), which may be attributed to the decrement of Taylor-hardening as observed for Al-Pd-Mn. Therefore, work softening, directly observed after yielding, is a feature of quasicrystal plasticity, which is only

observed in a certain range of strain rate and temperature. It should not be regarded as a general feature of quasicrystal plasticity under any experimental conditions. More significant than the course of the stress-strain curve is the observation of the decrease of the dislocation density at high strains in Al-Pd-Mn (Schall *et al.* 1999) as well as in Zn-Mg-Dy (present work). The decrease of the dislocation density is observed due to recovery processes, which take place at high strains in the increasingly disordered material. The correlated evolution of dislocation density and disordering can therefore be regarded as a fundamental plastic property of icosahedral quasicrystals.

6.2 Microstructural plastic deformation properties

In Zn-Mg-Dy quasicrystals three types of planar defects were observed and discussed in the present work: antiphase boundaries, stacking faults, and phason defects. These defects appear in different proportions in samples that were prepared under various conditions, and they can be distinguished by their appearance under given imaging conditions.

In Zn-Mg-Dy quasicrystals antiphase boundaries were observed in heat-treated and deformed samples. It was shown, that Ostwald ripening of the domains takes place due to diffusional rearrangement of the structure. Al-Pd-Mn, as Zn-Mg-Dy, possesses a face-centred hyperlattice. Hence, from the structural point of view the formation of antiphase boundaries by the movement of partial dislocations should take place in that material as well. However, antiphase boundaries were not observed in Al-Pd-Mn quasicrystals. In this respect, the post-mortem microstructure of these quasicrystals is distinctly different.

A possible explanation for the absence of antiphase boundaries in deformed Al-Pd-Mn quasicrystals may be found in the difference in diffusion dynamics between Al-Pd-Mn and Zn-Mg-Dy. In works by Galler (2003) and Mehrer *et al.* (2003) the diffusion of Zn in Zn-Mg-Ho and of Zn and Ga in Al-Pd-Mn was studied using radiotracer diffusion. In the present work plastic deformation experiments and subsequent microstructural analyses were performed at typical temperatures of 500 °C and 760 °C for Zn-Mg-Dy and Al-Pd-Mn, respectively. The diffusion coefficients at these temperatures are $D = 3.4 \times 10^{-14} \text{ m}^2/\text{s}$ for Zn-Mg-Ho and $D = 2.1 \times 10^{-11} \text{ m}^2/\text{s}$ for Al-Pd-Mn (Galler 2003). Hence, diffusion is faster in Al-Pd-Mn by about three orders of magnitude. The diffusion behaviour was reported to be very similar in Zn-Mg-Ho and Zn-Mg-Y, hence it is expected to be similar in Zn-Mg-Dy as well (Galler 2003). It is suggested that fast diffusion in Al-Pd-Mn leads to rapid dissolution of antiphase boundaries, that, from the structural point of view, may exist shortly after creation. It has been shown that antiphase boundaries in Zn-Mg-Dy already reflect progressed Ostwald ripening in samples that were cooled at 300 °C h⁻¹ (Figure 2.14). The direct observation of antiphase boundaries in Al-Pd-Mn quasicrystals may only be possible in in-situ straining experiments at low temperature, i.e. in a temperature regime, where brittle fracture of the sample may occur.

The strong difference in the diffusion coefficient may also influence the mode of dislocation motion. It was shown in the present work that plastic deformation in Zn-Mg-Dy is mainly taking place by pure dislocation glide. Climb processes were shown to take place as well, but in a lower proportion. The higher diffusion mobility in Al-Pd-Mn, on the other hand, supports non-conservative dislocation mobility. TEM studies by Caillard *et al.* (2000, 2002a, 2002b) indicate that dislocation climb has to be considered a mode of deformation at high temperatures in Al-Pd-Mn. The analysis of moving dislocations in an in-situ TEM study (Feuerbacher *et al.* 2003c) provides direct evidence for dislocation climb during deformation.

6. Generalizing discussion: The plasticity of Zn-Mg-Dy and Al-Pd-Mn quasicrystals

Therefore, the difference in the appearance of preferential glide or climb in Zn-Mg-Dy and Al-Pd-Mn should not be interpreted as a fundamental difference in the mode of plastic deformation, but as a gradual difference on the background of a different diffusion dynamics.

The present results confirm the basic similarity of the plastic deformation processes in Al-Pd-Mn and Zn-Mg-Dy and furnish evidence that the plastic properties observed are characteristic for other icosahedral quasicrystals rather than just for both icosahedral phases investigated in the present work. Furthermore, it has been shown that the constitutive model successfully describes the complex deformation behaviour of quasicrystals in a wide experimental range. Therefore, it is assumed that the constitutive model universally describes the plastic deformation properties of other icosahedral phases.

7. Plasticity of Pd-Ni-Cu-P bulk metallic glass

7.1 Introduction

The lack of long-range order and the absence of sharp diffraction peaks are the main attributes of a class of materials called amorphous metals or metallic glasses. In good glass forming alloys like Pd-Ni-Cu-P (He *et al.* 1996) or Zr-based alloys (Peker and Johnson 1993, Inoue *et al.* 1993), large ingots of amorphous material can be produced by direct casting from the melt. Structurally, in a first approximation, metallic glasses can be interpreted as frozen liquids. An alternative interpretation of the structure as an assembly of microcrystals has been demonstrated not to be adequate (Cargill 1970).

A successful approach for the description of the structure of metallic glasses is the so-called dense random packing (DRP) approach of hard spheres. The DRP was initially studied by Bernal (1960) who characterized a mechanical model of single-sized spheres, arranged without translational symmetry. Although the average number of nearest neighbours and the interatomic distances are very similar to close-packed crystalline structures, the angular arrangements are different. In a later work by Frost (1982) it has been shown that most of the polyhedra formed by connection of the centres of neighbouring spheres are tetrahedra. While in a close-packed crystal (FCC or HCP) the ratio of tetrahedral to octahedral configurations is 2, Bernal (1964) determined the ratio of tetrahedral to octahedral configurations in a DRP as 15. The tetrahedral configuration of 4 spheres represents the configuration with the highest local density (cf. Spaepen 1981). The DRP can therefore be considered as the structure that maximizes the local density. Figure 7.1 illustrates local arrangements of a sphere surrounded by 12 equally-sized spheres. In a DRP icosahedral arrangements of atoms can be found, because these represent the densest arrangement of 20 vertex-sharing tetrahedra. In a face-centred cubic structure the arrangement of nearest neighbour atoms around a central atom is given by a cuboctahedron, i.e. 8 tetrahedra and 6 half-octahedra sharing a vertex (Figure 7.1 b).

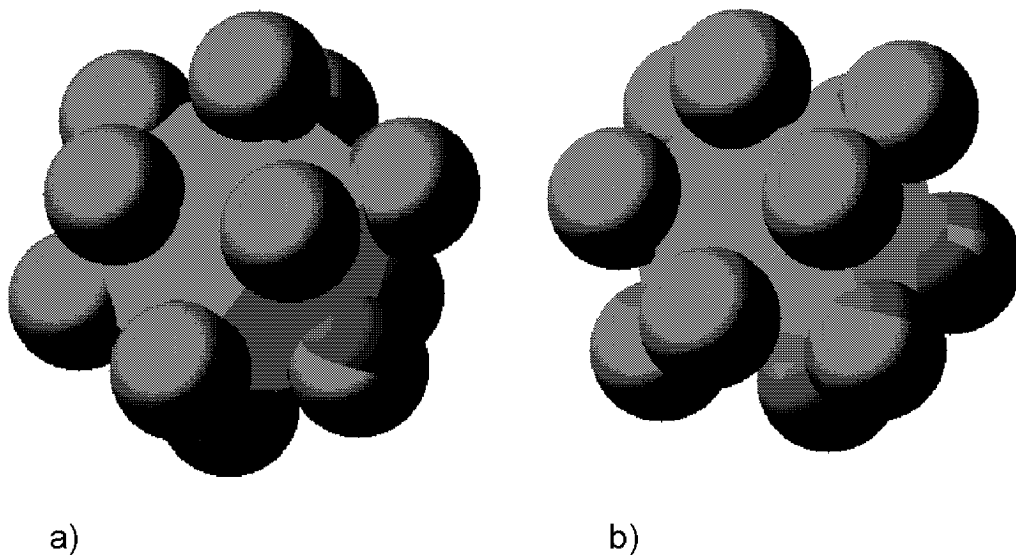


Figure 7.1: Local arrangement of a sphere surrounded by 12 spheres: (a) icosahedron, (b) cuboctahedron.

The lack of translational symmetry in amorphous materials, however, does not exclude a high degree of structural order. The chemical short range order in most amorphous alloys is very high, and the coordination numbers and distances are almost identical to those in crystalline intermetallic compounds of similar composition (Spaepen 1981). Alamgir (2001) studied short range order around the constituent atoms of Pd-Ni-P bulk metallic glass using extended X-ray absorption fine structure (EXAFS) and extended energy loss fine structure (EXELFS). The environment around the atoms was shown to be very similar to that of the binary Phosphides. The nearest neighbour distance is even reduced in the metallic glass.

7.2 Structural defects in metallic glasses

Plastic deformation in crystals and quasicrystals is governed by the motion of localized defects like dislocations or vacancies. However, the introduction of these defects into an amorphous structure in direct analogy to crystalline structures leads to strong difficulties. When a vacancy is introduced into an amorphous structure, e.g. by removing an atom during a molecular dynamics simulation (Bennett *et al.* 1979), it loses its identity by breaking up into smaller voids which eventually distribute over the whole system. This is an explicit difference to vacancies in crystals, which remain localized and keep their identity even during movement.

The introduction of a dislocation with a fixed Burgers vector into an amorphous structure is impossible because of the lack of translational and orientational symmetry. However, the existence of so-called generalized dislocations has been postulated by some authors (Gilman 1973, Li 1976). According to the definition of Gilman, local fluctuations of the length and magnitude of the Burgers vector can occur along the dislocation line. Hence, only an average Burgers displacement can be attributed to these dislocations. In a molecular simulation work by Chaudhari (1979), dislocations were introduced into an amorphous structure. This was done by cutting an amorphous monatomic cluster along a halfplane and displacing both parts of the cluster by a distance of the order of an atomic diameter. After static annealing the structure was studied visually and by stress analysis. It was shown that only screw-type dislocations are stable, while edge dislocations are unstable and dissolve. Furthermore the direct experimental observation of a dislocation in an amorphous metal would be difficult. Direct imaging by TEM is ruled out due to the absence of sharp reflections in the electron diffraction patterns. A positron annihilation study of deformed and undeformed amorphous metals by Chen and Chuang (1975) also gave no evidence for the existence of atomic scale dislocation cores in amorphous metals. Yet, there is no direct experimental evidence for the existence of dislocations in metallic glasses. Furthermore, the previous considerations indicate that the description of defects in amorphous materials in terms of dislocations and vacancies is not very successful.

The characterization of the atomic-scale structure, the dynamics of motion and the creation and annihilation of defects governing plastic deformation remains a challenging task. Widely used for the description of defects in amorphous structures is the free volume model (Cohen and Turnbull 1959), in which the defects governing plastic flow are density fluctuations with greater volumes than a critical value v^* . The defect concentration is described as

$$c_f \equiv \exp\left(-\frac{v^*}{v_f}\right) = \exp\left(-\frac{1}{x}\right), \quad (7.1)$$

where γ is a geometrical-overlap factor between 0.5 and 1, and v_f is the average free volume per atom. The quantity $x = v_f / \gamma v^*$ is termed reduced free volume.

The basic feature of a flow defect is that, under an externally applied shear stress, it undergoes a local shear transformation which is transferred elastically to the specimen surface to produce macroscopic strain. When enough free volume is collected locally, the atoms can, under the action of an applied stress, produce a local shear strain. Figure 7.2 illustrates a local shear transformation in a volume v_0 involving the motion of two atoms (hatched circles) and the rearrangement of the surrounding atoms. A local shear strain γ_0 is produced, which is transferred elastically to the specimen surface. The shear transformation is illustrated as joint motion of two atoms for reason of simplicity. Generally, it is believed that a joint motion of groups of 10 to 100 atoms takes place in a single shear event. During such a shear event additional free volume is created by squeezing atoms into holes of slightly smaller volumes than the atomic volume (cf. Spaepen 1977). The process of free volume creation by plastic deformation is described in more detail in Chapter 7.3.

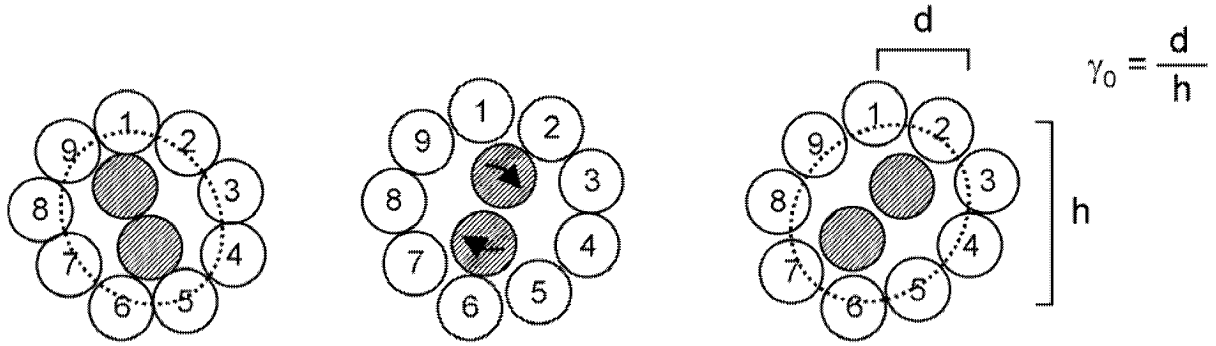


Figure 7.2: Simple model of a local shear transformation involving the motion of two atoms (hatched circles) in a volume v_0 (dotted ellipse). Under action of an applied stress a local shear γ_0 is produced.

7.3 Flow equations

Figure 7.3 illustrates the plastic deformation of a sample under an applied shear stress τ . Local shear transformations in an average volume v_0 produces a local shear strain γ_0 (cf. Figure 7.2). The local strain field is transferred elastically to the sample surface. The concentration of flow defects is given by c_f and can be expressed in terms of the free volume using Equation (7.1). If no stress is applied, the jump rate between the unstrained and strained position due to thermal fluctuations of an atom is given by k_f . Under an applied stress the jump rate between the unstrained and strained position is biased by the factor (Spaepen 1977)

$$\beta = \sinh\left(\frac{\varepsilon_0 v_0 \sigma}{2kT}\right), \quad (7.2)$$

where k is Boltzmann's constant, ε_0 is the local strain, and T is the absolute temperature. The stresses σ and strains ε are, as in the previous chapters, quantities referring to the uniaxial compression geometry of the experiments performed (cf. Appendix B). Since plastic deformation is a shear process, similar equations in terms of shear stresses τ and shear strains γ_0 are often found in the literature.

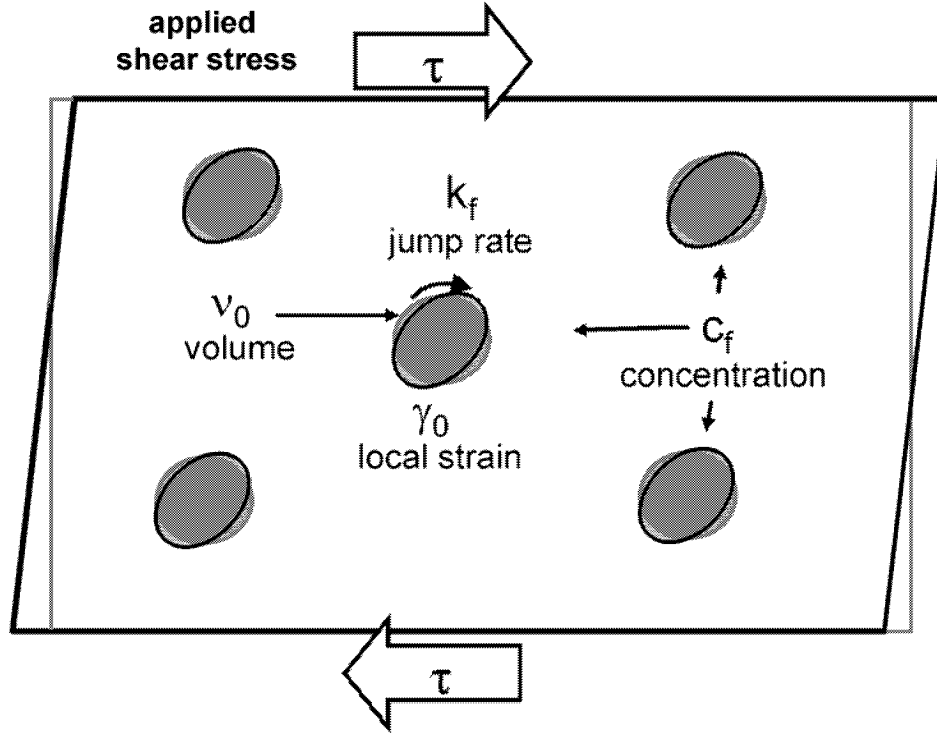


Figure 7.3: Schematic of plastic deformation of a sample under an external shear stress τ (see text.)

Expression (7.2) can be derived by rate theory (Spaepen 1977) and is given by the difference between the forward and backward jump rates between the unstrained and strained positions (cf. Figure 7.2) under action of an applied stress. The macroscopic strain rate can be written as (Spaepen 1977)

$$\dot{\epsilon}_{plast} = 2c_f k_f \frac{\epsilon_0 v_0}{\Omega} \sinh\left(\frac{\epsilon_0 v_0 \sigma}{2kT}\right), \quad (7.3)$$

where Ω is the atomic volume. The product $\epsilon_0 v_0$ can be interpreted as an activation volume of the local jump process. Expression (7.3) originates from a general flow equation which is an analogue to the Orowan equation for dislocation motion in crystals. The strain rate $\dot{\epsilon}_{plast}$ expressed by Equation (7.3) represents the plastic strain rate, i.e. a strain rate referring to plastic irreversible straining.

If the stress is small, i.e. $\sigma < 2kT/\epsilon_0 v_0$, the hyperbolic-sine function can be approximated by its argument

$$\dot{\epsilon}_{plast} = \frac{c_f k_f (\epsilon_0 v_0)^2}{\Omega kT} \sigma. \quad (7.4)$$

In this regime the flow is newtonian viscous, since $\dot{\epsilon}_{plast} \propto \sigma$. The viscosity is defined by

$$\eta \equiv \frac{\sigma}{\dot{\epsilon}_{plast}} \approx \frac{\Omega kT}{c_f k_f (\epsilon_0 v_0)^2}. \quad (7.5)$$

Annihilation of flow defects

Above the melting temperature T_m the liquid phase of a glass forming melt is in stable equilibrium. The free volume is in an equilibrium condition. When the temperature decreases below T_m , the free volume decreases rapidly, resulting in a rise of the viscosity (see Equation 7.5). When the viscosity reaches a certain value, the necessary configurational rearrangements kinetics to come to structural equilibrium are too slow; the material can then be considered configurationally frozen. The temperature at which this takes place depends on the cooling rate. By definition, the glass transition temperature T_G corresponds to an equilibrium viscosity of 10^{12} Pas. Below this temperature the atomic jump rate is so low that the material essentially behaves like a solid. However, annealed at temperatures below the glass transition temperature T_G , the amorphous material undergoes a structural relaxation, during which the defect concentration continuously decreases. The annihilation of defects takes place by a *bimolecular* process, the rate of which can be described as

$$\left. \frac{dc_f}{dt} \right|^- = -k_r c_f^2, \quad (7.6)$$

where k_r is a rate constant. The validity of this Ansatz has been verified by viscosity measurements during relaxation of the glass. In these measurements the viscosity, which at low stresses is inversely proportional to c_f (Equation 7.5), increases *linearly* with time (Taub and Spaepen 1980, Tsao and Spaepen 1985), as implied by Equation (7.6). Duine *et al.* (1992) have shown that during isothermal annealing at temperatures close to T_G , the viscosity of amorphous Pd-Ni-P reaches a saturation value. Since $\eta \propto c_f^{-1}$, the authors have concluded that the defect concentration reaches a metastable equilibrium defect concentration c_{eq} . It was found by Duine *et al.* (1992) from fitting viscosity and calorimetric data, that the change of c_f towards equilibrium can be well described by the rate equation

$$\left. \frac{dc_f}{dt} \right|^- = -k_r c_f (c_f - c_{eq}). \quad (7.7)$$

Bimolecular annihilation of defects also occurs in covalently bound amorphous materials (Lille 1933, Roberts *et al.* 1965, Witvrouw *et al.* 1993), where it is plausibly explained by the mutual annihilation of pairs of dangling bonds. In amorphous metals, however, the bimolecular annihilation mechanism is less obvious; it may be related to the formation of holes that are sufficiently oblate to collapse and thereby decrease their volume elastically (Spaepen 1994).

Creation of flow defects

The shear deformation of a random close-packed structure is accompanied by dilatation, as is well known from soil mechanics (Taylor 1948). Accordingly, the flow events governing plastic deformation of amorphous metals are accompanied by dilatation. The corresponding increase of free volume implies an increase of the number of flow defects. This mechanism has been invoked to explain the strain softening observed at high stresses in amorphous metals, which leads to the formation of shear bands (Spaepen and Turnbull 1974, Spaepen 1977, Steif *et al.* 1982). For the creation of flow defects a number of descriptions have been proposed (Spaepen and Turnbull 1974, Spaepen 1977, Argon 1979, de Hey *et al.* 1998). Most recently, de Hey *et al.* (1998) assumed that each flow event produces a specific amount of free volume. For the free-volume production rate they write

$$\left. \frac{dx}{dt} \right|^+ = a_x \dot{\epsilon}, \quad (7.8)$$

which, using Equation (7.1), translates to

$$\left. \frac{dc_f}{dt} \right|^+ = a_x \dot{\epsilon} c_f (\ln c_f)^2 \quad (7.9)$$

for the flow-defect production rate. Equation (7.9), together with the bimolecular annihilation Equation (7.7), was used by de Hey *et al.* (1998) to describe tensile stress-strain curves of $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$ metallic glass ribbons. The authors determined defect concentrations by calorimetric measurements at various strains and showed that a steady state, showing equal creation and annihilation rates, is established at large strains, independent of the initial state of the glass. The lower part of Figure 7.4, taken from the work of de Hey *et al.* (1998), shows five overlapping stress-strain curves of samples deformed under the same constant strain rate up to different amount of strain. The final amount of strain of the respective curves is indicated by an open circle. The upper part shows the free volume as a function of strain according to calorimetric measurements of the samples after deformation. The increase of free volume with increasing amount of strain is obvious.

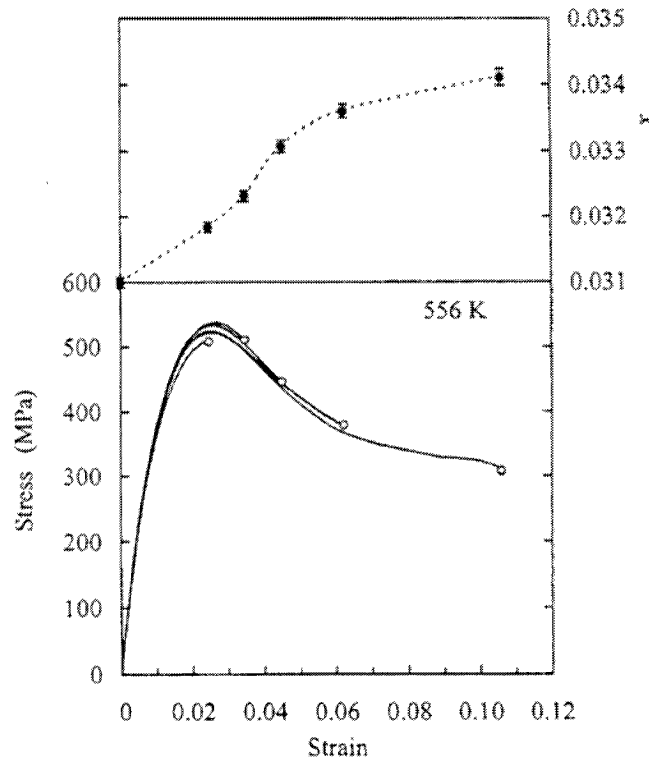


Figure 7.4 Lower part: stress-strain curves for five samples of amorphous Pd-Ni-P, measured at 556 K and $\dot{\epsilon} = 1.7 \times 10^{-4} \text{ s}^{-1}$. Upper part: reduced free volume after deformation as function of strain. The dotted line is a guide to the eye (from de Hey *et al.* 1998).

7.4 Plastic deformation behaviour

Anelastic behaviour

As discussed in the previous section, a metallic glass sample shows plastic behaviour, i.e. irreversible straining, which is described by the flow Equation (7.3). In a constant-true-stress creep experiment the strain rate $\dot{\epsilon}$ is constant if the flow-defect concentration c_f remains constant. Besides the plastic behaviour, metallic glass samples show elastic behaviour, i.e. fully reversible, linear and instantaneous straining, and anelastic behaviour, i.e. time dependent and reversible straining (Murata *et al.* 1976). The anelastic response is a transient behaviour resulting from a sudden stress change. The anelastic part ϵ_A of the total strain can be described by a sum of exponential-decay functions $\epsilon_A = \sum_j \epsilon_j^A (1 - e^{-t/\tau_j})$ (Berry and Pritchett 1973, Argon and Kuo 1980, Taub and Spaepen 1981), where t is the time, τ_j is a series of time constants and ϵ_j^A is the anelastic strain part at the appropriate time constant. The anelastic response to load changes can be seen in Figure 7.5.

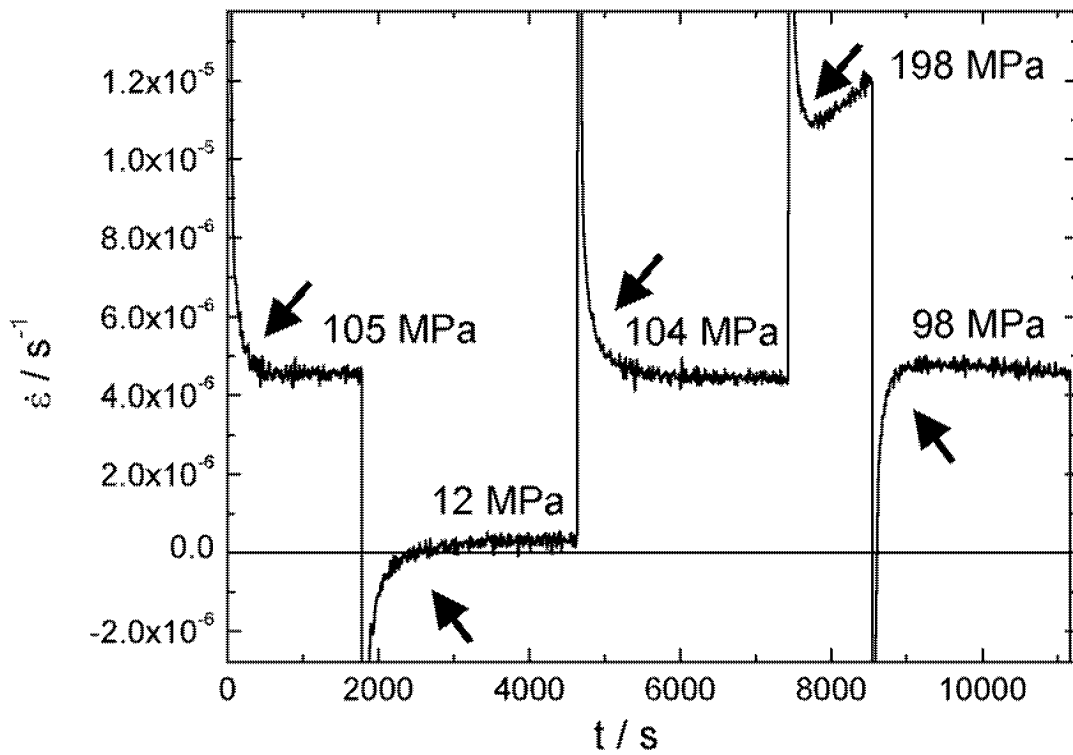


Figure 7.5: The creep curves show $\dot{\epsilon}$ as a function of time. Load changes were performed. Arrows indicate the anelastic response to load changes.

When the sample is loaded to 105 MPa, the strain rate, decreasing from high values, approaches a constant strain rate of $4.6 \times 10^{-6} \text{ s}^{-1}$ after about 500 s. This value corresponds to the constant plastic strain rate, as described by Equation (7.3). If a load change from high to low load is performed, the anelastic response is reversed, i.e. the strain rate converges to the plastic strain rate from lower values, as can be seen after the load change from 198 to 98 MPa. The anelastic response can even result in negative strain rates as is observed after the load change from 105 to 12 MPa. For accurate determinations of the plastic strain rate the anelastic contribution has to be negligibly small. This implies the conduction of creep experiments of sufficiently long duration, such that the plastic strain rate can be accurately determined after the decay of the anelastic response.

Homogeneous and inhomogeneous deformation

At low stresses and high temperatures plastic deformation is homogeneous, i.e. each volume element of the specimen equally contributes to the strain (cf. Spaepen 1981). The sketch in the middle left part of Figure 7.6 illustrates homogeneous deformation on the shape of a sample in a tensile test: the sample becomes uniformly longer and thinner.

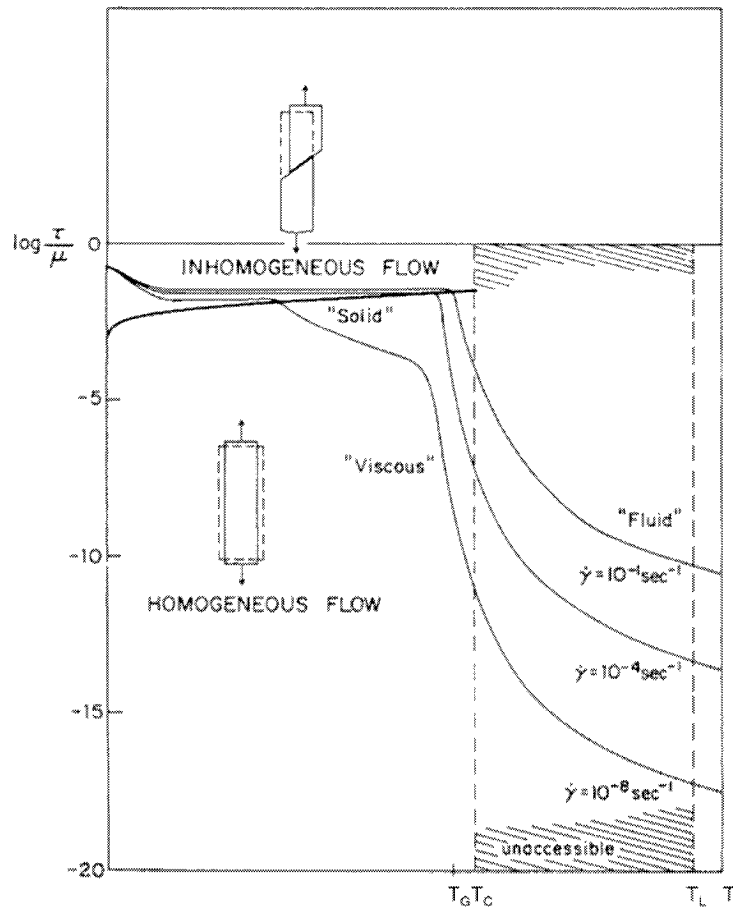


Figure 7.6: Schematic deformation map for an amorphous metal, showing the temperature and stress regimes for homogeneous and inhomogeneous deformation (from Spaepen 1977). Contours of different shear rates $\dot{\gamma}$ are plotted against temperature and normalized shear stress. τ is the shear stress and μ is the shear modulus. T_G , T_C , and T_L are the glass transition temperature, the crystallization temperature, and the liquidus temperature, respectively.

At high stresses and low temperatures inhomogeneous flow occurs. The strain is then localized in a number of very thin slip bands. The formation of a slip band is a very rapid process which is illustrated in Figure 7.6 for a specimen plastically deformed in tension. The band nucleates at a surface-stress singularity, e.g. a crack at the edge of the sample, and propagates through the sample at an angle close to 45° with respect to the tensile axis. The shear band consists of amorphous material that has undergone a structural change, producing local softening. The softening is a result of decreasing viscosity due to a rapid increase of the density of flow defects. If diffusion and structural relaxation cannot impede localization, this is an amplifying feedback process: A local rise of flow defects determines higher local strain which produces local disordering and thus additional flow defects. A schematic deformation map is given in Figure 7.6. Strain-rate contours are plotted for normalized stress and temperature. The temperature regime between the crystallization temperature T_C and the liquidus temperature T_L is inaccessible to experimental investigations of the amorphous state, since here the amorphous state is no longer stable. Near and below the glass transition temperature T_G the mode of plastic deformation and the strain rate depends on the temperature and the applied stress. The strain-rate contours in the inhomogeneous flow region are closely spaced, illustrating that the strain rate is highly stress sensitive, i.e. the stress exponent $m = \frac{\partial \ln \dot{\epsilon}_{plast}}{\partial \ln \sigma}$ is large. Values as high as $m = 30$ were measured for Pd-Si by Murata *et al.* (1978). In the homogeneous flow regime at low stresses, plastic flow is newtonian viscous, i.e. $m = 1$.

7.5 Experimental procedure

Metallic glass samples of composition $\text{Pd}_{41}\text{Ni}_{10}\text{Cu}_{29}\text{P}_{20}$ were provided by J. Schroers (Californian Institute of Technology) and D. M. Herlach (Deutsches Zentrum für Luft- und Raumfahrt). Samples of approximately $5 \times 2 \times 2 \text{ mm}^3$ in size were cut from the metallic glass casts. The faces were prepared by grinding and polishing. The surfaces, in contact with the compression anvils, were aligned accurately parallelly and were ground on a glass plate using diamond paste to avoid any concavity of the surface. Before the mechanical testing, some of the samples were annealed at the temperature of the experiment to ensure a high degree of structural relaxation.

The plastic deformation tests were carried out in a modified Zwick Z050 uniaxial testing machine under compression (Appendix B). Creep deformation was performed under constant true stress, i.e. the load, L , was controlled to take into account the change of the specimen cross section upon straining. For homogeneous plastic deformation at constant volume the true stress is then given by

$$\sigma_{true} = \frac{L}{A_0}(1 - \epsilon_{tech}), \quad (7.10)$$

where A_0 is the initial specimen cross section and ϵ_{tech} is the uniaxial technical strain. The creep experiments were performed by a stepwise increase of the load. The duration of the individual creep tests was chosen much longer than the decay time of the anelastic response arising from the load changes.

7.6 Results

Figure 7.7 shows creep curves taken at 550 K and constant true stresses of 30, 60, 90, 119 and 148 MPa. Before mechanical testing the sample was annealed for 5×10^5 s at 550 K. After the decay of the anelastic response due to the change of the creep stress, constant creep rates are approached within the accuracy of measurement. The strain rate peaks in Figure 7.7 correspond to the loading steps at 10^{-4} s $^{-1}$ between the creep experiments. These creep curves demonstrate the high sensitivity of measurement that was achieved at very low strain rates.

The stress dependence of the creep rates at 550 K is plotted as full squares in Figure 7.8. The numbers indicate the sequence of the creep experiments. At low stresses a linear stress-strain dependence is found; in this range plastic flow is newtonian viscous (cf. Equation (7.4)). At higher stresses the stress exponent m is greater than unity.

Up to 225 MPa, the strain rate remains constant over the duration of a single experiment, between 1.4×10^5 to 1.2×10^4 s. At the highest stress value of 255 MPa, the creep rate increases from 2.5×10^{-7} to 4.2×10^{-7} s $^{-1}$ over the experiment duration of 8×10^4 s. The square in Figure 7.8 indicates the initial strain rate in the creep experiment at 255 MPa, the arrow indicates the increase of the strain rate with time. The creep curve for that stress is shown in Figure 7.9 as a solid line. After an anelastic response of approximately 8000 s following the stress change, the curve shows a continuous increase of the creep rate.

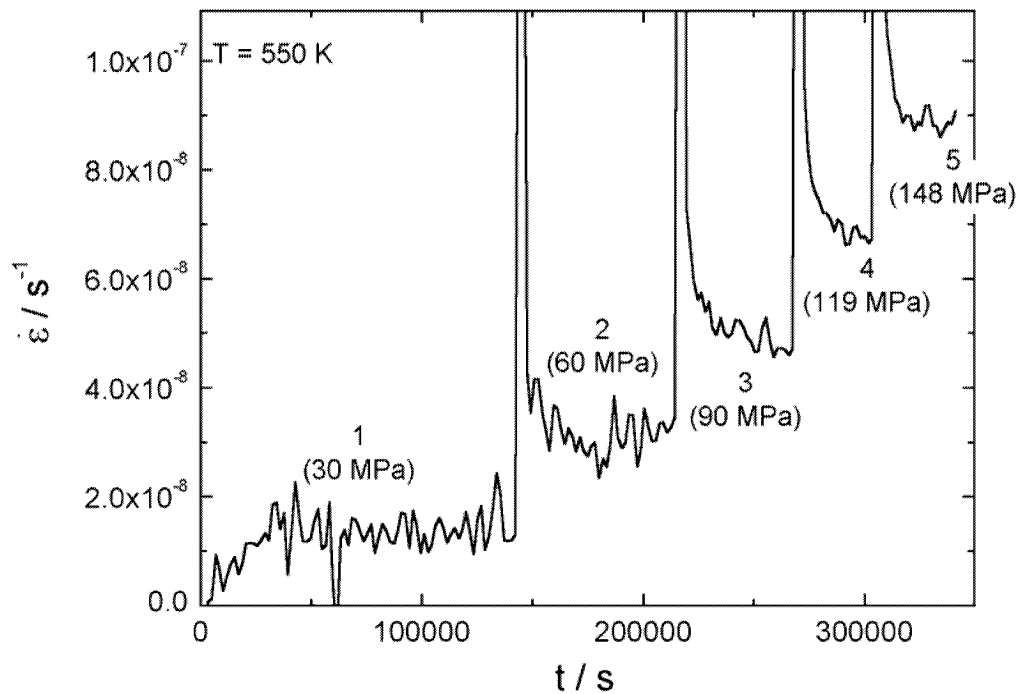


Figure 7.7: Creep curves at 550 K at constant true stresses of 30, 60, 89, 119 and 148 MPa.

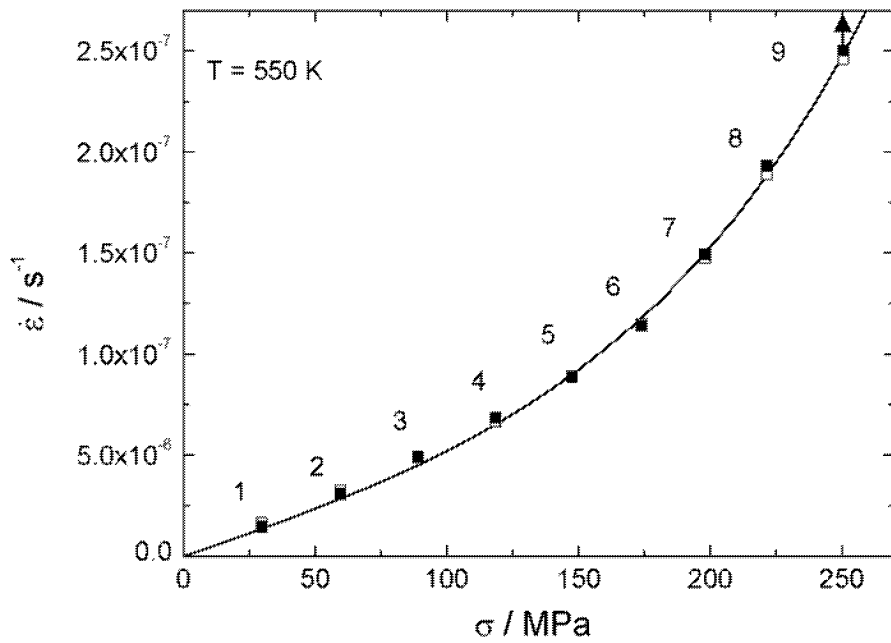


Figure 7.8: Experimental (full squares) and computed (open squares) stress dependence of the creep rates at 550 K. The arrow indicates an increase of the creep rate with time in the creep experiment at 255 MPa. Up to 225 MPa, the measured strain rate remains constant. The solid line is a fit to Equation (7.3). The numbers indicate the sequence of the creep experiments.

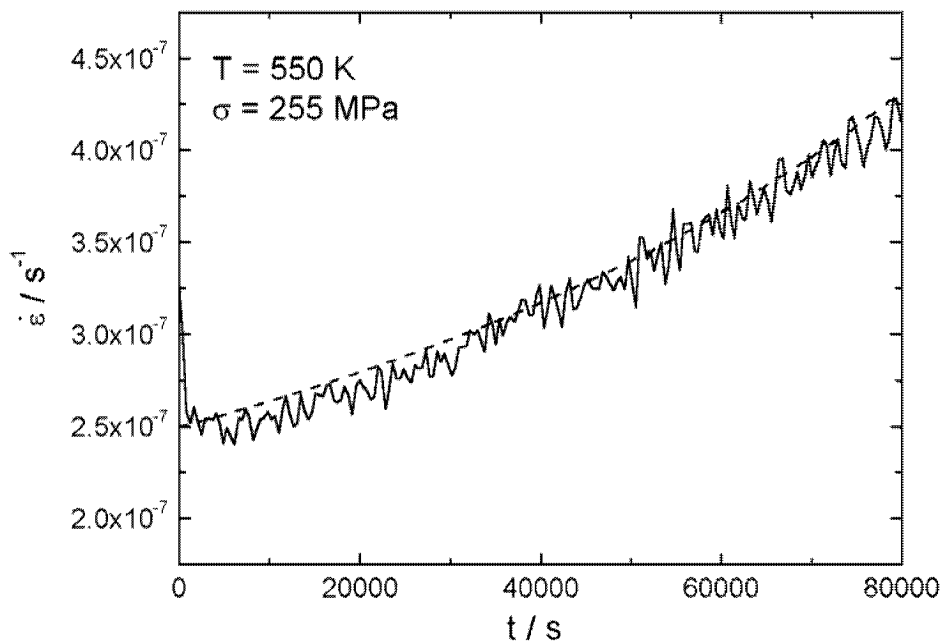


Figure 7.9: Experimental (solid line) and computed (broken line) creep curve at 550 K and a stress of 255 MPa.

The line in Figure 7.8 represents a fit of Equation (7.3) to the data points. The best fit is obtained with $\varepsilon_0 v_0 = (141.6 \pm 3.2) \text{ \AA}^3$ and a prefactor $2k_f c_f \varepsilon_0 v_0 \Omega^{-1} = (4.85 \pm 0.24) \times 10^{-8} \text{ s}^{-1}$. Nevertheless, a closer inspection reveals a systematic deviation of the experimental data from the fitted curve. The first four data points show slightly larger strain rates while the fifth to seventh data point show slightly smaller strain rates than those predicted by Equation (7.3). Since the defect density c_f increases at high plastic strain rates according to Equation (7.9), the prefactor in Equation (7.3) is no longer constant. Therefore, it is assumed that a more reliable fit to the data is obtained if only the lowest strain-rate values are taken into account. For the first four strain-rate values the best fit is obtained using the parameters $\varepsilon_0 v_0 = (126.3 \pm 11.2) \text{ \AA}^3$ and $2k_f c_f \varepsilon_0 v_0 \Omega^{-1} = (5.97 \pm 0.65) \times 10^{-8} \text{ s}^{-1}$.

The stress dependence of the creep rates at $T = 555$ and 565 K at low stresses is plotted as full squares in Figure 7.10 a and b, respectively. The numbers indicate the sequence of the creep experiments. During the creep experiments 1-6 in Figure 7.10 a, the strain rates remain constant. A slight increase of the creep rate was recorded in creep experiment 7, while in experiment 8 a strong increase could be observed. This is indicated by arrows in Figure 7.10 a.

Likewise in Figure 7.10 b an increase of the creep rate was recorded in creep experiment 9, during the other creep experiments the creep rate remained constant. The lines indicate a fit of Equation (7.3) to all the experimental data points. For $T = 555$ K the best fit to all creep rates is obtained with $\varepsilon_0 v_0 = (152.0 \pm 10.8) \text{ \AA}^3$ and a prefactor $2k_f c_f \varepsilon_0 v_0 \Omega^{-1} = (3.5 \pm 0.4) \times 10^{-7} \text{ s}^{-1}$ and $\varepsilon_0 v_0 = (143.8 \pm 2.0) \text{ \AA}^3$ and $2k_f c_f \varepsilon_0 v_0 \Omega^{-1} = (4.6 \pm 0.1) \times 10^{-6} \text{ s}^{-1}$ for $T = 565$ K, respectively.

Figure 7.11 shows an Arrhenius plot of $1/\eta$ according to Equation (7.5). From the slope of the linear fit, an apparent activation energy $E = 9.27$ eV was calculated.

A closer inspection of the data points in Figure 7.10 a again reveals that the creep rates of experiments 1-3 are higher than the fit curve. After the low-stress creep experiment 4, the creep rates in experiments 5 and 6 are lower than the fit curve but approach the fit curves in the subsequent experiments 7 and 8. A similar systematic deviation can be observed during the creep experiments at 565 K shown in Figure 7.10 b.

Figure 7.12 shows experimental creep curves at 397 , 537 and 636 MPa and a temperature of 550 K as a solid line. During creep at 397 MPa a slight increase of the creep rate from 2.4×10^{-6} to $2.7 \times 10^{-6} \text{ s}^{-1}$ over 2000 s was recorded. At 537 MPa the strain rate changed from a minimum value of 6.1×10^{-6} after the decay of the anelastic response to $8.5 \times 10^{-6} \text{ s}^{-1}$ within 900 s. The creep experiment at the highest stress value of 636 MPa shows strongly accelerating creep. An increase of the strain rate from 1.5×10^{-5} to $8.1 \times 10^{-4} \text{ s}^{-1}$ was observed. The creep curve shows a concave curvature on the logarithmic scale, i.e. the dependence of the creep rate over time is faster than an exponential increase. During this experiment, the sample was continuously observed by means of a video camera.

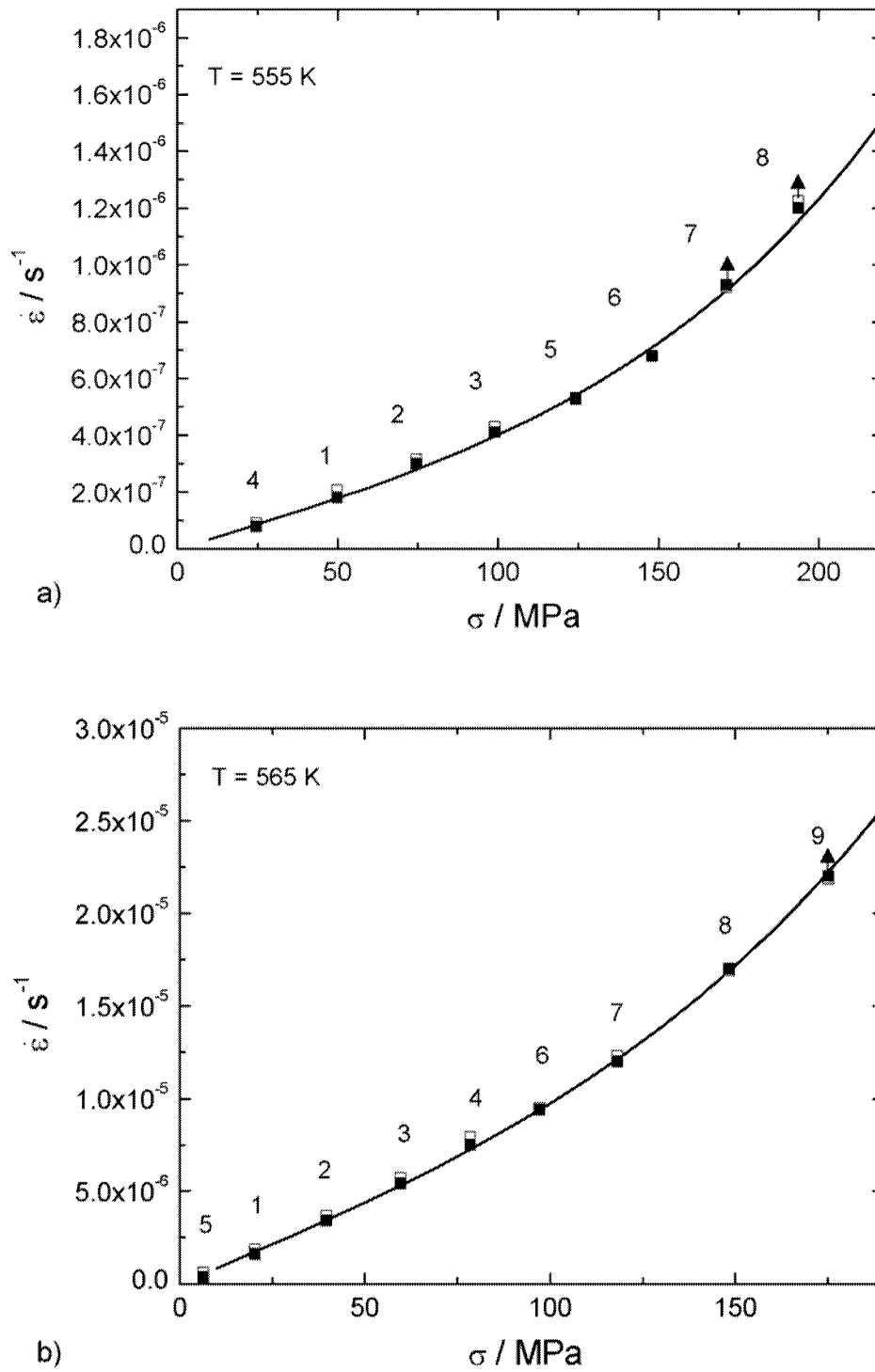


Figure 7.10: Experimental (full squares) and computed (open squares) stress dependence of the creep rates at (a) 555 K and (b) 565 K, respectively. The arrows indicate an increase of the creep rate with time. The solid lines are fits to Equation (7.3). The numbers indicate the sequence of the creep experiments.

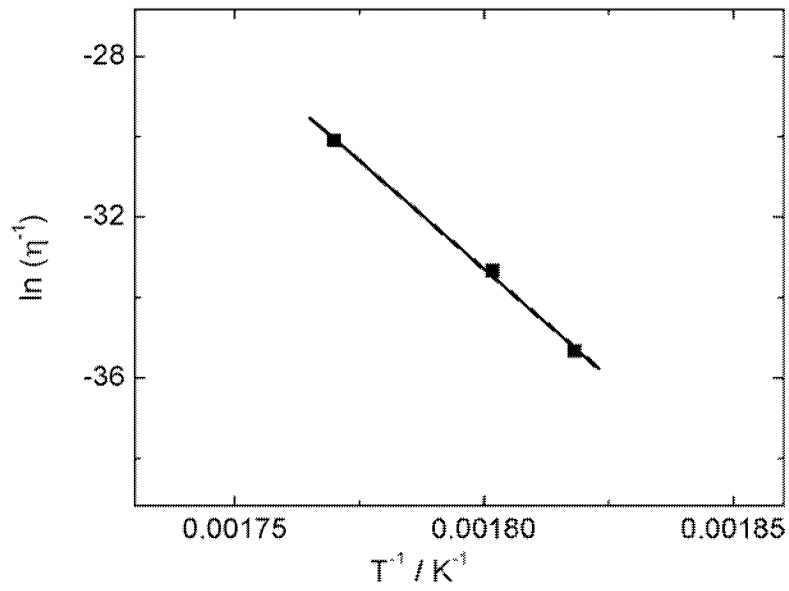


Figure 7.11: Arrhenius plot of $1/\eta$. The line is a linear fit to the data points.

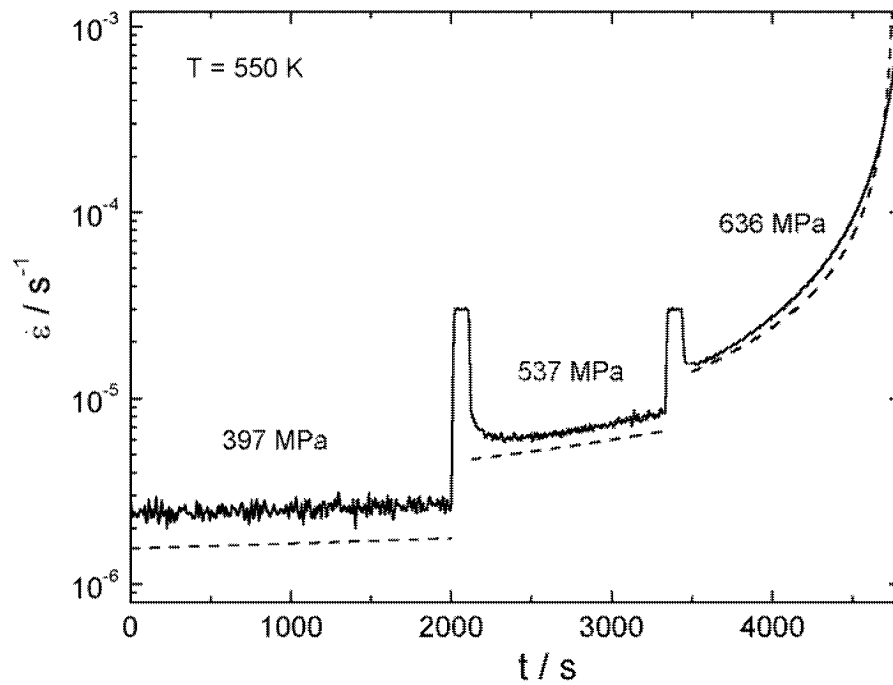


Figure 7.12: Experimental (solid line) and computed (broken line) creep curves at 397, 537 and 636 MPa and $T = 550$ K.

Figure 7.13 shows four still images at different times according to Figure 7.12. The cuboid-shaped compression sample is situated between two compression anvils as sketched on the left-hand side of Figure 7.13. An arrow indicates the view direction of the still images. The sample is oriented with one edge to the camera so that two side faces can be seen. During the last seconds the sample shows a little buckling but the deformation is still homogeneous. The formation of a shear band is not observed. Sample fracture occurred at the end of the experiment on a fracture plane inclined in almost 45° angle to the compression direction. The fracture surface shows the typical vein pattern of shear fracture (Figure 7.14). The vein pattern occurs due to an instability in the motion of the interfaces between the low-viscosity layer and the air. This phenomenon was first described by Taylor (1958) and applied to the fracture phenomenon by Spaepen (1975). According to these visual observations a shear band can have formed only during the very last instant of the test, leading to immediate fracture. Plastic deformation during all of the experiment, therefore, took place in the homogeneous mode.

Figure 7.15 shows experimental creep curves at 111, 250, 286 and 303 MPa and $T = 565$ K as solid lines. As in Figure 7.12, $d\dot{\epsilon}/dt$ increases with increasing stress.

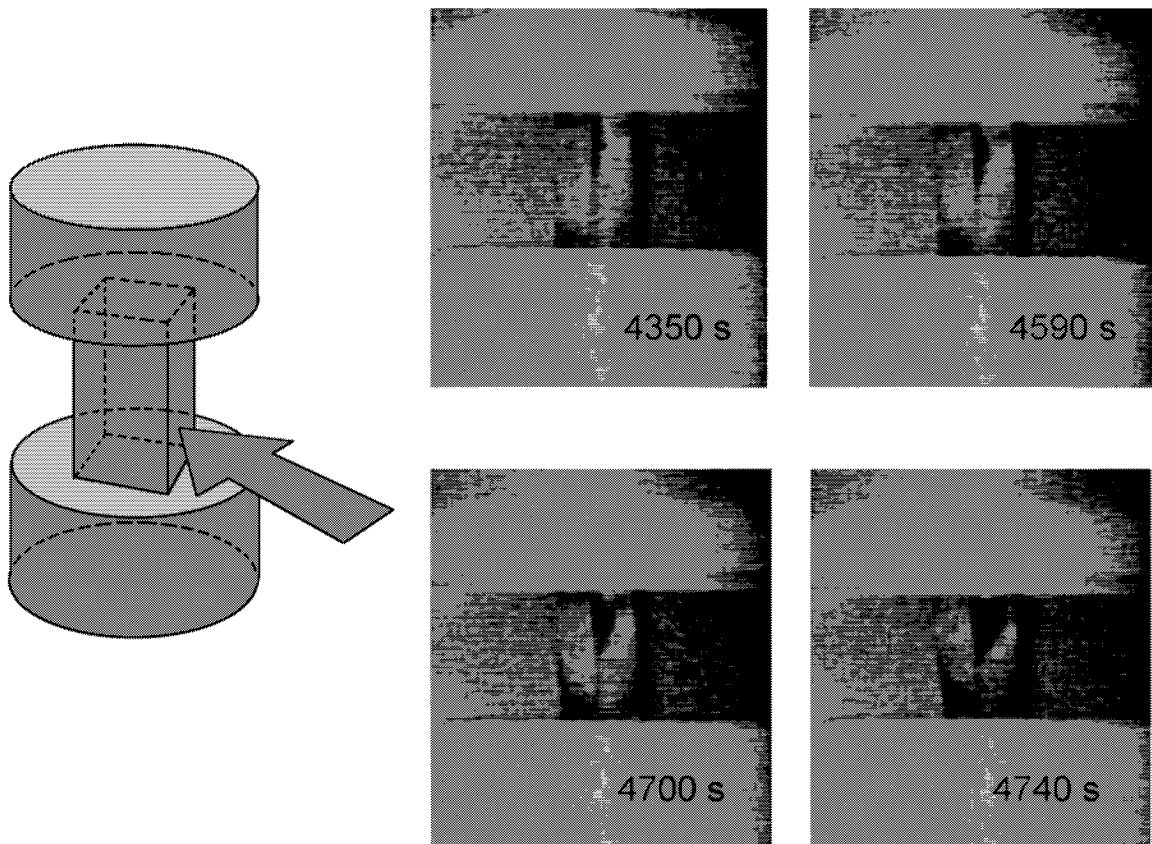


Figure 7.13: Still images, taken from a video sequence of the creep experiments according to Figure 7.12. The cuboid-shaped compression sample is situated between two compression anvils as sketched on the left-hand side. An arrow indicates the view direction of the still images. The sample is oriented with one edge to the camera so that two side faces can be seen.

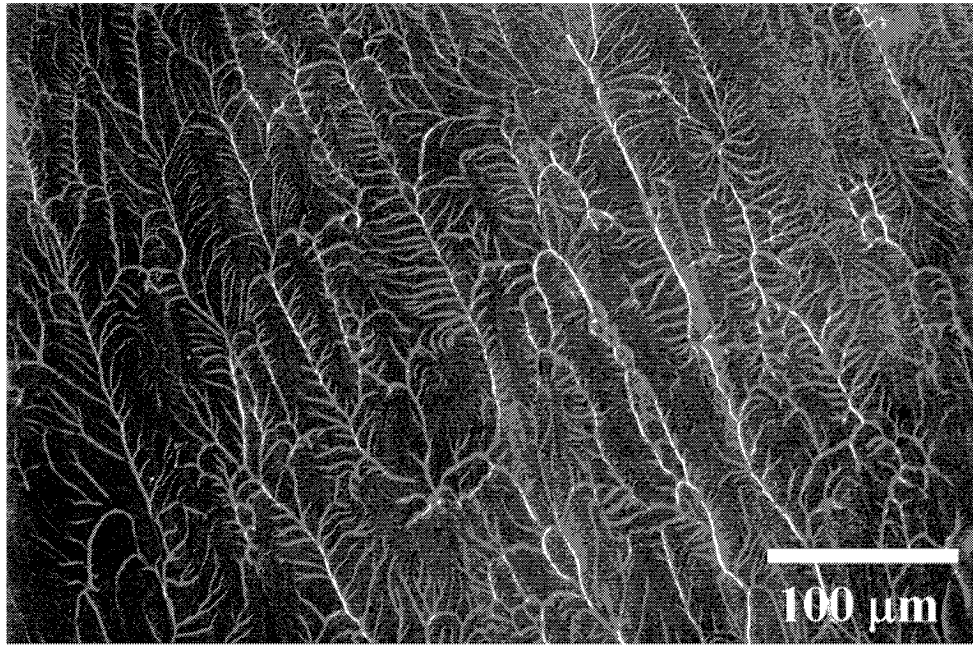


Figure 7.14: Fracture surface of a sample showing the typical vein pattern of shear fracture.

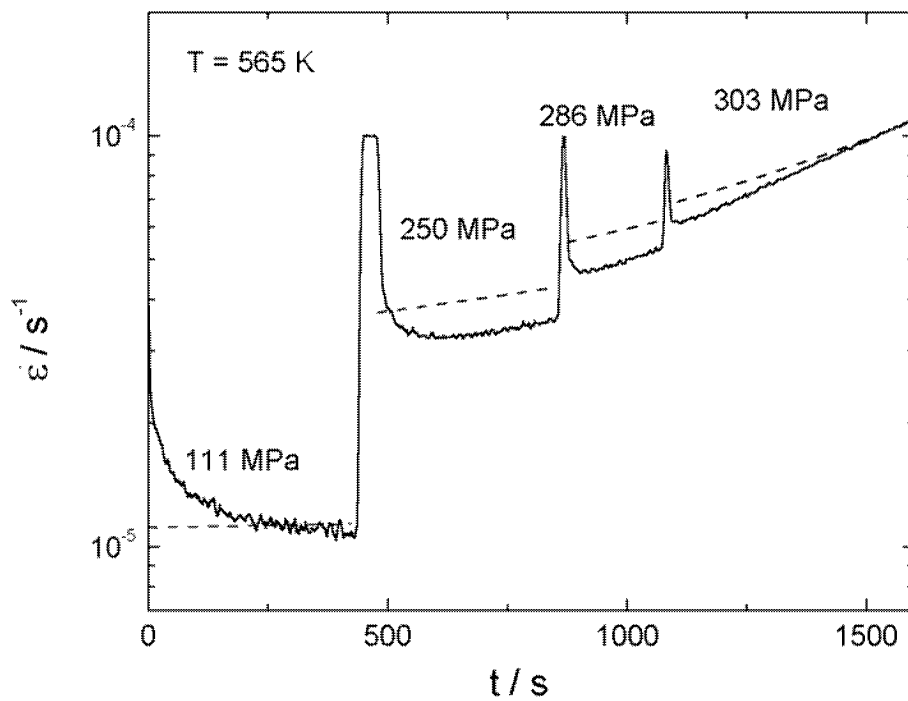


Figure 7.15: Experimental (solid line) and computed (broken line) creep curves at 111, 250, 286 and 303 MPa and $T = 565$ K.

Computation of creep curves

The computation of creep curves was performed by two subsequent steps. In a first step the experimental creep curves at 550 K (Figures 7.8, 7.9, 7.12) were computed using the defect-creation Equation (7.8) according to de Hey *et al.* (1998). By means of this model satisfying computations of creep curves were not possible using one set of parameters for all stress ranges. Hence, in a second step the model was modified in a way that a description of creep curves in all stress ranges became possible using one set of parameters. Furthermore, the modified model was applied to experimental creep curves at 550, 555, and 560 K.

The evolution of the defect concentration during the creep tests was calculated by numerical integration of Equations (7.6) and (7.9). Since the production rate of flow defects is small at low stresses, the value $\varepsilon_0 v_0$ was taken from the fit of Equation (7.3) to the first four experimental creep rates. The atomic volume was taken as $\Omega = 13.2 \text{ \AA}^3$ (Lu *et al.* 2000). The initial defect concentrations were chosen according to de Hey *et al.* (1998) as 1.7×10^{-14} and 3.2×10^{-14} for the chosen pre-annealing times of 5×10^5 and 8×10^4 s, respectively. With the values for c_f , the parameter k_f can be obtained from the prefactor of the fit of Equation (7.3) to the first four data points. The remaining free parameters, k_r and a_x , were adjusted to fit the complete set of data points at 550 K as it is shown in Figures 7.8, 7.9, and 7.12. The parameters k_r and a_x could be varied within narrow limits (less than 20 %). The complete set of parameters is given in Table 7.1. The experimental curves are fitted with constant parameter values for $\varepsilon_0 v_0$, k_f , k_r . However, reasonable fits to the experimental creep curves can only be achieved if the parameter a_x is varied according to the range of creep stresses. With increasing creep stress a_x is found to increase. The computed evolution of the defect concentration shows that c_f even at low creep stress is not constant. Starting with the defect concentration 1.7×10^{-14} , c_f decreases to a value of 1.44×10^{-14} after the first creep experiment and reaches a minimum value of 1.32×10^{-14} after the fourth creep experiment. At higher stresses c_f increases.

	30 to 225 MPa	255 MPa	397 to 636 MPa
$\varepsilon_0 v_0 / \text{\AA}^3$	126	126	126
k_f / s^{-1}	2.3×10^5	2.3×10^5	2.3×10^5
k_r / s^{-1}	9×10^7	9×10^7	9×10^7
a_x	6.5×10^{-3}	1.25×10^{-2}	1.75×10^{-2}

Table 7.1: Parameters used to fit the creep data at 550 K; $\varepsilon_0 v_0$: activation volume (Equation (7.3)); k_f : jump frequency of the flow defects (Equation (7.3)); k_r : rate constant for bimolecular annihilation of the defects (Eq (7.6)); a_x : proportionality constant in the production of free volume (Eqs. (7.8) and (7.9)).

In a second step the computation of creep curves was applied to creep experiments at 550, 555, and 565 K. The annihilation of flow defects shows different behaviour at high temperatures. At 550 K the viscosity is shown to increase linearly with time within the timescale of the experiment, which can be described according to the defect-annihilation Equation (7.6). At 555 K a long time creep experiment was performed at 15 MPa (Figure 7.16) which is a low stress and hence corresponds to a low defect-creation rate. The evolution of the viscosity shows a saturation behaviour, which cannot be described by Equation (7.6).

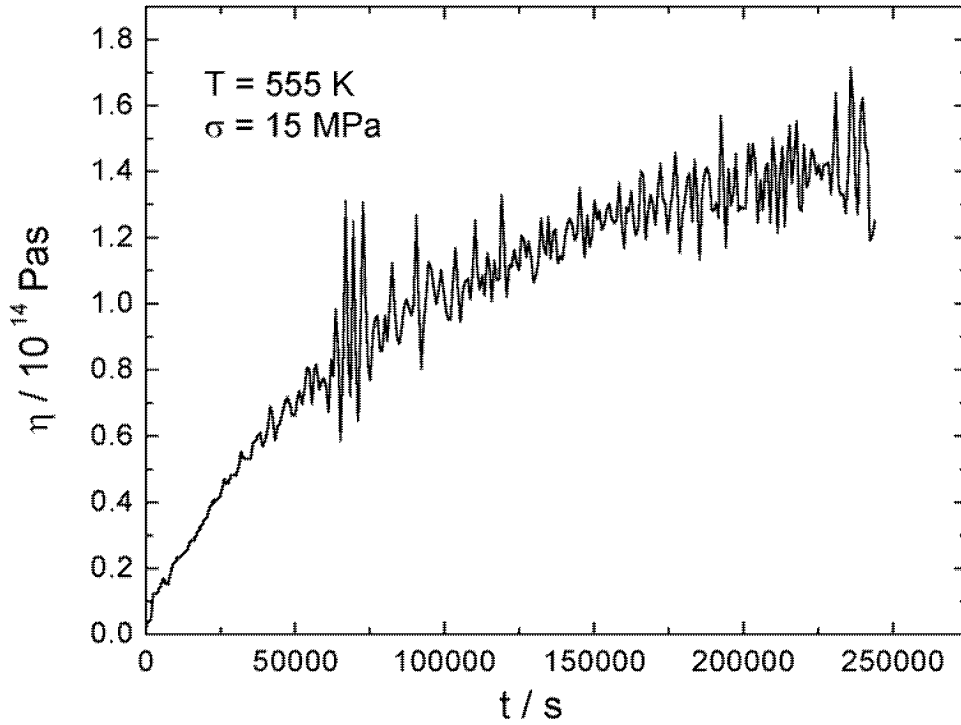


Figure 7.16: Increase of the viscosity with time during a creep experiment at 15 MPa and $T = 555$ K.

Accordingly, the defect annihilation Equation (7.7) after Duine *et al.* (1992) was used, in which a finite equilibrium defect concentration c_{eq} is assumed. Equation (7.7) approaches Equation (7.6) in the limit $c_f \gg c_{eq}$. Thus, a linear change of c_f with time, as it was observed at 550 K, is well described under this condition. The parameter c_{eq} was determined by de Hey *et al.* (1998) for different temperatures for $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$. These values were adopted in the present work (Table 7.2).

Since a_x was found to follow an approximately linear stress dependence (cf. Table 7.1), a new Ansatz for the description of the defect creation, explicitly introducing a linear stress-dependence, was chosen

$$\left. \frac{dx}{dt} \right|^{+} = a'_x \sigma \dot{\epsilon}. \quad (7.11)$$

The evolution of the defect concentration during creep experiments was calculated by the numerical integration of Equations (7.7) and (7.11). Subsequently creep curves were calculated according to Equation (7.3), and the standard deviation between the computed and the experimental creep curves at 550, 555 and 565 K (Figures 7.8, 7.9, 7.10, 7.12 and 7.15) was calculated. The parameters k_f , k_r and a'_x were used as free parameters for each temperature. They were varied to minimize the standard deviation between the experimental data and the computed curves. The parameters resulting in the best fit are given in Table 7.2.

	550 K	555 K	565 K
$\varepsilon_0 v_0 / \text{\AA}^3$	106	106	106
k_f / s^{-1}	2.45×10^5	2.21×10^6	3.82×10^7
k_r / s^{-1}	5.15×10^7	2.67×10^8	3.31×10^9
a'_x / Pa^{-1}	5.05×10^{-11}	3.61×10^{-11}	1.88×10^{-11}
c_{init}	5×10^{-14}	5×10^{-14}	5×10^{-14}
c_{eq}	2×10^{-15}	8×10^{-15}	2.1×10^{-14}
(de Hey <i>et al.</i> 1998)			

Table 7.2: Parameters used to fit the creep data at 550, 555 and 565 K; $\varepsilon_0 v_0$: activation volume; k_f : jump frequency of the flow defects; k_r : rate constant for bimolecular annihilation of the defects; a'_x : proportionality constant in the production of free volume; c_{init} : flow defect concentration of non-annealed samples; c_{eq} : equilibrium density of flow defects.

Unlike in the first set of computations using Equations (7.6) and (7.8), the pre-annealing procedure was also taken into account in the advanced computations. The initial defect concentration c_{init} , i.e. the defect concentration of the as-cast material, was assumed to be equal for all deformation samples. The value was estimated as $c_{init} = 5 \times 10^{-14}$ from viscosity data during preannealing experiments. First, the evolution of the defect concentration is computed according to the experimental annealing conditions, and after that the defect evolution during the individual creep experiments is calculated. The c_f value computed at the end of each creep experiment is taken as starting value for the subsequent creep experiment.

It was shown earlier that even in the sample pre-annealed for 5×10^5 s the defect concentration is not constant during a low-stress creep experiment. Structural relaxation takes place during creep experiments 1 to 4. The decrease of c_f results in a lower activation volume $\varepsilon_0 v_0$ and in a higher prefactor $2k_f c_f \varepsilon_0 v_0 \Omega^{-1}$ than for calculations at constant c_f according to Equation (7.3). The best fits were achieved with $\varepsilon_0 v_0 = 106 \text{ \AA}^3$, which is lower than the value $\varepsilon_0 v_0 = 126.3 \text{ \AA}^3$ calculated according to Equation (7.3).

The computed strain rates at low stresses at 550, 555 and 565 K are plotted in Figures 7.8, 7.10 as open squares. Good agreement with the experimental strain rates is found. In Figure 7.8 the computed data shows the same systematic deviation from the fit curve according to Equation (7.3) as the experimental data: The first four experimental and computed data points show slightly larger strain rates while the fifth to seventh data points show slightly smaller strain rates than the values corresponding to the hyperbolic-sine curve.

Figure 7.17 shows the evolution of the flow defect concentration c_f during the creep experiments at 550 K and low stress. The individual creep experiments are numbered according to Figure 7.8. The squares indicate the start of the individual creep experiments. Up to the end of the third creep experiment, c_f decreases, during the fourth creep experiment c_f remains almost constant at a value of 1.8×10^{-14} . At higher stresses c_f increases rapidly.

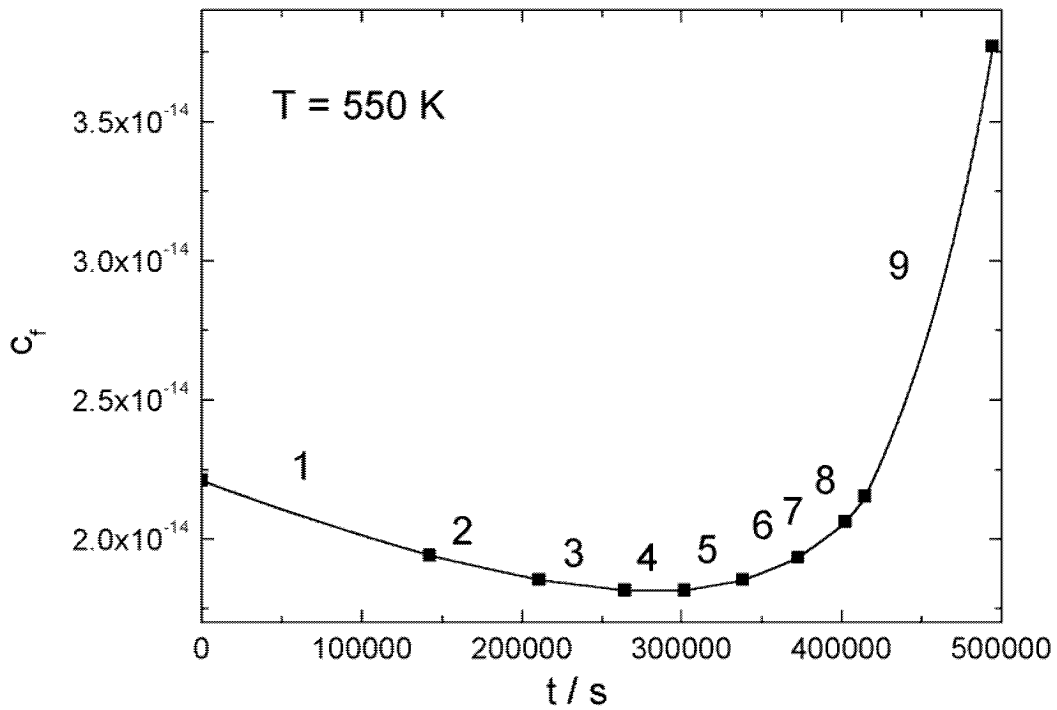


Figure 7.17: Computed evolution of the flow defect concentration c_f during the creep experiments at 550 K and low stress. The creep experiments are numbered according to Figure 7.8.

In Figure 7.18 a dc_f/dt is plotted as a function of c_f for three stresses according to Equations (7.7) and (7.11). The stresses correspond to the creep experiments 3, 4 and 5 in Figure 7.17. The curve at 119 MPa is close to zero at $c_f = 1.8 \times 10^{-14}$, i.e. c_f is approximately constant at a value of 1.8×10^{-14} . At 90 MPa c_f strives for an equilibrium value of 4×10^{-15} . In a creep experiment at 90 MPa over a long period of time the strain rate decreases asymptotically from 5×10^{-8} to the limit of $1.1 \times 10^{-8} \text{ s}^{-1}$. Figure 7.18 b shows the same dc_f/dt over c_f plot on a double logarithmic scale. At 148 MPa c_f increases at $c_f = 1.8 \times 10^{-14}$ with increasing rate dc_f/dt .

In Figure 7.19 the steady-state defect concentration c_{st} , i.e. the free volume c_f for $dc_f/dt = 0$ at a given stress, is plotted versus stress. The value c_{st} increases strongly at $\sigma > 100 \text{ MPa}$. Figure 7.20 shows a computed long duration creep experiment at 148 MPa. The creep rate increases up to a maximum value of $2.2 \times 10^{-5} \text{ s}^{-1}$. This strain rate corresponds to the steady-state defect concentration of 4.5×10^{-12} in Figure 7.19. This value, however, is only reached after $3.1 \times 10^6 \text{ s}$ and 1000 % strain. Hence, the steady-state defect concentration and constant-strain-rate stage in high-stress creep experiments is never reached in practice. Under ordinary laboratory conditions only the continuously accelerating rise of the strain rate can be observed in high-stress creep experiments.

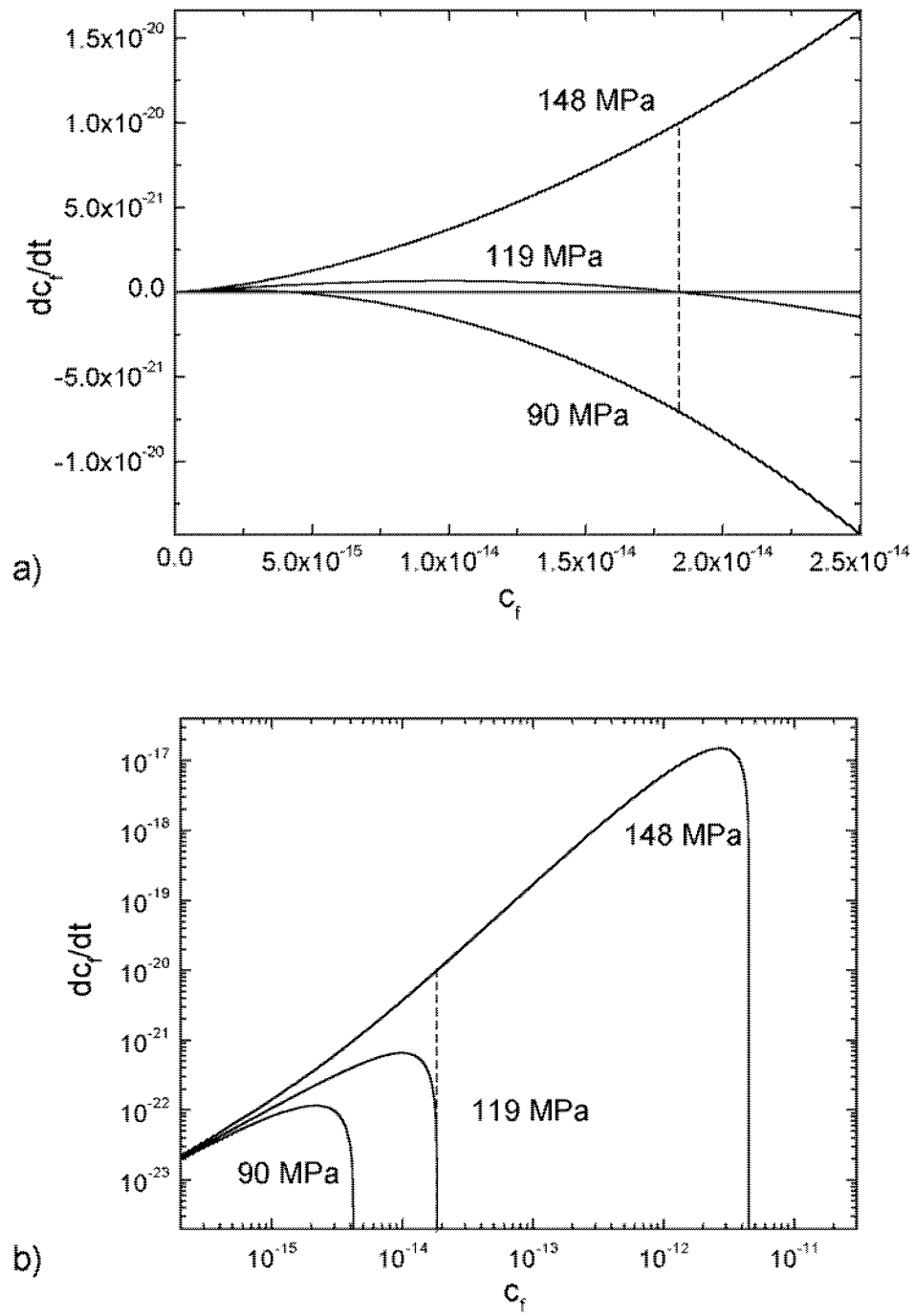


Figure 7.18: dc_f/dt plotted as a function of c_f (a) on a linear and (b) on a double-logarithmic scale for three stresses according to the Equations (7.7) and (7.9). The dotted line represents the defect density c_f in creep experiment 4 (119 MPa).

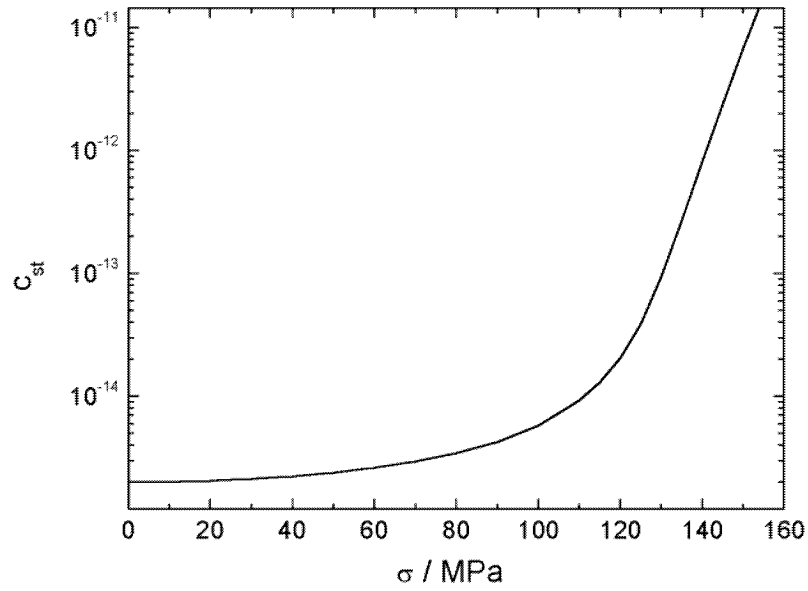


Figure 7.19: Steady-state defect concentration c_{st} plotted versus stress.

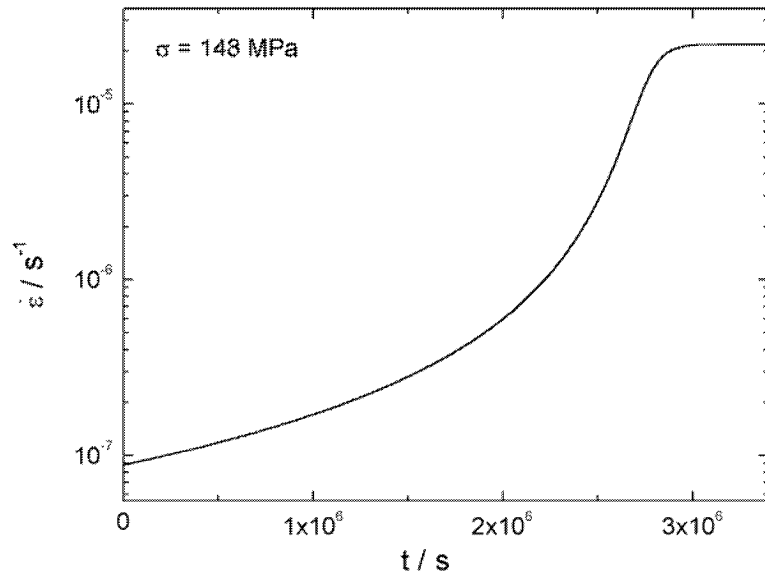


Figure 7.20: Computed long-duration creep experiment at 148 MPa.

Figures 7.21 a and b show the evolution of the defect concentration for the creep experiments at 555 and 565 K corresponding to Figures 7.10 a and b, respectively. In both cases, the creep experiments were not performed in a series of ascending stresses; the creep experiment with the lowest stress is No 4 in Figure 7.21 a and No 5 in Figure 7.21 b, respectively. During the low-stress creep experiments structural relaxation takes place and the flow defect concentration drops. Thus, the subsequent creep experiments 5 and 6 in Figure

7.21 a and 6 and 7 in Figure 7.21 b show lower flow-defect concentrations, and the corresponding strain rates in Figures 7.10 a and b are distinctly lower compared to the fit curves according to Equation (7.3).

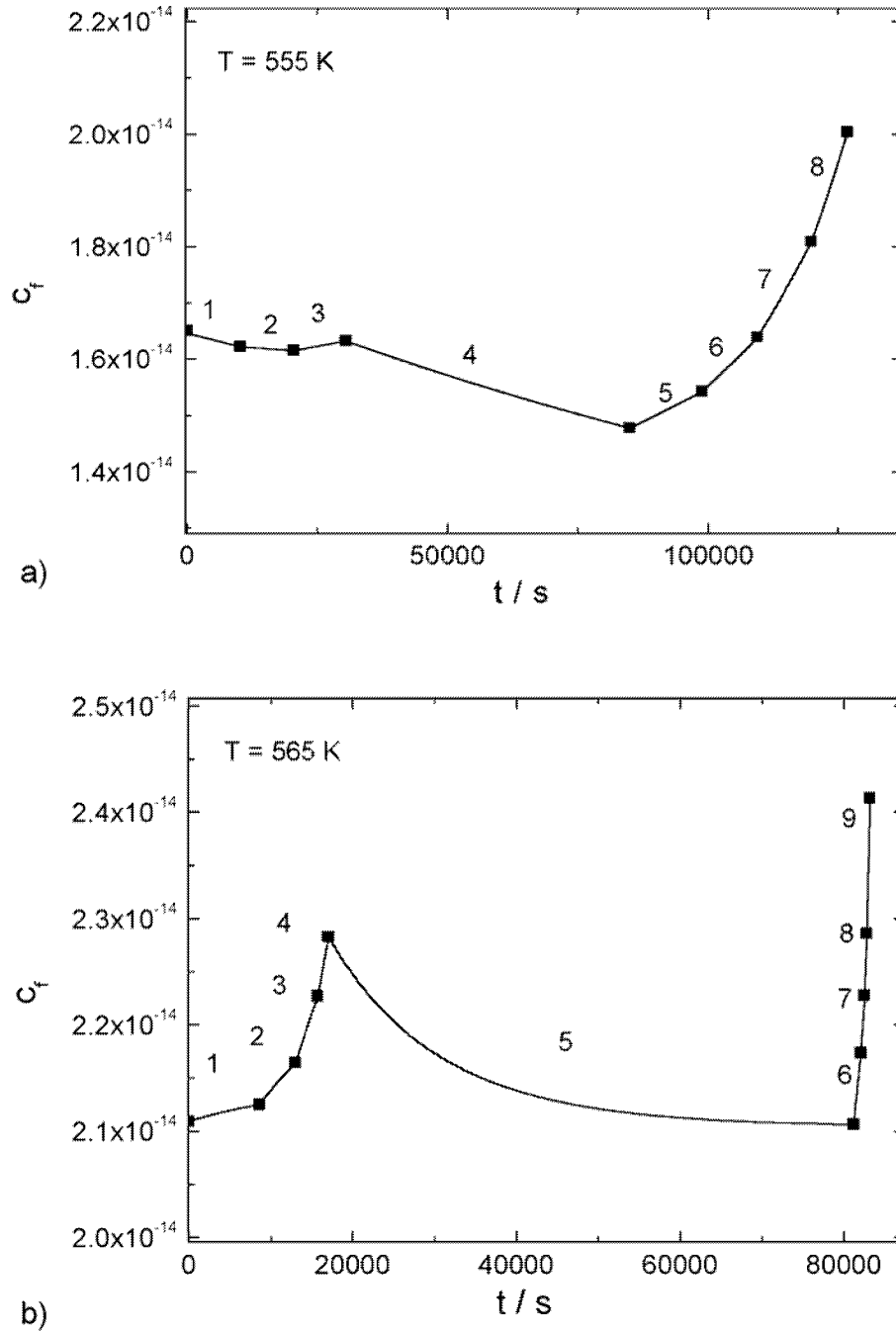
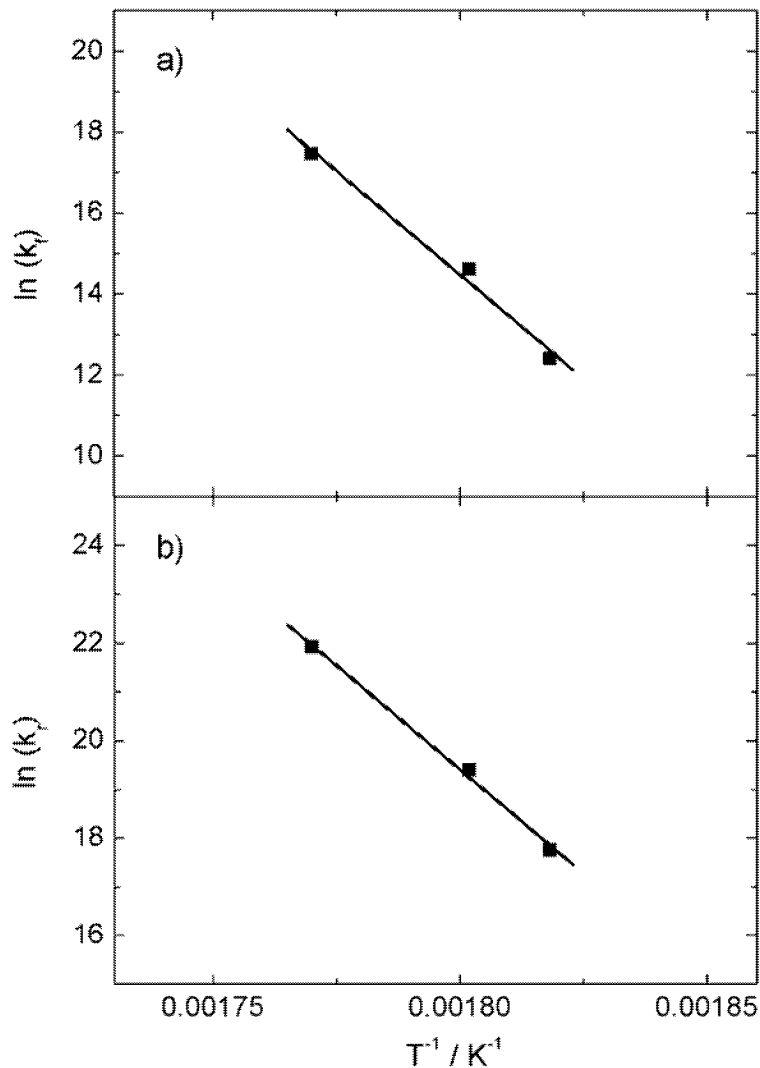


Figure 7.21: Computed evolution of the flow defect concentration c_f during the creep experiments at (a) 555 K and (b) 565 K at low stress. The creep stages are numbered according to Figure 7.10 a and b, respectively.

The computed curve of creep experiment 9 at 255 MPa is plotted as a broken line in Figure 7.9. The absolute values and the curvature compares very well to the experimental data. Computed high-stress creep curves are plotted as broken lines in Figures 7.12 and 7.15. The very fast increase of the strain rate in Figure 7.12 at 636 MPa over 1200 s is reproduced, as well as the very slow evolution of the creep rate over 8×10^4 s in Figure 7.9. Discrepancies between the fits and the data in Figure 7.15 may be the result of the transients corresponding to the stress changes. During these changes, which can take up a substantial fraction of the time, the evolution of the defect concentration was not taken into account.

Figures 7.22 a and b show Arrhenius plots for the parameters k_r and k_f in Table 7.2. The corresponding activation energies are $E_{kr} = 7.35$ eV and $E_{kf} = 8.83$ eV, respectively. The temperature dependence of a'_x is shown in Figure 7.23: a'_x decreases with increasing temperature. The broken line is a guide to the eye.



Figures 7.22: Parameters (a) k_f and (b) k_r (Table 7.2) displayed in an Arrhenius plot.

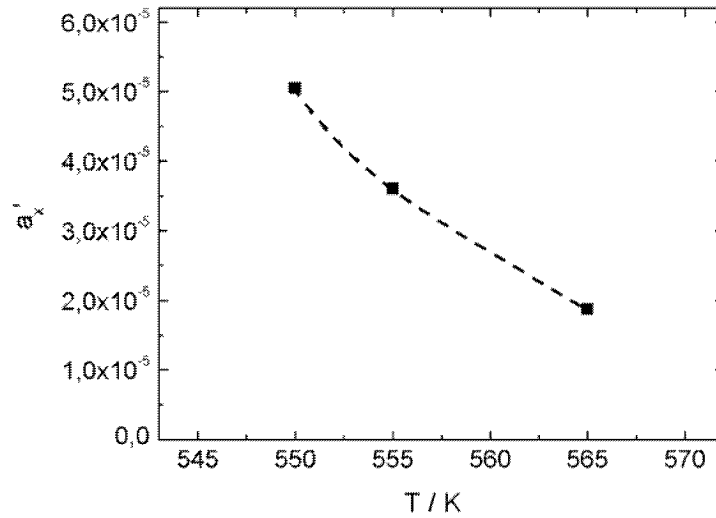


Figure 7.23: Temperature dependence of Parameter a'_x (Table 7.2). The broken line is a guide to the eye.

7.7 Discussion

High precision plastic deformation experiments were performed on Pd-Ni-Cu-P bulk metallic glass. A highly sensitive strain measurement and very constant deformation conditions enabled us to measure strain rates down to 10^{-8} s^{-1} at high accuracy. For the first time constant-true-stress creep experiments were performed on bulk metallic glasses, and structural disordering, a very stress sensitive process, could be studied. The creep behaviour was described within the framework of the free-volume theory. For the description of the defect evolution a similar approach to that used by de Hey *et al.* (1998) was made, which was, however, subjected to modifications in order to get satisfying results.

The experimental strain rate vs. stress dependence at low stress is described well by Equation (7.3) to a first approximation. However, a perfect fit to Equation (7.3) can only be obtained if the defect concentration c_f is constant. Slow changes in the defect concentration are directly reflected in the difference between the experimental data points and the strain rates according to the fit to Equation (7.3). The fit to Equation (7.3) represents a strain rate vs. stress behaviour with a constant defect concentration c_f , which can be interpreted as an average defect concentration. The experimental and computed data at lower stress, however, show higher strain rates than the fit to Equation (7.3) since the defect concentration is slightly higher than the average concentration and decreases during creep (Figure 7.17). At higher stresses, on the other hand, the strain rates are lower than the fit to Equation (7.3), since the defect concentration, even though it is increasing, is still below the average concentration. At 550 K the computations show that only at 119 MPa the defect concentration c_f is close to steady state, i.e. the strain rate is constant in time. At lower stresses the defect concentration c_f

is higher than the steady-state value c_{sf} . Structural relaxation occurs, i.e. $\left. \frac{dc_f}{dt} \right|^- > \left. \frac{dc_f}{dt} \right|^+$, and the strain rate decreases. At stresses higher than 119 MPa, the defect concentration c_f is below

the steady-state value c_{st} . Accordingly structural disordering is dominant, i.e. $\left. \frac{dc_f}{dt} \right|^- < \left. \frac{dc_f}{dt} \right|^+$,

and the strain rate increases. In the stress range between 110 and 130 MPa the transition between the two stages of different creep behaviour takes place. The exact value depends on the defect concentration c_f at the beginning of a creep experiment (cf. Figure 7.19). The steady-state defect concentration c_{st} increases strongly with increasing stress. Therefore, steady-state defect concentration and constant strain rate cannot be attained at stresses higher than about 130 MPa under conventional experimental conditions (Figure 7.20).

The dramatic increase of the creep rate at high stresses (Figures 7.12, 7.15) is the result of a fast increase in the defect concentration by the creation of free volume as can be seen from the calculated curve showing the same behaviour. The present results demonstrate that this increase is not the result of necking or macroscopic void formation (tertiary creep), as has been claimed for similar increases observed in tensile creep experiments (Gibeling and Nix 1978, Taub and Spaepen 1980). In our experiments, the deformation was observed to remain homogeneous and the cross-section to remain uniform over the entire length of the sample. Inhomogeneous deformation, leading to sample fracture, took place instantaneously at the very end of the experiment. Necking and void formation are ruled out by the compression geometry.

The strong stress dependence of the equilibrium defect concentration is shown in Figure 7.19. Correspondingly, the defect-creation rate strongly depends on the applied stress. Figure 7.24 a shows the true stress plotted versus time in a creep experiment. This experiment was not performed under constant-true-stress but under constant-technical-stress conditions, i.e. at constant load, which is the common procedure to perform creep experiments as described in the literature. With increasing strain the sample diameter increases and thus the true stress decreases. Figure 7.24 b shows the evolution of the strain rate in this experiment. Initially, the strain rate increases but approaches a constant value after approx. 1.3×10^4 s. After reaching a maximum strain rate of $2.6 \times 10^{-6} \text{ s}^{-1}$ the strain rate starts to decrease very slowly.

Kato *et al.* (2001) described a similar behaviour as that shown in Figure 7.24 in compression tests of a Zr-Al-Ni-Cu metallic glass. Figure 7.25 was taken from the work of these authors. Figure 7.25 b shows the strong decrease of the true stress in creep experiments under different constant loads, i.e. constant technical stresses. Figure 7.25 a shows the corresponding creep curves as strain vs. time. It can be observed that the strain rate increases at first, then reaches a maximum value, subsequently, with decreasing true stress, the strain rate decreases. From Figure 7.19 it is obvious that a decrease of the true stress in the high-stress regime leads to a substantial decrease of the steady-state defect concentration. c_{st} may even drop below the current value of c_f which then leads to a decrease of the strain rate. This phenomenon can be observed in Figure 7.24 b and in the experiments of Kato *et al.* (2001) (Figure 7.25). The model states that in a creep experiment at constant true stress c_f and the strain rate increase if $c_f < c_{st}$. Theoretically, equilibrium can only be attained in very long creep experiments (cf. Figure 7.20) and when the difference between c_f and c_{st} is small.

The present results clearly indicate, that the conduction of constant-load creep experiments does not result in reliable data about the flow stress evolution at constant true stress. The defect creation in metallic glass is strongly stress dependent, hence it is necessary to control creep experiments to constant true stress, as it was performed for the first time in the present work.

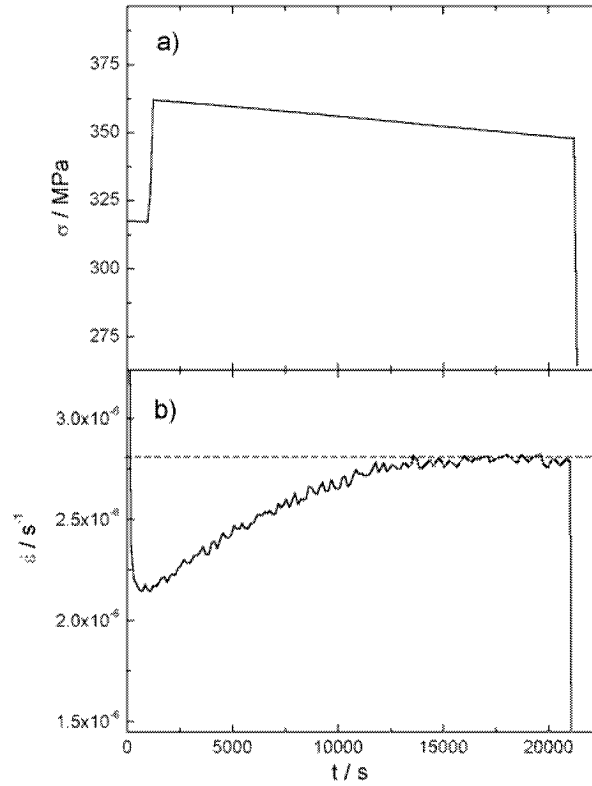


Figure 7.24: (a) True stress and (b) strain rate vs. time in a constant-load experiment.

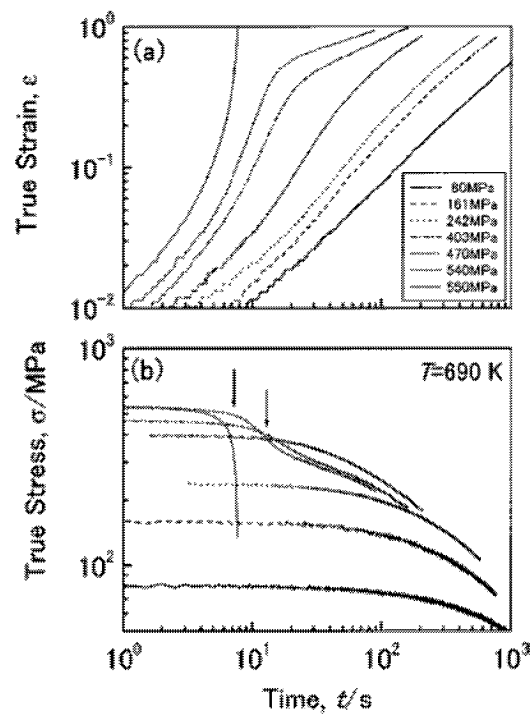


Figure 7.25: (a) Constant load curves of Zr-Al-Ni-Cu at a temperature of 690 K; (b) change of the true stress with time (Figure taken from Kato et al. 2001).

Figure 7.26 shows an experimental creep curve at 555 K and 445 MPa plotted as solid line. After this creep experiment the sample was unloaded to 14 MPa for 5.8×10^4 s to allow for structural relaxation. Subsequently the sample was reloaded to 445 MPa. The corresponding creep curve is plotted as broken line and shifted on the time axis to match to the first creep curve. The curves perfectly coincide with respect to their slope as well as their curvature. This shows that the microstructural state, i.e. the concentration of flow defects, is reversible. Hence the plastic behaviour does not depend on the history of the sample but only on the current flow defect concentration c_f . In other words, the flow defect concentration is the only essential structural parameter. It can be lowered by annealing and raised by plastic deformation or annealing at high temperature, i.e. close to T_G .

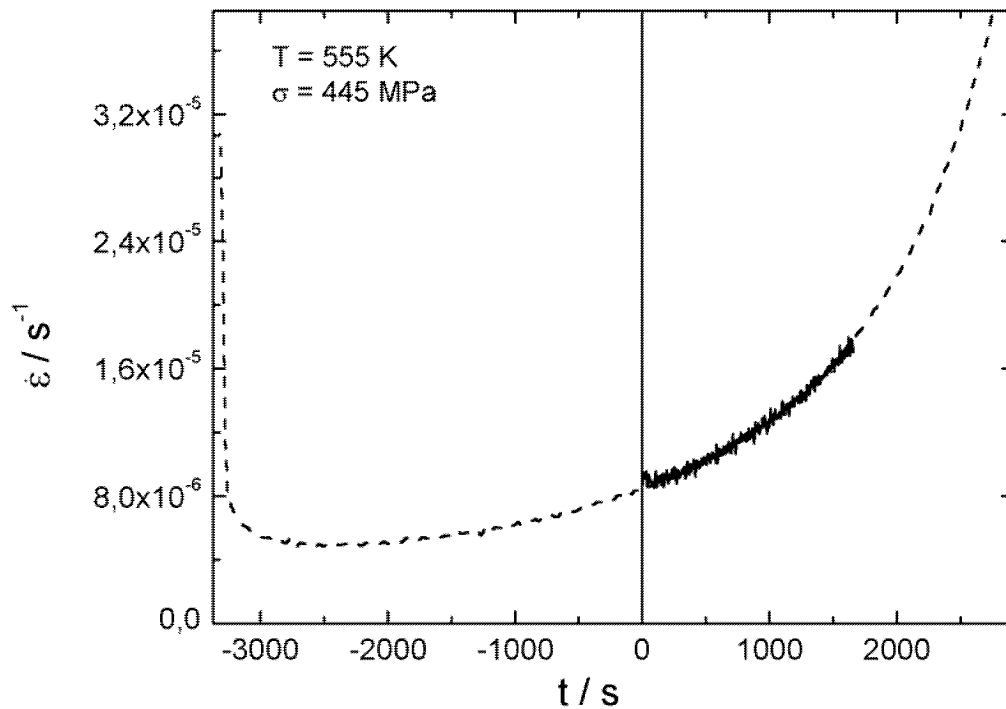


Figure 7.26: Experimental creep curves at 555 K and 445 MPa true stress. After the first experiment (solid line) the sample was loaded at 14 MPa for 5.8×10^4 s to attain structural relaxation and loaded at the same stress like in the first experiment again (dotted line). The second curve was shifted on the time axis to match the first curve.

Generally, our studies demonstrate that the strain rate as a function of stress and time can be well reproduced by a model based on deformation-induced free volume. The experimental data was fitted with a set of three parameters for each temperature: k_f , k_r and a_x . Additionally the common parameters $\varepsilon_0 v_0$ and c_{init} were used for all temperatures. Our parameter values are in accordance with those of de Hey *et al.* (1998), who used a similar approach to describe the stress-strain curves attained from tensile tests on Pd₄₀Ni₄₀P₂₀ ribbons. The value of the activation volume obtained from our experiments, $\varepsilon_0 v_0 = 126.3 \text{ \AA}^3$, is in perfect agreement with the value of $130 \text{ \AA}^3$ found by de Hey *et al.* (1998). Nevertheless the computed evolution of the flow defect concentration reveals that c_f changes during the creep experiments. Fitting

the data according to Equation (7.3), i.e. proposing constant c_f , leads to a too high value for the activation volume $\varepsilon_0 v_0$. The best agreement between computations and experimental data was obtained for $\varepsilon_0 v_0 = 106 \text{ \AA}^3$.

The computed creep rates presented fit the experimental curves very well, except for the high stresses at 565 K (see Figure 7.15). These discrepancies may be the result of relatively longer transient times between experiments or to a value of c_{eq} other than that measured by de Hey *et al.* (1998) for Pd-Ni-P. Because of sample preparation conditions, the initial defect concentration (c_{init}) may also differ between samples from the value assumed in the simulations.

In a first step Equation (7.8) was used to describe the defect creation: A constant amount of free volume is produced in each shear event. Thus, the rate of free volume production is proportional to the strain rate. A defect creation approach according to Equation (7.8) was used by de Hey *et al.* (1998) to describe the stress-strain curves of $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$ ribbons. At 556 K they used a value of $a_x = 0.043$. The authors found this parameter to be strongly temperature dependent, showing a decrease with increasing temperature. The temperature dependence was interpreted as a partial restoring of order during the flow event due the thermal motion of the atoms. From the present work, it appears, that the lower value of a_x is the result of the stress at the higher temperature being lower, leading, according to Equation (7.11), to a lower value of a_x . To compare de Hey's parameter $a_x = 0.043$ with those determined in the present experiments it has to be divided by the approximate stress of his experiment of 500 MPa. This yields a value of $8.6 \times 10^{-11} \text{ Pa}^{-1}$ which is of the same order of magnitude as our value at 555 K, where we found $a'_x = 3.61 \times 10^{-11} \text{ Pa}^{-1}$.

In the present work, satisfying results were only achieved when a stress variation of a_x was taken into account. Therefore, in a second step a linear stress dependence was introduced in Equation (7.11) describing the creation of defects. With a linear stress dependence in Equation (7.11) and the stress-independent parameter a'_x we find a good agreement of the computed curves and the experimental data. According to this Ansatz we can conclude that the rate of free volume production is proportional to the *mechanical power*, $\sigma \dot{\varepsilon}$, applied to the sample. The energy cost of free volume production has been estimated by van den Beukel *et al.* (1990). From calorimetric studies of structural relaxation the production of free volume requires energy according to $(\Delta U)_{fv} = \beta \Delta x$, where β is the proportionality factor between the energy of free volume production and the reduced free volume change. For amorphous $\text{Pd}_{77.5}\text{Cu}_6\text{Si}_{16.5}$ a value of $\beta = 0.4 \text{ eV}$ was estimated. The quantity $\beta' = \beta / \gamma^*$ can be interpreted as the formation energy of a vacancy of the size of one atomic volume (van den Beukel *et al.* 1990) for $\gamma^* = 0.143\Omega$, $\beta' = 2.9 \text{ eV}$. However, real vacancies in crystalline materials have smaller volumes due to lattice relaxation in the neighboring atomic arrangement. To compare the vacancy formation energy to those in pure metals, a more realistic estimate would be $1/2 \beta'$, which compares well to vacancy formation energies in Pd or Ni. Using the parameter a'_x from our fits, we can calculate a proportionality factor β_w between the mechanical work applied on the sample and the reduced free volume according to $\Delta W = \beta_w \Delta x$. With the quantity $\gamma^* = 0.143$ taken from van den Beukel *et al.* we can compute $\beta'_w = \beta_w / \gamma^*$. The results for 550, 555 and 565 K are compiled in Table 7.3.

7. Plasticity of Pd-Ni-Cu-P bulk metallic glass

The proportionality factor β'_w can be interpreted as the mechanical work that has to be introduced into the system for the formation of an amount of free volume with the magnitude of one atomic volume. The resulting value of β'_w is distinctly higher than the formation energy of a vacancy β' , calculated by van den Beukel *et al.* The ratio β'_w / β' is the mechanical efficiency of the formation process. Hence 9 to 24 % of the applied energy is used to form the vacancy, the rest is dissipated as heat.

	550 K	555 K	565 K
β'_w eV	12.0	16.6	31.9

Table 7.3: Proportionality factor between mechanical energy and free volume for 550, 555 and 565 K.

8. Generalizing discussion: The plasticity of quasicrystals and metallic glasses

In the present work two models describing the plastic deformation behaviour of quasicrystals and metallic glasses, respectively, were presented. The constitutive model of quasicrystal plasticity developed by Feuerbacher *et al.* (2001a) has been successfully applied to an extended range of experimental deformation conditions for icosahedral Al-Pd-Mn quasicrystals. Furthermore a model describing the creep behaviour of Pd-Ni-Cu-P bulk metallic glasses based on the free volume description (Cohen and Turnbull 1959) was developed in the present work.

In both models the state of *order* of the material during plastic deformation is the deciding microstructural parameter. The amount of order is not a fixed value. Disorder is introduced into both materials upon plastic deformation. The introduction of disorder is expressed by Equations (5.1) and (7.11) for quasicrystals and metallic glasses, respectively. On the other hand, annealing of a disordered structure leads to reordering in both materials.

In a metallic glass the amount of disorder is dependent on the free volume v_f (Spaepen 1977). For example, if a metallic glass has been rapidly quenched from the melt the amount of order is low and the free volume is high. On the contrary, if a metallic glass is annealed at a temperature well below T_G , the free volume decreases and the amount of order raises. The reordering of the metallic glass structure in the model is described according to Equation (7.7). In the constitutive model of quasicrystal plasticity the amount of order is expressed by the order parameter λ which has been introduced by Feuerbacher *et al.* (2001a) heuristically. Annealing of a disordered quasicrystal structure induces reordering of the structure according to Equation (5.1). In both materials, reordering is supported by diffusion (cf. Feuerbacher *et al.* 2001, Spaepen 1977).

The plastic deformation behaviour of both materials depends on the evolution of the respective order parameters. In both cases *softening* of the material, i.e. the decrease of the flow stress with increasing strain takes place. This behaviour is in distinct contrast to the plastic deformation behaviour of all conventional metals, which show work hardening upon plastic deformation (Basinski and Basinski 1979, Sevillano *et al.* 1993). It is demonstrated that the softening results from a decrease of order during plastic deformation. Figure 9.1 a and b show stress-strain curves at constant strain rates of 10^{-5} s^{-1} for Pd-Ni-Cu-P bulk metallic glass and an icosahedral Al-Pd-Mn quasicrystal, respectively. Both materials exhibit distinct work softening after yielding. In the constitutive model of quasicrystal plasticity the order parameter directly influences the reference stress $\hat{\sigma}$. A decrease of the order parameter lowers the “quasicrystal” stress contribution which leads to a decrease of the flow stress σ according to Equation (5.4). In the model describing the creep behaviour of Pd-Ni-Cu-P bulk metallic glasses, the amount of disorder, expressed by the free volume, is directly connected to the flow-defect concentration c_f (Equation 7.1). Hence, plastic deformation of a metallic glass is only possible if a certain amount of structural disorder is present in the material. If the amount of free volume is low, i.e. due to structural relaxation, the material embrittles. In a creep experiment the amount of free volume influences the creep rate via Equations (7.1) and (7.3) predicating that the creep rate increases with increasing disorder.

The model describing the creep behaviour of Pd-Ni-Cu-P bulk metallic glass is an one parameter model. The amount of disorder is directly related to the concentration of flow-

defects. In this sense plastic deformation is directly governed by structural disorder. The constitutive model of quasicrystal plasticity, on the other hand, is a two parameter model. Besides the order parameter λ , the dislocation density ρ , representing the amount of defects governing plastic deformation, is accounted for.

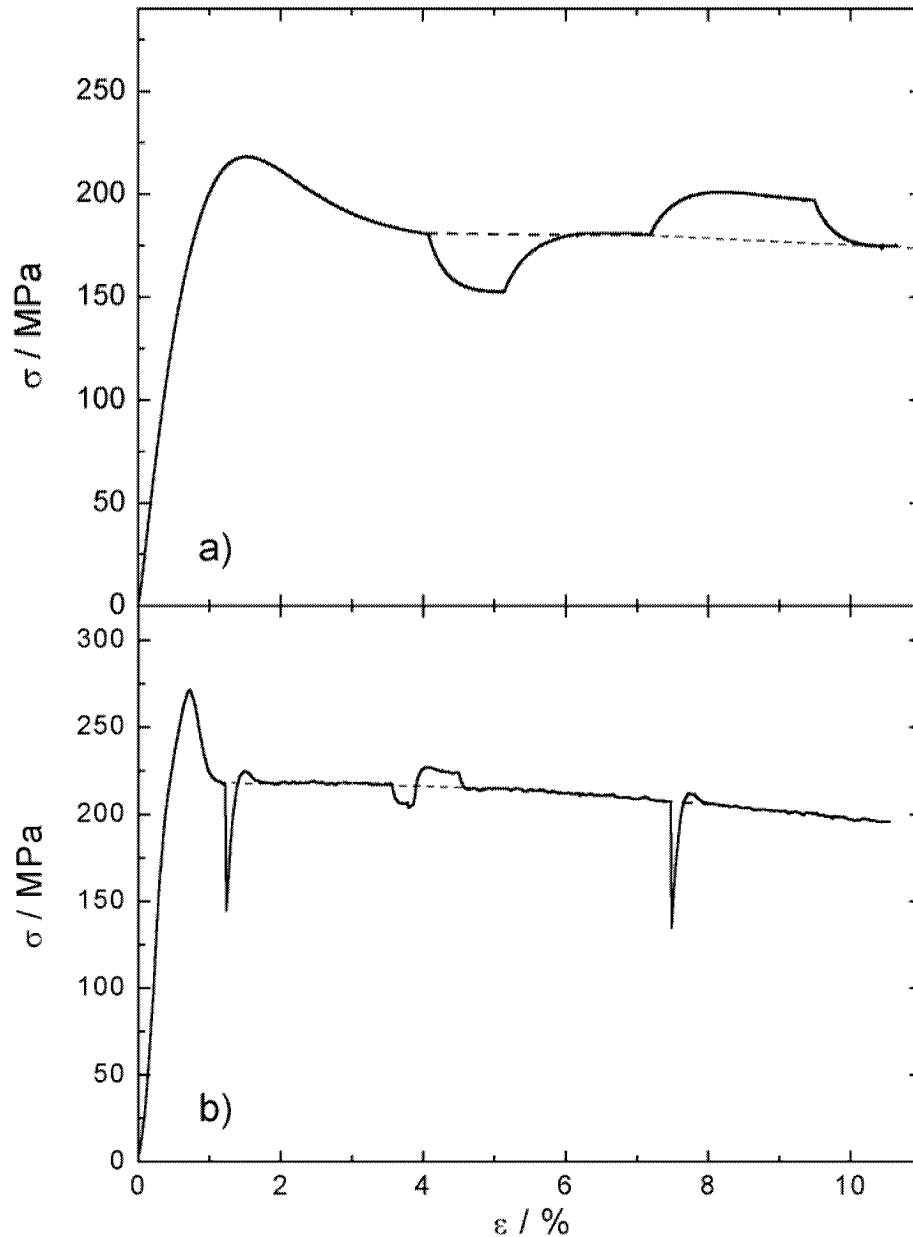


Figure 9.1: Stress-strain curves at constant strain rates of 10^{-5} s^{-1} for (a) Pd-Ni-Cu-P bulk metallic glass at 292 °C and (b) an icosahedral Al-Pd-Mn quasicrystal at 760 °C (including stress-relaxation tests and strain-rate changes). The interpolated courses of the stress-strain curves are plotted by broken lines.

A decisive and common structural feature of quasicrystals and metallic glasses is the lack of translational symmetry. If a simple crystal is traversed by a perfect dislocation, the crystal

structure remains unchanged. If a dislocation moves through a structure without translational symmetry, it is necessarily altered permanently, hence the material is in a different structural state after plastic deformation. Undeformed quasicrystals and metallic glasses generally represent a state of low free energy and the material possesses a high degree of order. Therefore in materials possessing no translational symmetry and a high state of structural order like quasicrystals and metallic glasses plastic deformation is accompanied by disordering.

The most significant structural difference between quasicrystals and metallic glasses concerns the long-range orientational symmetry. Quasicrystals, as crystals, possess a discrete autocorrelation function, which is exemplified e.g. by discrete diffraction patterns. Fixed atomic next-neighbour orientations and distances occur, and defined dense atomic planes are present in the structure. Dislocations and vacancies were shown to exist in quasicrystals as in crystals. Metallic glasses do not possess a discrete autocorrelation function. Next-neighbour distances can only be expressed in terms of distribution functions, and long-range orientational symmetry is absent. The description of metallic-glass plasticity in terms of dislocations and vacancies is not useful, since both defects lose their identity upon movement (cf. Chapter 7.2).

Although the mechanism of plastic deformation is very different in both materials, plastic deformation of quasicrystals and metallic glasses is mediated by the competing processes of structural disordering upon plastic deformation and structural reordering upon static and/or dynamic annealing. At low strain rates a dynamic equilibrium between both processes is attained. The amount of order is constant during plastic deformation (Figures 5.8 and 7.17). Steady-state deformation for both materials is reached (e.g. Figures 5.2 and 7.7) which is reflected by a constant stress or strain rate, respectively. On the contrary the predominance of structural disordering weakens the structure of both materials and leads to work softening (e.g. Figures 5.1 and 7.12), and the amount of order decreases during plastic deformation (Figures 5.8 and 7.17).

9. Metadislocations in ξ' -Al-Pd-Mn

9.1 Introduction

Elementary metallic materials with body-centred cubic, hexagonal close packed and face-centred cubic structure usually possess 2, 2, and 4 atoms per unit cell. Some intermetallic compounds are more complex. For example γ' -Ni₃Al and Fe₃Al have ordered structures with 4 and 16 atoms per unit cell, respectively.

Since the 1950s the structures of many metallic compounds have been determined, which are by far more complex than the examples given above. These materials contain from a few hundreds to about one thousand atoms in the unit cell. For example the intermetallic compound NaCd₂ has 1152 atoms per unit cell (Pauling 1955). The lattice parameter is 30.56 Å and the space group is Fd $\bar{3}$ m. Today a few hundred structurally complex alloy phases are known which possess large unit cells (Villars *et al.* 1986, Tamura 1997). Often the structure of these materials is cluster-based, e.g. they are based on the 55 atom Mackay cluster or on the 117 atom Bergman cluster (see Chapter 1.1) (Tamura 1997). An example is the complex intermetallic phase Mg₃₂(Al,Zn)₄₉, which has 162 atoms in the cubic unit cell (Bergman *et al.* 1957). The basic structural element of this phase is the Bergman cluster. 60 % of the atoms in this structure possess icosahedral coordination. Nowadays these materials are often referred to as structural complex alloy phases (SCAPs) (Urban *et al.* 2003).

The structure of SCAPs can be described with reference to a six-dimensional hyperlattice in the framework of the cut procedure (Chapter 1.1). However the lattice is constructed using a rational cut rather than an irrational one as for the construction of a quasicrystal lattice. Therefore SCAPs in alloy systems containing quasicrystalline phases are referred to as rational approximants to quasicrystals in the literature (Janot 1994). The increasing interest in SCAPs during the last decade is partly due to the structural similarity of the short range order to quasicrystals. However, up to now the scientific work on SCAPs, with a few exceptions, concerns only crystallography. The physical properties of SCAPs are largely uninvestigated.

The focus of the present work is on the plastic deformation behaviour of SCAPs. Because of their complex structure and the occurrence of large lattice parameters, the direct application of the dislocation concept to these materials is not straightforward. The introduction of a perfect dislocation into a structurally complex alloy phase implies large Burgers vector moduli and hence high elastic energies (Appendix D), that might exceed physically reasonable values. The nature of structural defects carrying plastic deformation and the mechanisms of plastic deformation of SCAPs are largely unknown. The only structurally complex alloy phase the plasticity has been investigated of, orthorhombic ξ' -Al-Pd-Mn, has revealed a new mechanism of plastic deformation. The ξ' -phase possesses large lattice parameters of $a_{\xi'} = 23.89$ Å, $b_{\xi'} = 16.56$ Å and $c_{\xi'} = 12.56$ Å (Klein *et al.* 1996). Microstructural investigations of deformed ξ' -Al-Pd-Mn revealed the presence of a novel type of structural defect called metadislocation (Klein *et al.* 1999).

Figure 9.1 is a schematic of a metadislocation in ξ' -Al-Pd-Mn seen along the [0, 1, 0]-direction of the structure. The flattened hexagons (1 and 2), which are present in two different orientations, are tiles representing basic structural elements of ξ' -Al-Pd-Mn. The boxed region, labelled (3), represents the unit cell. The ψ -Al-Pd-Mn phase can be regarded as a superstructure of the ξ' -phase. The unit cell of the ψ -Al-Pd-Mn phase is labelled (4) in Figure

9.1. This orthorhombic phase possesses the same a and b cell parameters as the ξ' -Al-Pd-Mn phase. The cell parameters in the c -direction of the ψ - and the ξ' -phase are related by the factor $(\tau+3)$ where τ is the irrational number of the golden mean. Hence, $c_\psi = (\tau+3)c_{\xi'}$ $c_{\xi'} = 58.00 \text{ \AA}$ (Klein *et al.* 1996). In Figure 9.1 the structure of the ψ -phase is represented by flattened hexagons (1 and 2) and two additional polygons (5 and 6). The polygon (7) represents the core of the metadislocation. The tiles representing the ψ - and the ξ' -phase (1, 2, 5 and 6) can not tile the polygon (7).

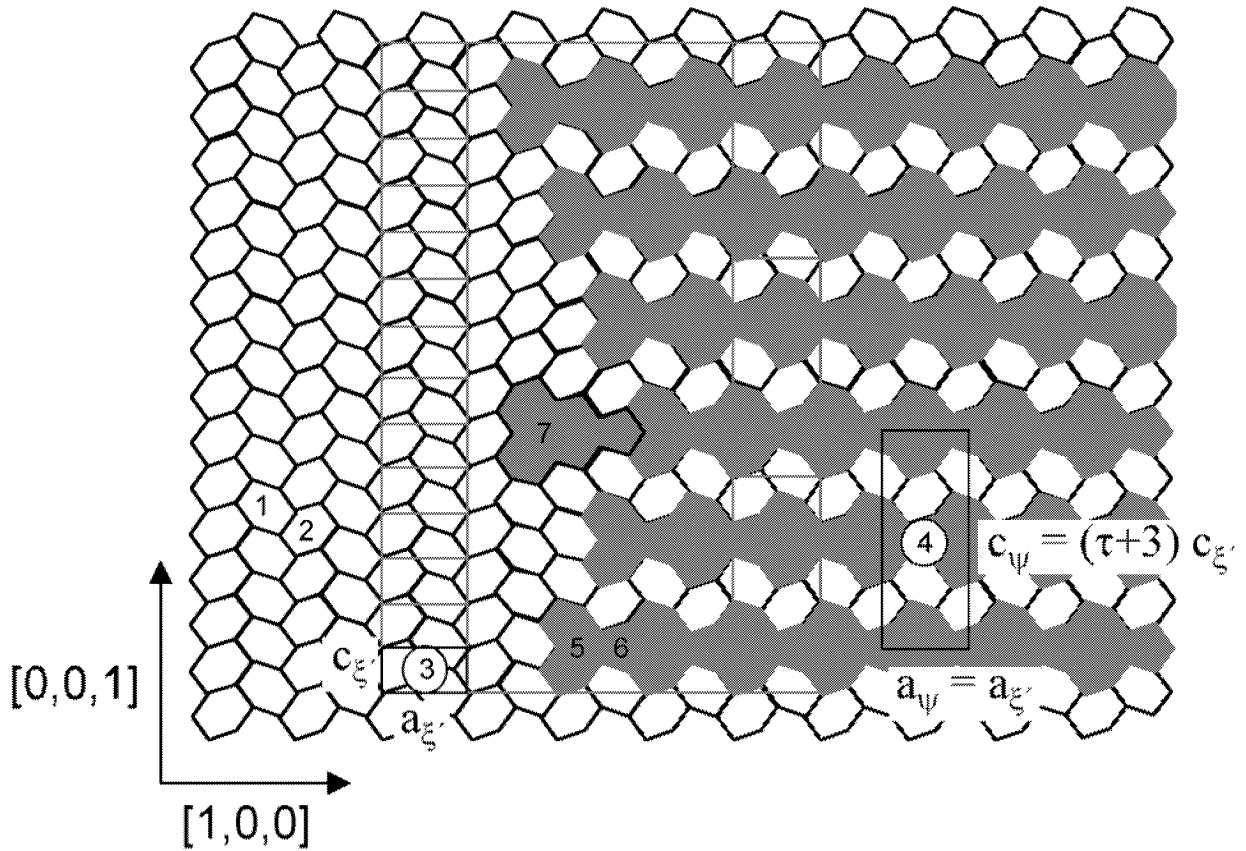


Figure 9.1: Schematic of a metadislocation along the $[0, 1, 0]$ -direction (see text).

In Figure 9.2 the polygon representing the core of the metadislocation is embedded into an arrangement of flattened hexagons. However the tile representing the core of the metadislocation can not be embedded perfectly into the flattened hexagons in the sense that no gaps are present between the tiles. A Burgers circuit along the edges of the flattened hexagons (indicated by black arrows) reveals a Burgers vector of $\vec{b} = \tau^{-4}c_{\xi'}[0, 0, 1]$. The Burgers vector is indicated by a grey arrow. In Figure 9.1 the tiles around the metadislocation core are strained to obtain a tiling without gaps between the tiles.

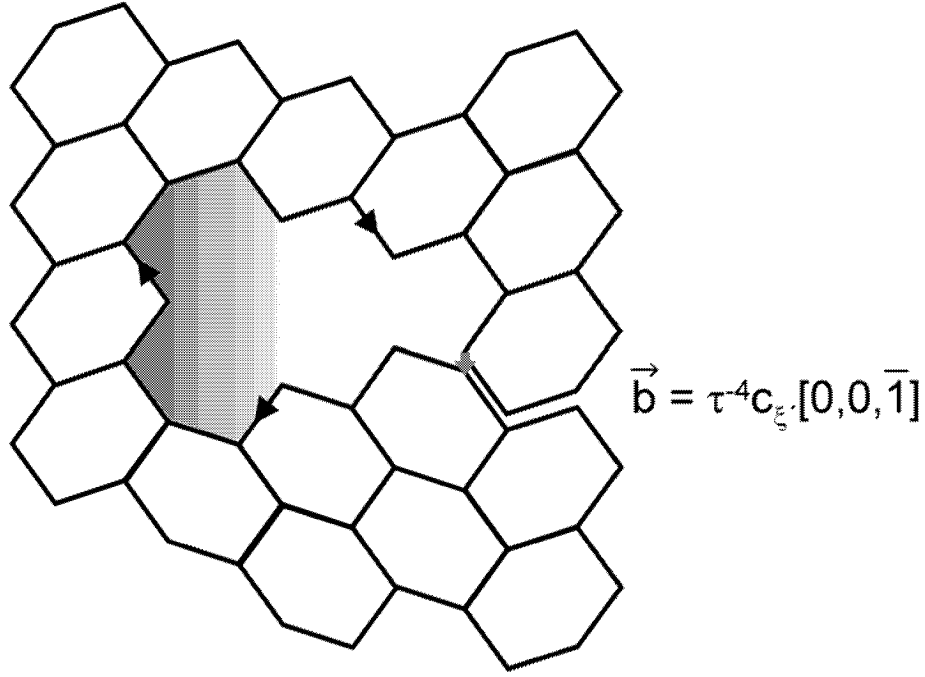


Figure 9.2: Arrangement of flattened hexagons (black) surrounding a polygon representing the core of a metadislocation. A Burgers circuit along the edges of the flattened hexagons (indicated by black arrows) reveals a Burgers vector (grey arrow).

In Figure 9.1 the grey tiles (5 and 6) are arranged in chains along the $[1, 0, 0]$ -direction. The tiles represent structural units in the ψ -phase which are arranged in planes parallel to the $[1, 0, 0]$ - and $[0, 1, 0]$ - direction. These planes are called phason planes. One “layer” of the ψ -phase with thickness $c_{\psi} = 58.00 \text{ \AA}$ includes two phason planes (see schematic unit cell 4 in Figure 9.1). Different metadislocation types can be distinguished by their number of phason planes. The schematic metadislocation shown in Figure 9.1 possesses six phason halfplanes (corresponding to three layers of the ψ -phase with thickness $3c_{\psi}$).

Figure 9.3 shows a lattice fringe image of a metadislocation obtained by TEM along the $[0, 1, 0]$ -direction. The location of the metadislocation core is indicated by a polygon. Six phason halfplanes (indicated by black lines) are attached to the metadislocation core. Here, the metadislocation is embedded into the ψ -phase. Some phason planes of the surrounding ψ -phase are indicated as grey lines.

The phason planes shown in Figure 9.3 are not arranged strictly parallel to the $[1, 0, 0]$ -direction. Figure 9.4 shows a schematic of tiles containing grey tiles, which represent basic structural units of phason planes. The uppermost chain of grey tiles is oriented parallel to the $[1, 0, 0]$ -direction as in Figure 9.1. However the tiles can be arranged in a way that chains of grey tiles are inclined to the $[1, 0, 0]$ -direction.

Different types of metadislocation have been experimentally observed possessing 16, 10, 6, and 4 phason halfplanes (Figure 9.5). Recently metadislocations possessing 2 phason halfplanes were observed (Feuerbacher 2003a). Metadislocations with different number of phason halfplanes possess different Burgers vectors as will be explained in the forthcoming subsection.

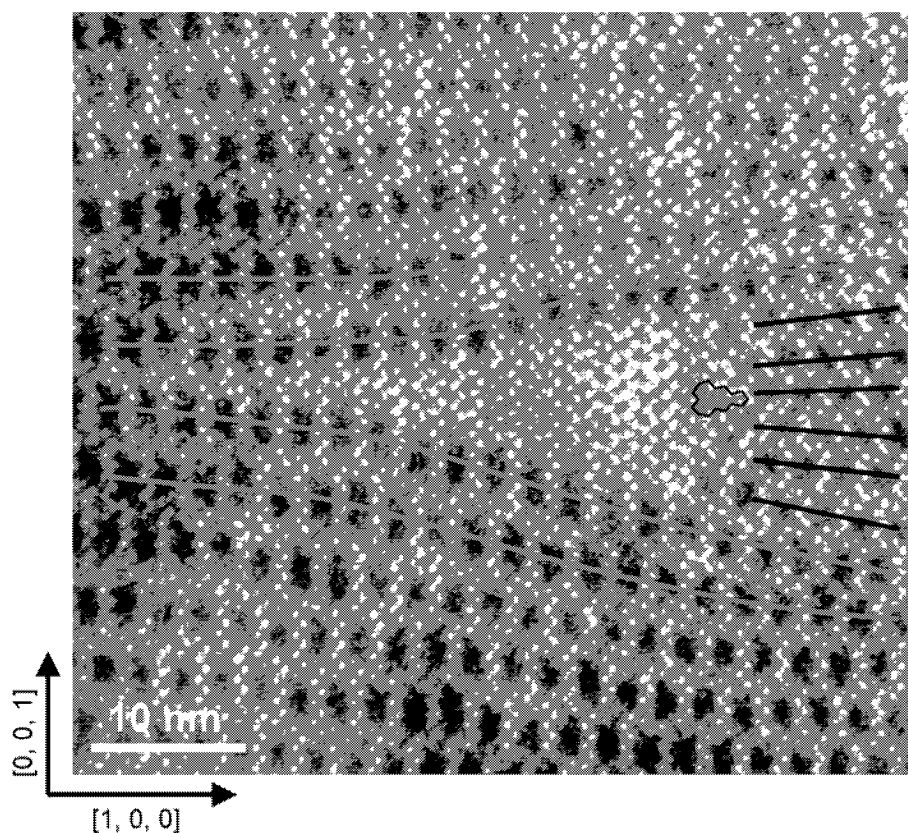


Figure 9.3: Lattice fringe image of a metadislocation along the $[0, 1, 0]$ -direction. The location of the metadislocation core is indicated by a black polygon. Six phason halfplanes of the metadislocation are indicated by black lines. The metadislocation is embedded into the ψ -phase. Some phason planes of the surrounding ψ -phase are indicated as grey lines.

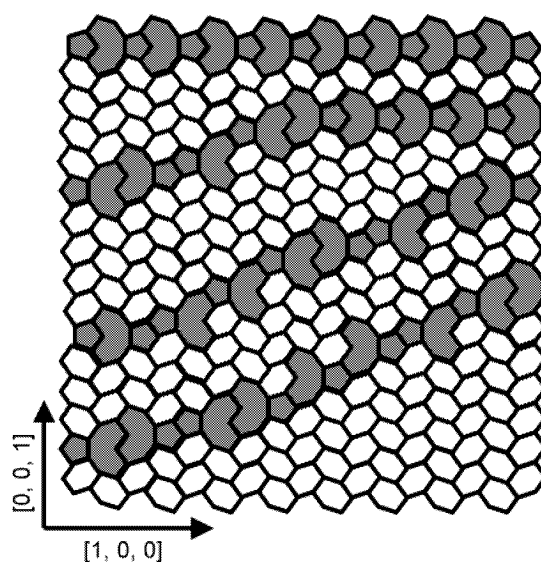


Figure 9.4: Schematic of tiles containing grey tiles, which represent basic structural units of phason planes. Some chains of grey tiles are inclined with respect to the $[1, 0, 0]$ -direction.

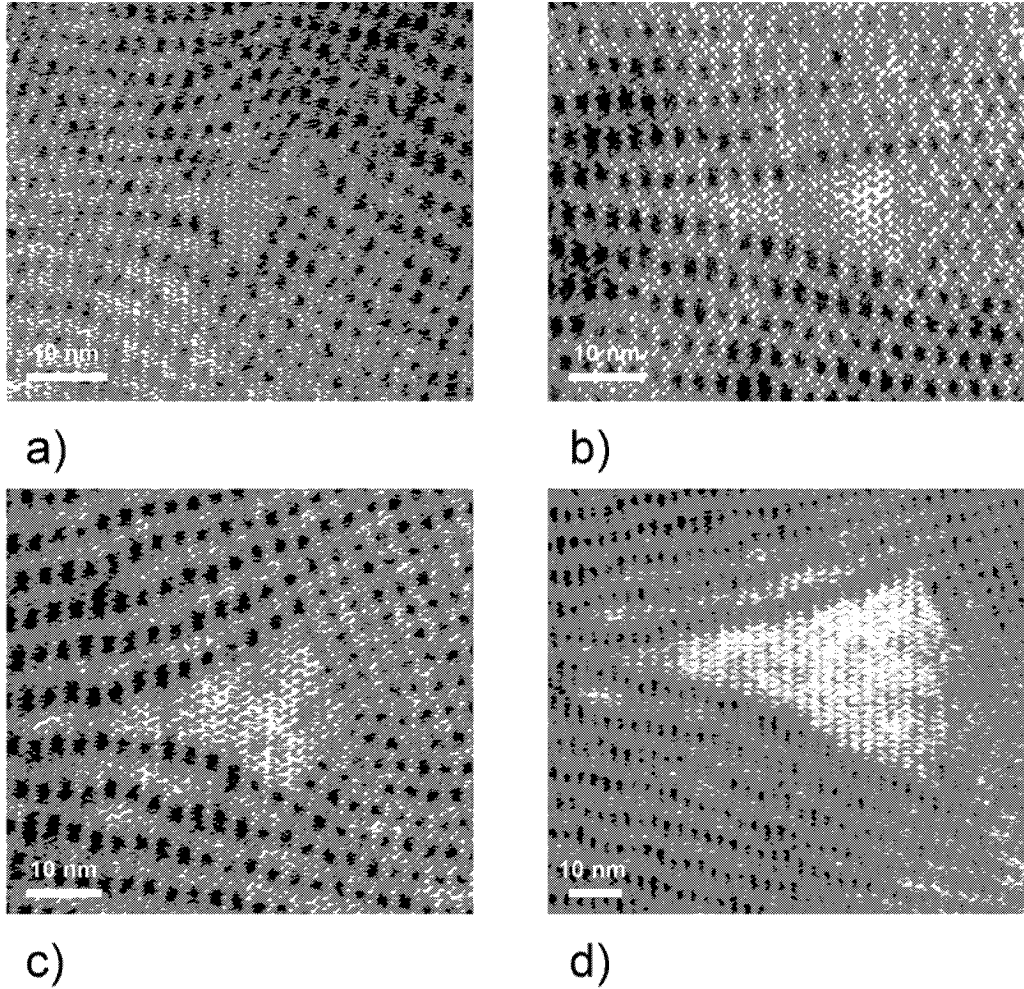


Figure 9.5: Different types of metadislocation have been experimentally observed possessing 4 (a), 6, (b), 10 (c), and 16 (d) phason halfplanes (from Feuerbacher 2003a).

9.2 The Burgers vector of a metadislocation

The Burgers vector of a metadislocation can be determined by a Burgers circuit around the tile representing the core of the metadislocation by embedding it in an arrangement of flattened hexagons as demonstrated in Figure 9.2.

In a simple alternative description the Burgers vector of a metadislocation can be interpreted as a lattice mismatch at the interface between the ξ' - and the ψ -phase. The determination of the lattice mismatch is demonstrated in Figure 9.1. On the right-hand side, the metadislocation core is accompanied by three layers of the ψ -phase (grey boxes). The “thickness” of the ψ -phase in $[0, 0, 1]$ -direction is $3 \times (\tau + 3) c_{\xi'} = 13.854 c_{\xi'}$. On the left-hand side, the metadislocation core is accompanied by 14 layers of the ξ' -phase (grey boxes), hence the extension of the ξ' -phase in $[0, 0, 1]$ -direction is $14 c_{\xi'}$. The lattice mismatch is $[3 \times (\tau + 3) c_{\xi'}] - 14 c_{\xi'} = -0.146 c_{\xi'} = -1.83 \text{ \AA}$. The Burgers vectors of metadislocations with different numbers of phason halfplanes can be calculated in the same way. For example a metadislocation involving 10 phason halfplanes possesses 5 layers of the ψ -phase. The

"thickness" of the ψ -phase in $[0, 0, 1]$ -direction is $5 \times (\tau + 3) c_{\xi'} = 23.09 c_{\xi'}$. The number 23.09 is close to the integer number 23. The number of layers of ξ' -phase at the metadislocation core corresponds to the integer number which is closest to the thickness of the ψ -phase in units of $c_{\xi'}$. By this way the lattice mismatch at the interface between the ξ' - and the ψ -phase is minimized. The lattice mismatch at the interface is $[5 \times (\tau + 3) c_{\xi'}] - 23 c_{\xi'} = 0.09 c_{\xi'} = 1.13 \text{ \AA}$. Hence the Burgers vector of a metadislocation possessing 10 phason halfplanes is $\vec{b} = 1.13 \text{ \AA} [0, 0, 1]$. Table 9.1 compiles the Burgers vectors of all metadislocations which have been experimentally observed so far. In the first and second column the number of phason halfplanes and the thickness of the ψ -phase in units of c_{ψ} are given, respectively. In the third column the thickness of the ψ -phase is given in units of $c_{\xi'}$. The numbers of the third column are calculated by multiplying the second column with the factor $(\tau + 3)$. In column four the integer number is given which is closest to the number in column three. This number represents the thickness of the ξ' -phase in units of $c_{\xi'}$. Subtracting the numbers of columns three and four yields the difference of the thickness of the ξ' - and the ψ -phase in units of $c_{\xi'}$. Multiplying these numbers with $c_{\xi'} = 12.56 \text{ \AA}$ yields the lattice mismatch at the interface between the ξ' - and the ψ -phase, i.e. the Burgers vector of the metadislocation. The Burgers vector of a metadislocation is always smaller than the lattice parameter $c_{\xi'}$. The lattice mismatch is $0.382 c_{\xi'}$ at maximum for the metadislocation possessing two phason planes.

Number of phason halfplanes	thickness of the ψ -phase in units of c_{ψ}	thickness of the ψ -phase in units of $c_{\xi'}$	thickness of ξ' -phase in units of $c_{\xi'}$	lattice mismatch in units of $c_{\xi'}$	Burgers vector
16	8	36.944	37	- 0.056	- 0.70 $\text{\AA}$
10	5	23.090	23	0.090	1.13 $\text{\AA}$
6	3	13.854	14	- 0.146	- 1.83 $\text{\AA}$
4	2	9.236	9	0.236	2.96 $\text{\AA}$
2	1	4.618	5	- 0.382	- 4.80 $\text{\AA}$

Table 9.1: Burgers vectors of metadislocations possessing different numbers of phason halfplanes (see text).

The sequence of metadislocations possesses interesting mathematical properties. The thickness of the ψ -phase in units of c_{ψ} (column 2 in Table 9.1) corresponds to a Fibonacci sequence (1, 2, 3, 5, 8, ...). The lattice mismatches in units of $c_{\xi'}$ are equal to the numbers $-\tau^{-6}$, τ^{-5} , $-\tau^{-4}$, τ^{-3} , and $-\tau^{-2}$. Hence the Burgers vectors, starting from low values, follow a sequence where the next value is calculated by multiplying a factor of $-\tau$. The Burgers vector moduli and the numbers of phason halfplanes are correlated in an opposite way, when the number of phason halfplanes is high the lattice mismatch is low and vice versa.

9.3 Metadislocation networks

Phason planes can only terminate at other metadislocation cores, at grain boundaries or at stacking faults. Therefore, a single metadislocation is, in principle, a defect structure of "unlimited" size. Frequently it is observed that metadislocations form networks in the sense that phason planes on both ends terminate at metadislocation cores. Figure 9.6 shows a network of metadislocations. The dark lines correspond to phason planes of metadislocations. The metadislocation cores are indicated by triangles. The metadislocation network is embedded into the ξ' -phase (bright background). The physical properties of metadislocation networks particularly their effect on plastic deformation has not been investigated so far.

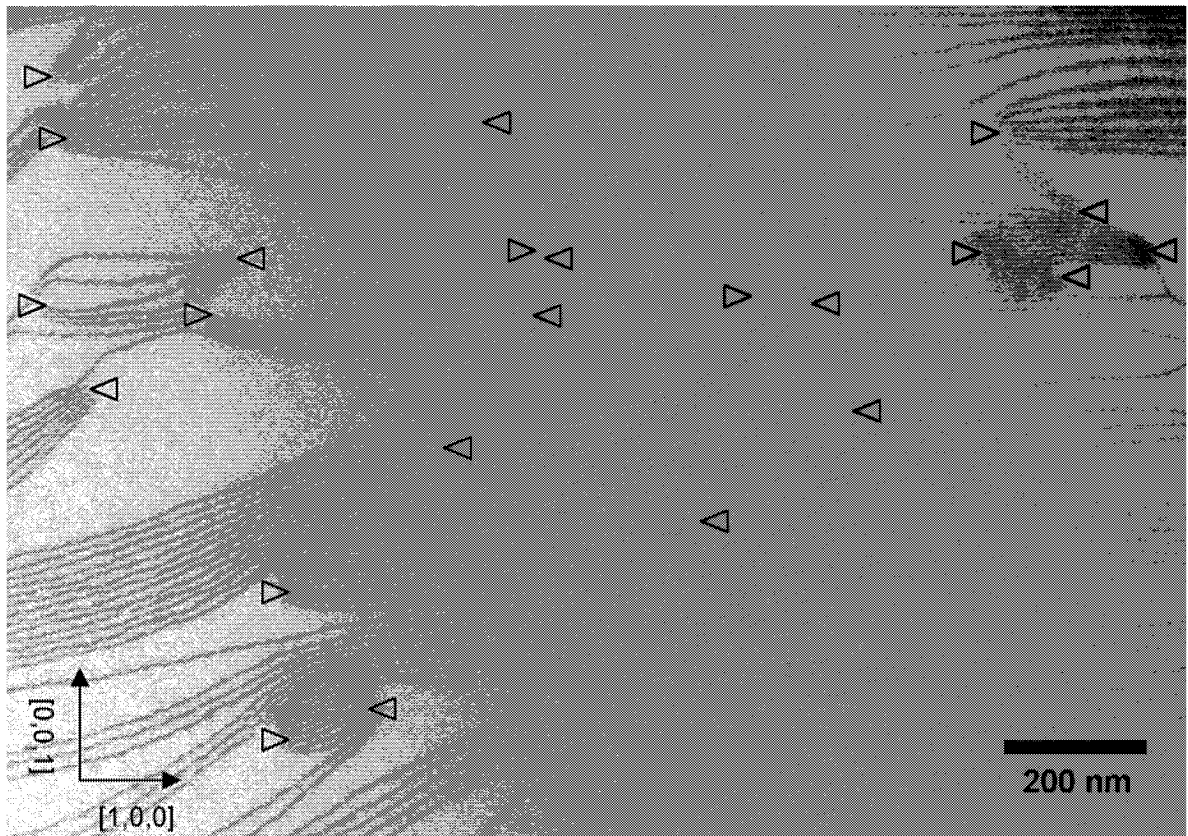


Figure 9.6 Micrograph of a metadislocation network (Klein 1998). The dark lines correspond to phason planes, metadislocation cores are indicated by triangles.

In this Chapter a basic theoretical investigation on metadislocation networks is performed. However only metadislocation networks are discussed which are limited to certain size in the sense that all phason planes terminate at metadislocation cores. A Burgers circuit can be performed around such type of metadislocation network entirely in one phase, the ξ' -phase. Therefore, these types of metadislocation networks possess fundamentally different topological properties than single metadislocations.

Figure 9.7 schematically shows simple examples of such metadislocation networks. The triangles symbolise the cores of metadislocations. Every core is accompanied by a number indicating the number of phason planes corresponding to the metadislocation. The phason planes are shown as black lines. The simplest example of a metadislocation network are two metadislocation cores connected by two phason planes. Such a network is named 2/2-metadislocation network in the further course of this work. A network of two

metadislocations possessing four phason planes is referred to as 4/4-metadislocation network (Figure 9.7 a). The Burgers vector of a metadislocation with four phason planes is $2.96 \text{ \AA} [0, 0, 1]$ (see Table 9.1). The Burgers vector of a 4/4-metadislocation network containing two metadislocation with four phason planes and oppositional direction is zero.

Metadislocation networks of two metadislocation of the same type as 2/2-, 4/4-, 6/6-, 10/10-, and 16/16-metadislocation networks always possess a Burgers vector equal to zero, i.e. a closed Burgers circuit around the network reveals no closure failure. Figure 9.7 b shows a metadislocation network containing one metadislocation with four phason planes and two metadislocation with two phason planes, i.e. a 4/2,2-metadislocation network.

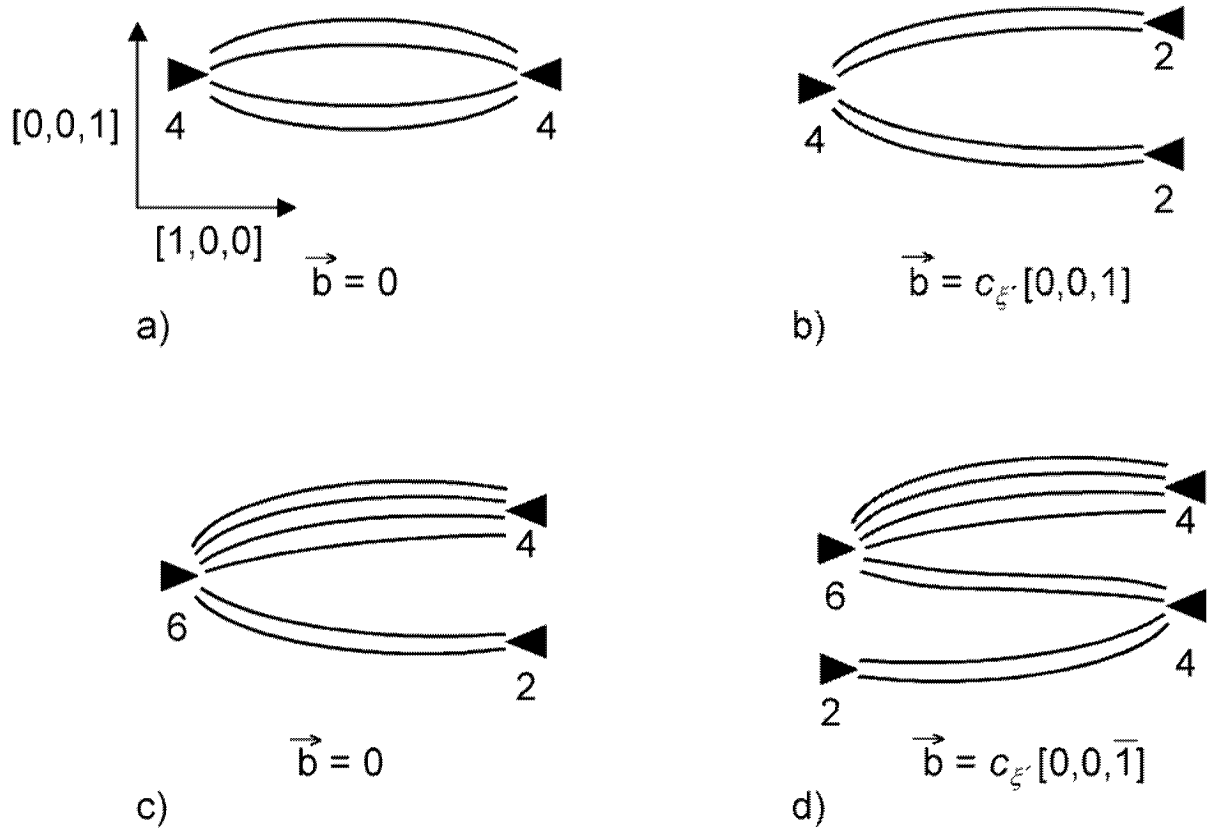


Figure 9.7: Schemes of 4/4- (a), 4/2,2 (b), 6/4,2- (c), and 6,2/4,4-metadislocation networks (d). The triangles symbolise the cores of metadislocations; phason planes are shown as black lines. The numbers indicate the number of phason planes connected to the metadislocation cores.

The modulus of the Burgers vector of a 4/2,2-metadislocation network according to Table 9.1 is $0.236 c_{\xi'} - (2 \times -0.382 c_{\xi'}) = c_{\xi'} = 12.56 \text{ \AA}$. Hence the Burgers vector is $\vec{b} = c_{\xi'} [0, 0, 1]$. A 4/2,2-metadislocation network is a perfect dislocation in the ξ' -phase. The Burgers vector modulus of a 6/4,2-metadislocation network (Figure 9.7c) is $0.146 c_{\xi'} - (0.236 c_{\xi'} - 0.382 c_{\xi'}) = 0 c_{\xi'}$. Figure 9.7 d shows a 6,2/4,4-metadislocation network. The Burgers vector modulus is $(-0.146 c_{\xi'} - 0.382 c_{\xi'}) - (2 \times 0.236 c_{\xi'}) = -c_{\xi'} = -12.56 \text{ \AA}$. Table 9.2 compiles the Burgers vectors for simple metadislocation networks possessing one metadislocation at one side.

metadislocation network	Burgers vector	metadislocation network	Burgers vector
2 / 2	0	16 / 16	0
4 / 4	0	16 / 10, 6	0
4 / 2, 2	$c_{\xi'} [0,0,1]$	16 / 10, 4, 2	0
6 / 6	0	16 / 10, 2, 2, 2	$c_{\xi'} [0,0,1]$
6 / 4, 2	0	16 / 6, 6, 4	0
6 / 2, 2, 2	$c_{\xi'} [0,0,1]$	16 / 6, 6, 2, 2	$c_{\xi'} [0,0,1]$
10 / 10	0	16 / 6, 4, 4, 2	0
10 / 6, 4	0	16 / 6, 4, 2, 2, 2	$c_{\xi'} [0,0,1]$
10 / 6, 2, 2	$c_{\xi'} [0,0,1]$	16 / 6, 2, 2, 2, 2, 2	$2c_{\xi'} [0,0,1]$
10 / 4, 4, 2	0	16 / 4, 4, 4, 4	$-c_{\xi'} [0,0,1]$
10 / 4, 2, 2, 2	$c_{\xi'} [0,0,1]$	16 / 4, 4, 4, 2, 2	0
10 / 2, 2, 2, 2, 2	$2c_{\xi'} [0,0,1]$	16 / 4, 4, 2, 2, 2, 2	$c_{\xi'} [0,0,1]$
		16 / 4, 2, 2, 2, 2, 2, 2	$2c_{\xi'} [0,0,1]$
		16 / 2, 2, 2, 2, 2, 2, 2, 2	$3c_{\xi'} [0,0,1]$

Table 9.2: Burgers vectors of metadislocation networks.

The metadislocation network shown in Figure 9.7 d possesses two metadislocation cores on both sides. The Burgers vector of the network can be calculated, as demonstrated before, using the lattice mismatches (or the Burgers vectors) for the metadislocations which are given in Table 9.1. Alternatively, the Burgers vector of a metadislocation network can be determined combining simple metadislocation networks, like those given in Table 9.2. In Figure 9.8 the "addition" of simple metadislocation networks is demonstrated. It should be emphasized here that the process shown in Figure 9.8 is only a simple graphical scheme which can be used for the determination of the Burgers vectors of metadislocation. Figure 9.8 does not show dynamical processes of metadislocation networks like the "annihilation" of metadislocations.

Figure 9.8 a shows a 6/4,2- and a 4/2,2-metadislocation network, respectively. The Burgers vectors of the metadislocation networks were taken from Table 9.2. In Figure 9.8 b the 4/2,2-metadislocation network is mirrored at the (1,0,0)-plane. The Burgers vector of a 2,2/4-metadislocation network is the negative Burgers vector of a 4/2,2-metadislocation network. In Figure 9.8 c both metadislocation networks are connected at metadislocation cores, possessing the same number of phason planes attached to them (2 in the present example) but opposite direction. The linking of metadislocation networks by this way does not change the Burgers vector of the network. In Figure 9.8 d the 6,2/4,4-metadislocation network is formed. The Burgers vector is determined by addition of the Burgers vectors of the two initial metadislocation networks in Figure 9.8 c.

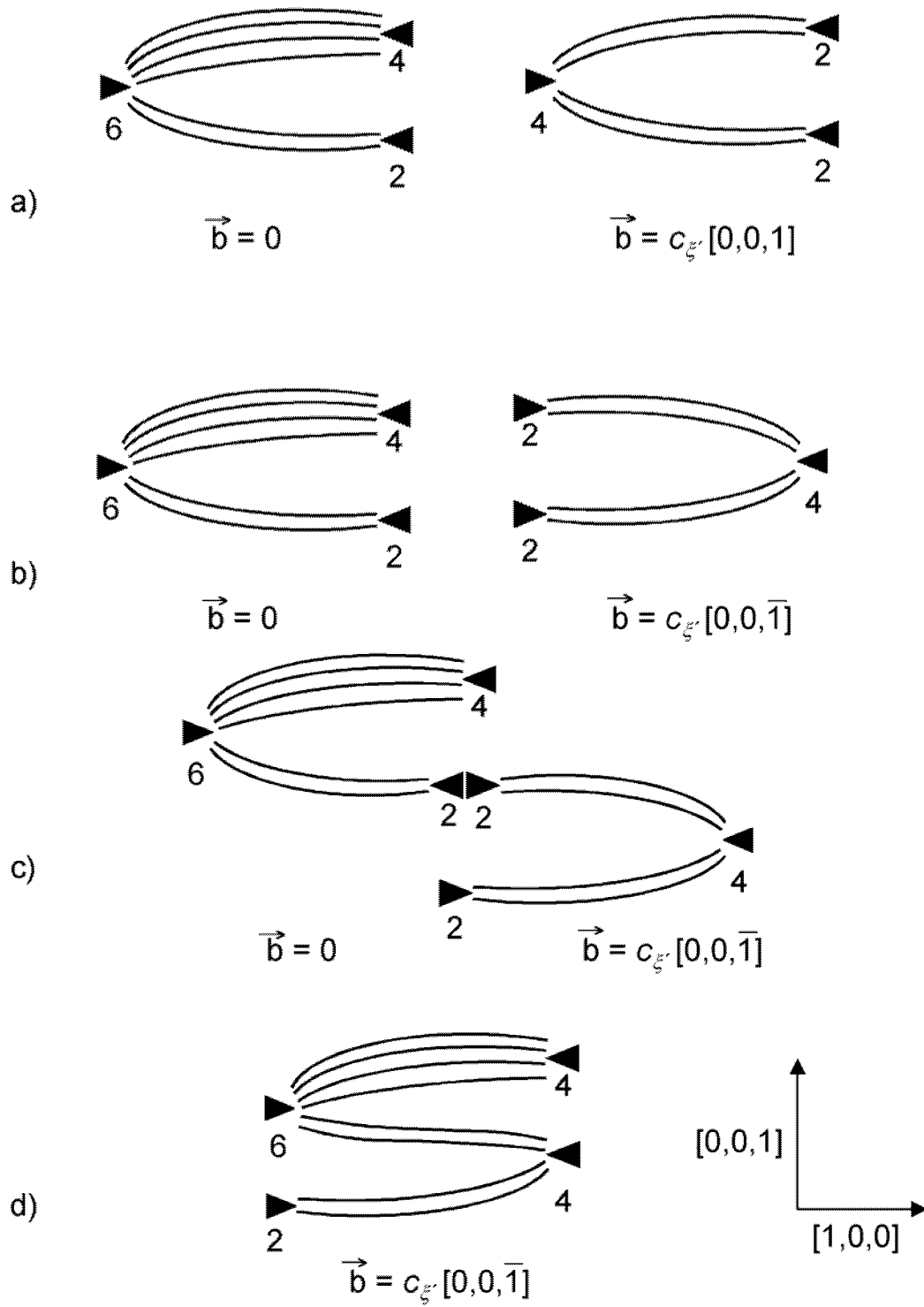


Figure 9.8: Graphical scheme for the determination of the Burgers vector of complex metadislocation networks by the "addition" of simple metadislocation networks.

9.4 Conclusion

In the present Chapter the basic characteristics of metadislocations were introduced. A metadislocation consists of a core region and phason halfplanes attached to the core. The phason planes possess structural elements which are present in the ψ -phase. A simple scheme for the determination of Burgers vectors of metadislocations is described. In this description the Burgers vector of a metadislocation is interpreted in terms of the lattice mismatch between the ξ' - and the ψ -phase. The Burgers vector of a metadislocation is not equal to the lattice parameter (or a rational fraction of the lattice parameter) as in simple crystals. The Burgers vector modulus of a metadislocation is the difference of multiples of the lattice parameters $c_{\xi'}$ and c_{ψ} .

Furthermore the properties of metadislocation networks were studied for the first time. The metadislocation networks discussed in the present Chapter have the common feature that all phason planes terminate at metadislocation cores (and not at a grain boundary or the surface of the crystal). A Burgers circuit can be performed around such types of metadislocation networks entirely in the ξ' -phase. It was shown that metadislocation networks can be constructed which are perfect dislocations in the ξ' -phase. The Burgers vector of these perfect dislocations is $\vec{b} = c_{\xi'} [0,0,1]$ or multiples of this vector. Although the Burgers vector modulus of such metadislocation networks is high (12.56 Å), the local strain at each metadislocation core is low. The Burgers vector modulus of a single metadislocation is $0.382 c_{\xi'}$ (4.8 Å) at maximum for a metadislocation possessing two phason halfplanes.

10. Defects in c_2 -Al-Pd-Fe

10.1 Introduction

In the present Chapter, the microstructure of plastically deformed c_2 -Al-Pd-Fe is investigated for the first time. c_2 -Al-Pd-Fe is a structurally complex alloy phase possessing about 255 atoms in the unit cell (Edler 1997). The phase diagram of the Al-Pd-Fe alloy system was published by Edler (1997) and has been reinvestigated by Balanetsky *et al.* (2003). The phases which are of importance in the present work are the cubic c_2 -Al₆₄Pd₃₁Fe₅ phase and the c_1 -Al₆₉Pd₁₀Fe₂₁ phase. Figure 10.1 shows an isothermal section of the ternary Al-Pd-Fe phase diagram at 900 °C (Balanetsky *et al.* 2003). Besides the cubic phases c_1 , c_2 and c additional phases (e.g. M, O, ϵ , δ and β) are present in this part of the isothermal section of the Al-Pd-Fe phase diagram (Figure 10.1). The orthorhombic phases O and ϵ and the monoclinic M-phase are structural complex phases possessing large lattice parameters as well. The c_2 -Al-Pd-Fe phase is stable up to the decomposition temperature of 975 °C. The phases c_1 - and c_2 -Al-Pd-Fe were recognized as rational approximants of a metastable face-centred-icosahedral phase by Sugiyama *et al.* (2000) and Shibuya *et al.* (2000).

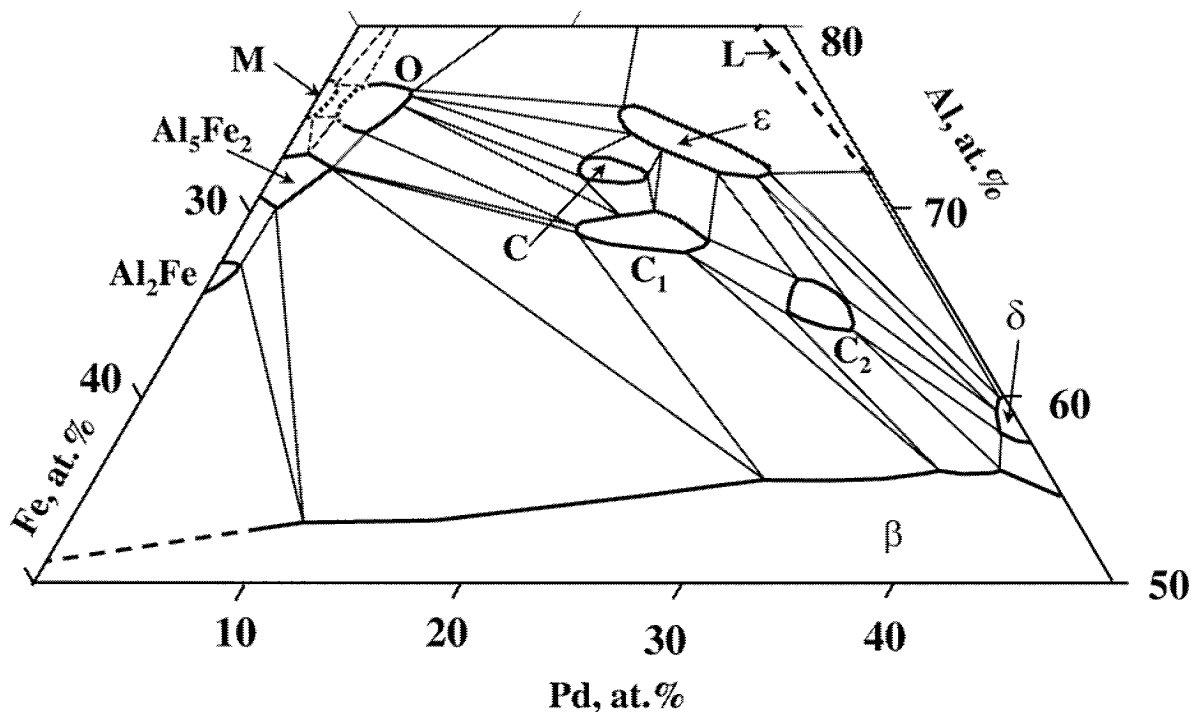


Figure 10.1: Partial isothermal section of the ternary Al-Pd-Fe phase diagram at 900 °C according to Balanetsky *et al.* (2003). The cubic phases c_1 , c_2 , c and additional phases (M, O, ϵ , δ and β) are indicated. The liquid is designated L. Provisional tie-lines and suggested regions of homogeneity of the phases are marked by broken and dotted lines, respectively.

The structure of c_2 -Al-Pd-Fe was determined by Edler and coworkers (Edler 1997, Edler *et al.* 1998). The space group of the c_2 -phase is $Fm\bar{3}$, i.e. it possesses a face-centred cubic (FCC) lattice. The lattice parameter amounts to $a = 15.52 \text{ \AA}$ (Sugiyama *et al.* 2000). The dominant structural motifs of the c_2 -phase are edge-sharing icosahedral cages with edge to edge diameter of $a/2$ are generated by Pd atoms. Figure 10.2 shows two icosahedral cages and three examples for the location of Pd atoms (dotted circles) at the vertices of the icosahedra. The icosahedra are filled with two different structural motifs. The first one (right-hand side of Figure 10.2) possesses a central atom site fractionally occupied by 22 % Fe and 78 % Pd. This central atom is coordinated by a rhombic dodecahedron which consist of a transition-metal cube (86 % Pd and 14 % Fe) and an Al octahedron. Hence, the coordination number (CN) for the central atom is 14. The eight transition-metal atoms forming a cube are sketched black and the six Al atoms forming the octahedron are grey.

The second cluster filling motif (left-hand side of Figure 10.2) is a central atom site fractionally occupied by 22 % Fe and 78 % Pd which is coordinated by an Al cube. Hence, the coordination number of the central atom is 8 (CN8). The Al cube is occurring in five different orientations. On the average these five different orientations form a regular pentagon-dodecahedron. Each of the 30 edges of the pentagon-dodecahedron represents a distance that is essentially too small for an Al-Al interatomic spacing. Since the site possesses a low occupancy of 40 %, too short next neighbour distances do not occur.

A striking detail of the structure model is the strong difference of the two filling motifs inside the icosahedral cages. Chemical disorder plays an important role on the transition-metal sites, however configurational disorder is only restricted to one type of the filling motifs, the Al cube (CN8 site). The ratio of configurationally ordered/disordered cluster filling motifs is $\frac{1}{2}$ in the c_2 -phase.

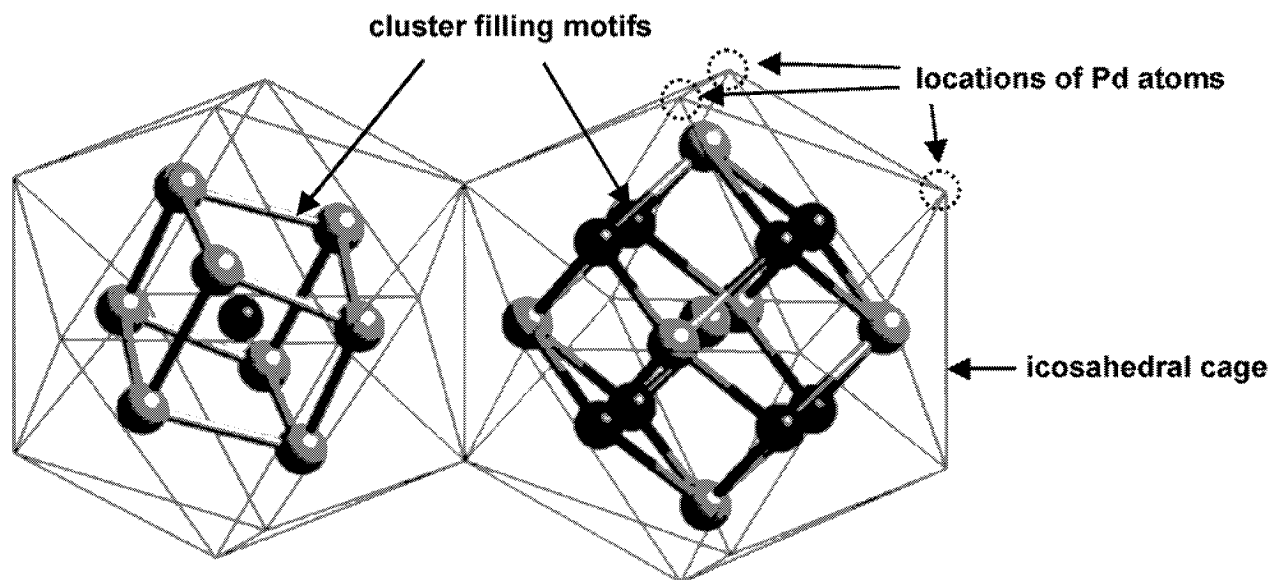


Figure 10.2: Sketch of the dominant structural motifs of the c_2 -phase. Edge-sharing icosahedral cages are generated by Pd atoms (dotted circles). The cages are filled with two different structural motifs. Left: A central atom is coordinated by a cube (left) and a rhombic dodecahedron (right). Transition-metal atoms and Al atoms are indicated black and grey, respectively (from Edler *et al.* 1998).

Figure 10.3 shows a network of the icosahedral cages containing the cluster filling motifs. Here, the second cluster filling motif, i.e. the Al cube which is present in five different orientations, is represented by the average structure, the pentagon dodecahedron. In the further course of this work, this filling motif is always referred to as pentagon-dodecahedral motif. The central atoms of both cluster filling motifs occupy the $(0, 0, 0)$ and $(0, 0, \frac{1}{2})$ positions of the unit cell. The icosahedral cages are filled alternately with both cluster filling motifs. Due to the face centred order, cages of equal type can never share a common edge.

Besides the structural elements introduced so far a small icosahedron consisting of a central Pd atom surrounded by 12 Al atoms is present on the $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ lattice positions and fills the spacings between the icosahedral Pd cages. The small icosahedra are not shown in Figure 10.3.

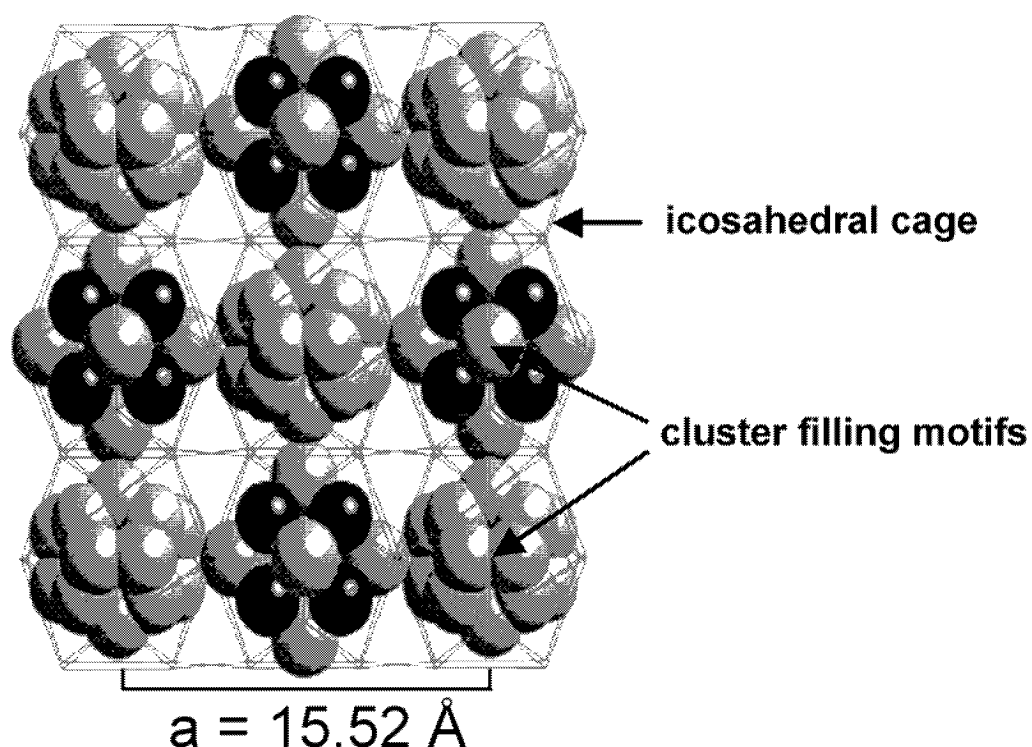


Figure 10.3: Sketch of the unit cell of the c_2 -phase according to Edler (1997). The main structural elements are edge-sharing icosahedral cages of Pd atoms (indicated as lines) alternately filled a rhombic dodecahedron and a pentagonal dodecahedron (grey: Al atoms, black: transition-metal atoms).

Figure 10.4 a shows a scheme of the distribution of cluster motifs in the unit cell. The distribution of the cluster filling motifs is schematically shown in two layers ($z = 0$ and $z = \frac{1}{2}$) of the unit cell. Filled and open circles denote the rhombic-dodecahedral (CN14) and the pentagon-dodecahedral (CN8) cluster motifs, respectively.

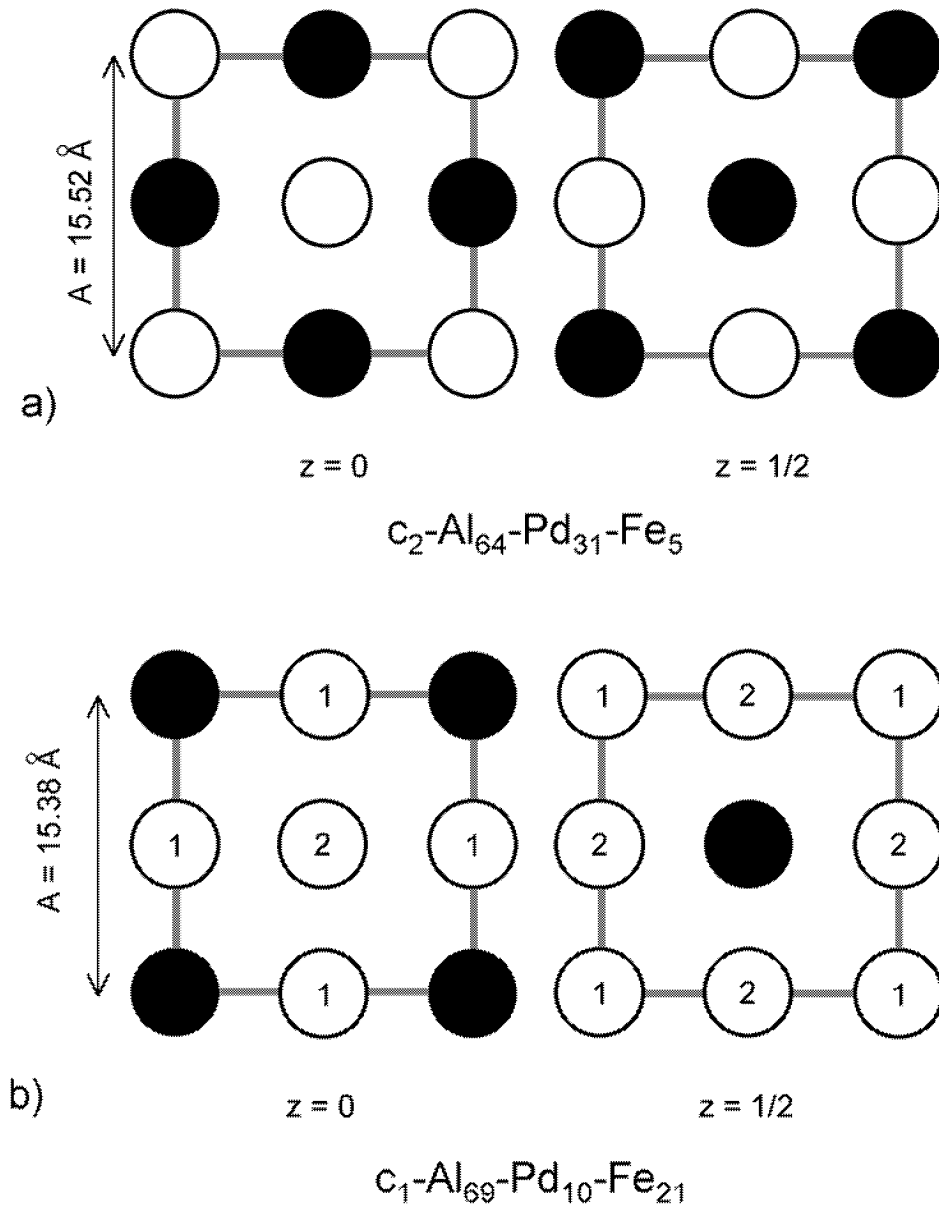


Figure 10.4: Scheme of the distribution of cluster motifs in the unit cell of (a) the c_2 -phase and (b) the c_1 -phase according to Edler (1997) (filled circles: rhombic-dodecahedral cluster motifs; open circles: pentagon-dodecahedral cluster motifs; “1” and “2” denote different pentagon-dodecahedral clusters).

Another structurally complex alloy phase in the Al-Pd-Fe alloy system is the c_1 -Al₆₉Pd₁₀Fe₂₁ phase. The space group is $Im\bar{3}$, i.e. it possesses a body-centred cubic (BCC) lattice. The lattice parameter is 15.38 Å (Sugiyama *et al.* 2000), i.e. 1 % smaller than the lattice parameter of the c_2 -phase. The structure of the c_1 -phase is very similar to the c_2 -phase. The main structural elements are icosahedral cages of Pd atoms which are alternately filled with different types of cluster motifs. Figure 10.4 b shows a scheme of the distribution of cluster motifs in the unit cell. The filled circles denote rhombic-dodecahedral cluster motifs. The open circles “1” and “2” denote different pentagon-dodecahedral clusters which are massively under-occupied and disordered. The ratio of ordered/disordered coordinations is $\frac{1}{4}$ in the c_1 -phase. Besides the c_1 - and c_2 -phase a structurally related simple-cubic high-temperature phase, the c-phase, was found. This phase possesses a lattice parameter of

7.654 Å and shows one disordered cluster filling motif of the icosahedral Pd cages (Edler 1997). Hence, the ratio of ordered/disordered coordinations is zero.

The phases c_1 , c_2 and c in the Al-Pd-Fe alloy system are structurally related to other phases like $\text{Al}_{63}\text{Pd}_{27}\text{Co}_{10}$ (Yurechko 2002 a, b), $\text{Al}_{68}\text{Pd}_{20}\text{Ru}_{12}$ (Mahne and Steurer 1996), $\text{Al}_5\text{Cu}_6\text{Mg}_2$ (Samson 1949) or $\text{Al}_{72}\text{Rh}_{28}$ (Grin *et al.* 1997). All these phases are cubic with similar lattice parameters and possess edge-sharing icosahedral cages which are filled with cluster motifs comparable to those presented in Figure 10.3. Therefore, the determination of the plastic deformation mechanism of the c_2 -Al-Pd-Mn phase is potentially significant for a sizable group of structurally related phases.

10.2 Experimental procedure

Polycrystalline single-phased c_2 -Al-Pd-Fe was produced by preparing an ingot of composition $\text{Al}_{61}\text{Pd}_{34}\text{Fe}_4$ by levitation melting and subsequent annealing for 90 h at 900 °C according to phase-diagram investigations of Edler (1997) and (Balanetskyy *et al.* 2003). Figure 10.5 shows the ingot after the annealing procedure. TEM investigations revealed the presence of polycrystalline single-phase c_2 -Al-Pd-Fe material. The size of single grains is approximately 5 µm.

Samples of $5 \times 2 \times 2 \text{ mm}^3$ in size were cut from the ingot and their faces were prepared by grinding and polishing. Plastic deformation tests were carried out in a modified Zwick Z050 uniaxial testing machine under compression (Appendix B) at a strain rate of 10^{-5} s^{-1} . Samples were deformed at 800 and 750 °C, which is well below the temperature of decomposition of the c_2 -phase.

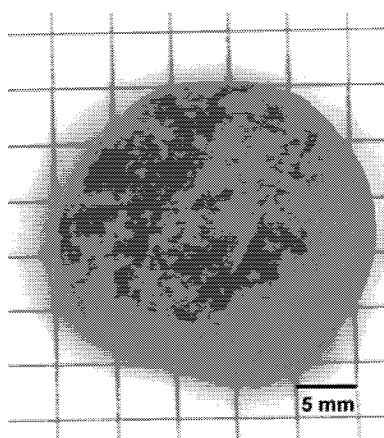


Figure 10.5: c_2 - $\text{Al}_{61}\text{Pd}_{34}\text{Fe}_4$ ingot after the annealing procedure.

Plastically deformed and undeformed samples were prepared for TEM by slicing, grinding, polishing and argon-ion milling. Firstly, microstructural analyses including Bragg-contrast imaging of defects in deformed c_2 -Al-Pd-Fe were carried out in a JEOL 4000FX transmission electron microscope. Lattice fringe pictures were taken in a JEOL 4000EX transmission electron microscope. A Philips CM 20 transmission electron microscope equipped with an energy dispersive x-ray (EDX) microanalysis system was used for composition analysis. The lattice fringe analysis was performed using the software Digital Micrograph by Gatan Inc. (Appendix E).

10.3 Results

Figure 10.6 shows a stress-strain curve of a c_2 -Al-Pd-Fe sample deformed at 750 °C at a strain rate of 10^{-5} s^{-1} . After elastic loading of the sample, plastic yielding was attained at a stress of 80 MPa. The stress drops in Figure 10.6 correspond to additional stress-relaxation experiments. After about 0.5 % of plastic straining the sample was unloaded and subjected to a microstructural analysis.

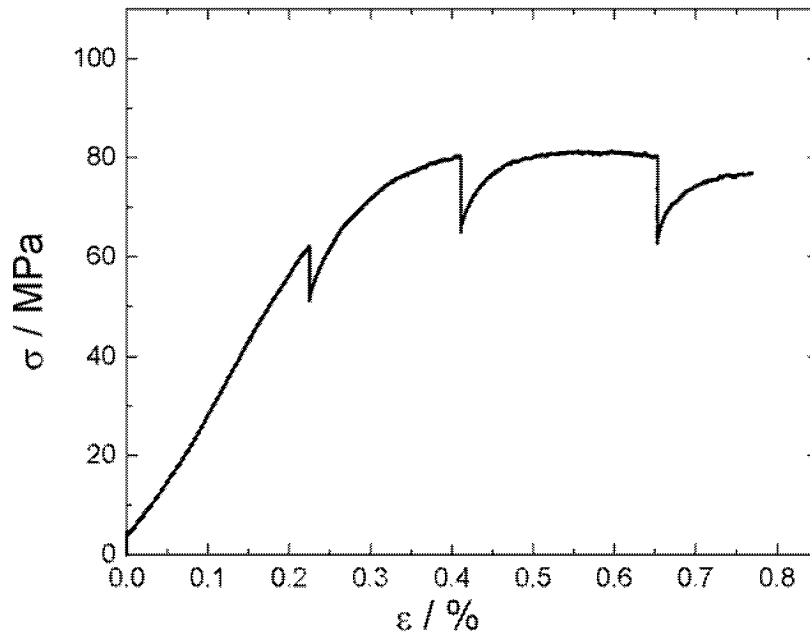


Figure 10.6: Stress-strain curve of a c_2 -Al-Pd-Fe sample deformed at 750 °C at a strain rate of 10^{-5} s^{-1} . The stress drops correspond to additional stress-relaxation experiments.

Figure 10.7 shows a diffraction-contrast image using bright-field conditions. Arrow (1) points at a planar fault showing fringe contrast. The planar nature of the fault was verified by tilting the sample with respect to the optical axis, resulting in a change of the projected lateral width of the fault. The planar fault is terminated by lines (2), the contrast of which resembles that of a dislocation. The inset in Figure 10.7 shows an enlarged image of a termination of a planar defect. It can be seen that the image contrast widens up and possesses an almost rectangular shape. The same behaviour can be observed in the diffraction-contrast image, shown in Figure 10.8. Here, a planar fault is imaged in an almost edge-on orientation (1). At the planar defect regions are observed (2) where the image contrast widens up as well.

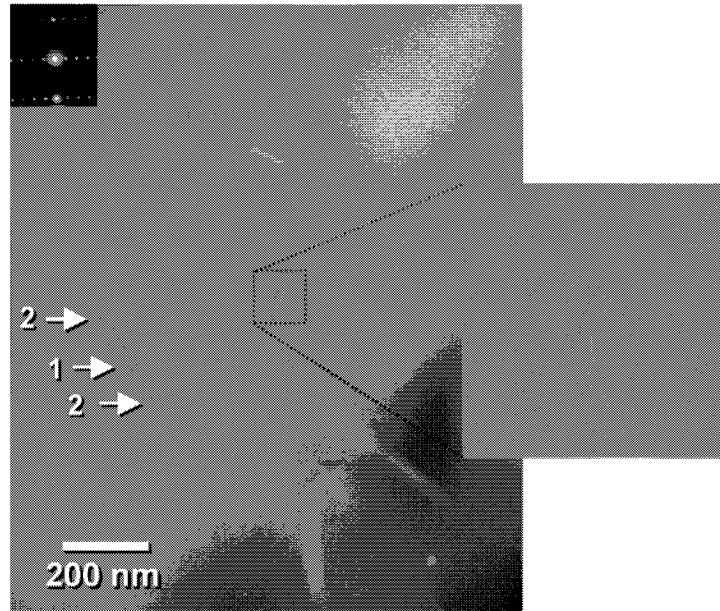


Figure 10.7: Diffraction-contrast image using bright-field conditions. The inset shows an enlarged image of the boxed region. A planar fault (1) is terminated by lines (2), the contrast of which resembles that of a dislocation.

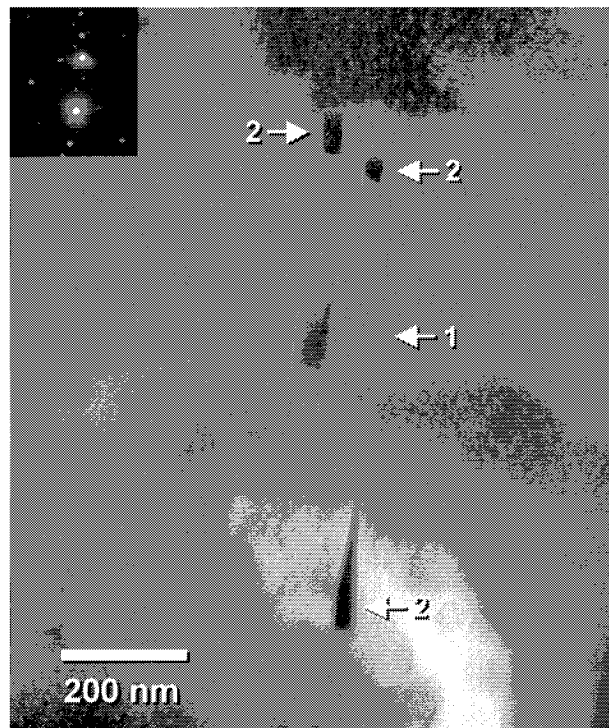


Figure 10.8: Diffraction-contrast image using bright-field conditions of a deformed c_2 -Al-Pd-Fe sample. Planar fault in an almost edge-on orientation (1) showing widened contrast at the end (2).

Figure 10.9 shows a lattice fringe picture of a defect, of which the part indicated by (3) is a planar defect oriented almost in edge-on orientation. The optical axis is along the $[\bar{1}, 1, 0]$ -direction of the sample. The regions (1) and (2) at the end of the planar fault show an almost rectangular shape and an image contrast which is, as the planar fault itself, brighter than the background. At the interface between the regions (1) and (2) and the bulk, small regions showing a non-uniform bending contrast can be observed (4 and 5). In region (4) particularly the image contrast changes from the left to the right from bright to dark. The length of the whole defect is 200 nm.

This micrograph was subjected to a detailed lattice fringe analysis using Fourier-processing. Figure 10.10 a shows a power spectrum of the bulk region outside the defect (6). The peak distribution of the power spectrum can be compared with the diffraction pattern of the sample parallel to the optical axis. Positions of low indexed reciprocal-lattice spots of the c_2 -phase structure along a $(\bar{1}, 1, 0)$ -reciprocal-lattice-direction are indicated by circles. They correspond to the intensity peaks of the power spectrum. Figure 10.10 b shows a power spectrum of region (1), i.e. within the defect structure. Here, the peak distribution does not correspond to a FCC-structure. For example no intensity peak is observed at the $\{1, 1, 1\}$ positions, which are indicated as dotted circles in Figure 10.10 b. The peak distribution corresponds to a BCC-structure, the low-index reciprocal-lattice positions of which along a $(\bar{1}, 1, 0)$ -reciprocal-lattice-direction are indicated as solid circles in Figure 10.10 b.

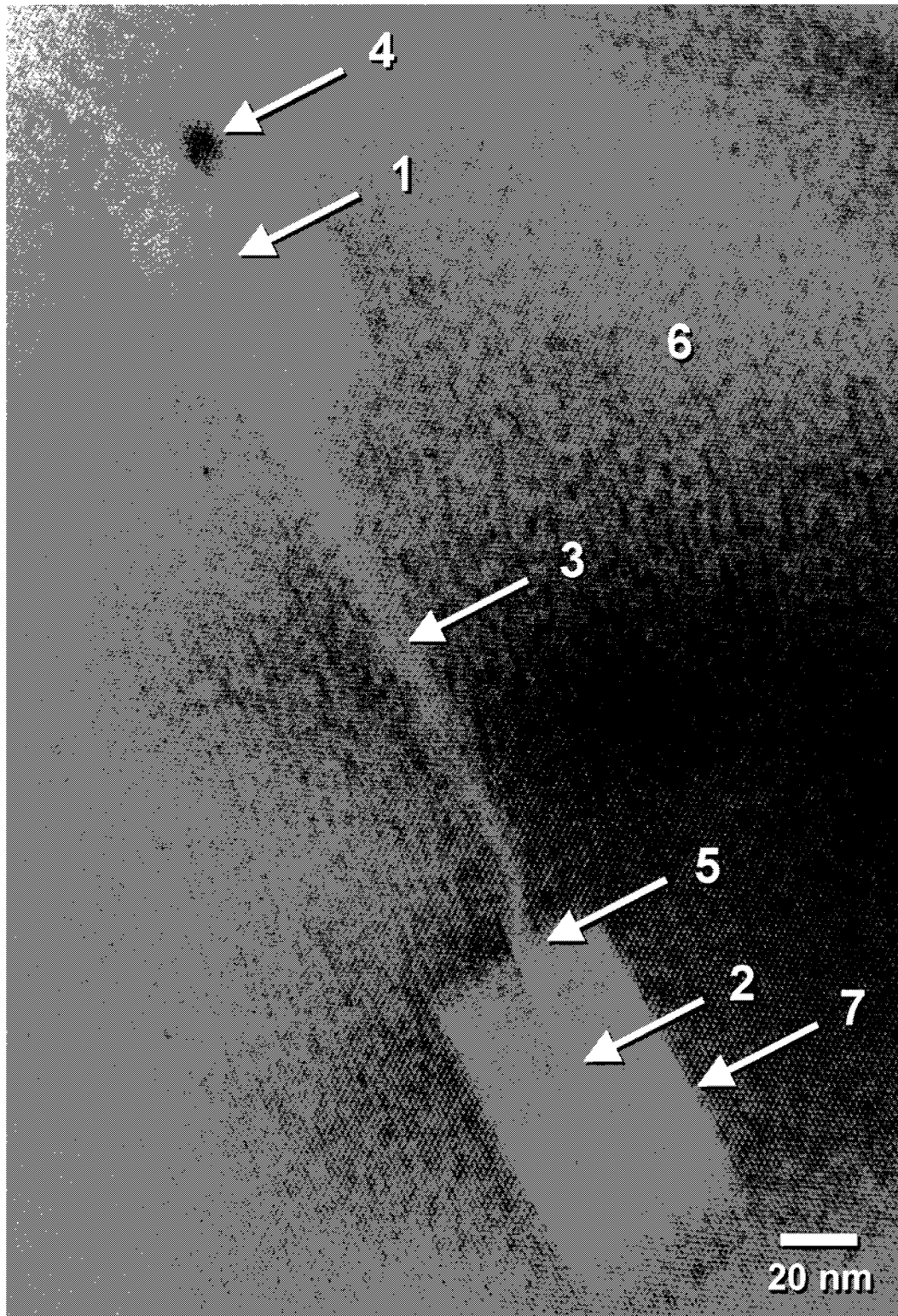


Figure 10.9: Lattice fringe picture of a defect containing a planar fault (3) oriented in edge-on orientation. The regions (1) and (2) at the end of the planar fault show an almost rectangular shape (4-7 see text). The optical axis is oriented along the $[\bar{1}, 1, 0]$ -direction of the sample.

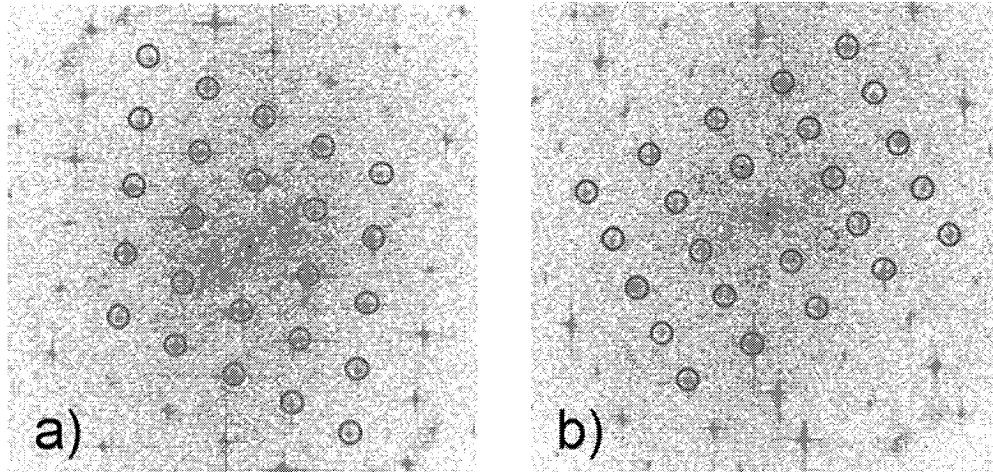


Figure 10.10: Power spectra corresponding to the sample region (6) (a) and (1) (b) in Figure 10.9. The peak distribution of the power spectra can be compared to diffraction patterns of (a) a FCC-structure (b) a BCC-structure. Corresponding reciprocal-lattice vectors are indicated as circles.

Figure 10.11 shows a Fourier-filtered enlarged image of the interface between the defect and the bulk (labelled (7) in Figure 10.9) using low spatial frequencies only, i.e. for back Fourier transformation, Fourier components corresponding to $(1, 1, 1)$, $(1, \bar{1}, \bar{1})$, $(1, 1, 0)$, $(2, 2, 0)$, $(0, 0, 2)$ reciprocal-lattice vectors were used. The projection of the c_2 -Al-Pd-Fe unit cell along the $[\bar{1}, 1, 0]$ -direction is shown schematically in the bulk region and in the defect region in Figure 10.11.

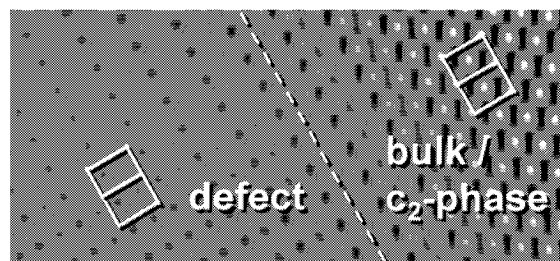


Figure 10.11: Fourier-filtered enlarged image of the interface (dashed line) between defect and bulk (indicated by (7) in Figure 10.9) using low spatial frequencies.

Fourier filtering of the regions (4) and (5) in Figure 10.9 reveals the presence of a non-coherent interface. Figure 10.12 a shows an enlarged Fourier-filtered image of the sample region (4) in Figure 10.9 using Fourier components corresponding to a $(0, 0, 2)$ -reciprocal-lattice vector and reveals the presence of an inserted half plane which is terminated at the interface between defect and bulk. A Burgers circuit around this region yields a Burgers-vector component in the $(\bar{1}, 1, 0)$ image plane of $\vec{b}_{(\bar{1},1,0)} = \frac{a_0}{2} [0, 0, \bar{1}]$, i.e. $|\vec{b}_{(\bar{1},1,0)}| = 7.76 \text{ \AA}$.

The same Burgers-vector component is found, analysing the $(0, 0, 2)$ -Fourier-filtered image corresponding to the sample region (5) in Figure 10.9 (Figure 10.12 b). In this region, the inserted half plane is terminated at the interface between defect and bulk, as well.

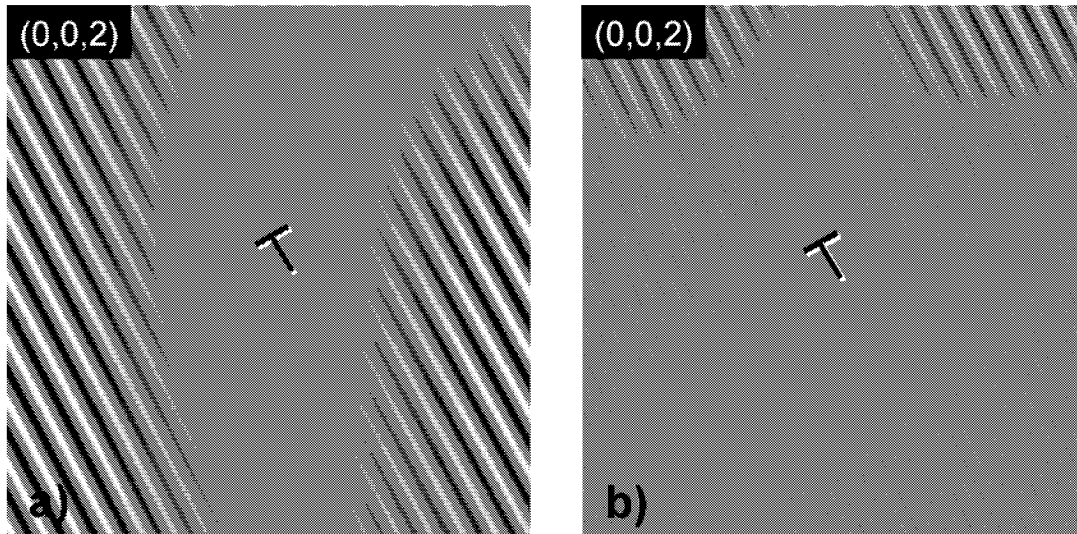


Figure 10.12: Enlarged Fourier-filtered image of the sample region (4) (a) and (5) (b) in Figure 10.9 using Fourier components corresponding to a $(0, 0, 2)$ -reciprocal-lattice vector.

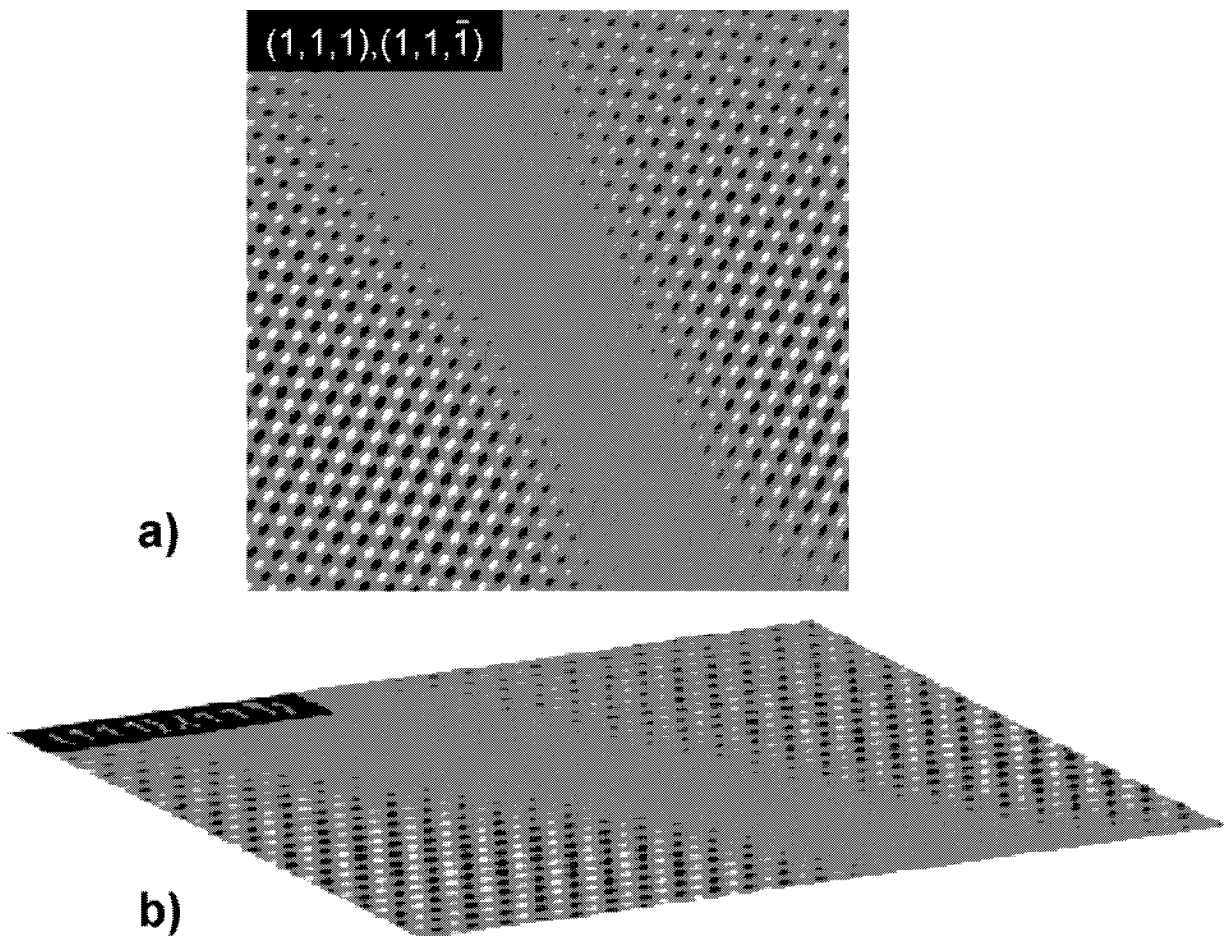


Figure 10.13 (a) Fourier-filtered image of the sample region (3) in Figure 10.9 using Fourier components corresponding to $(1, 1, 1)$ and $(1, 1, \bar{1})$ reciprocal-lattice vectors. (b) The same image in a grazing view along the lattice fringes.

Figure 10.13 a shows a Fourier-filtered image of the sample region (3), i.e. at the location of the planar defect, using Fourier components corresponding to $(1, 1, 1)$ and $(1, 1, \bar{1})$ reciprocal-lattice vectors. Figure 10.13 b shows Figure 10.13 a in a grazing view along the lattice fringes. At the location of the planar defect, the fringes show a shift of π along the planar fault. The interfaces of the defect regions (1) and (2) with the bulk (6) are fully coherent (cf. Figure 10.11) with exception of the regions (4) and (5) where a Burgers circuit yields the presence of inserted lattice planes. A Burgers circuit around the whole defect yields a Burgers-vector component of $\vec{b}_{(\bar{1},1,0)} = a_0[0, 0, \bar{1}]$ in the image plane, i.e. $|\vec{b}_{(\bar{1},1,0)}| = 15.52 \text{ \AA}$.

Figure 10.14 shows lattice fringe picture of a defect imaged along the $[\bar{1}, 1, 0]$ -direction. The defect has a rectangular size of approximately $38 \times 57 \text{ nm}$. Again, the inside region of the defect (1) shows a power spectrum which does not correspond to a FCC-structure but to a BCC-structure. At the upper and lower interface in Figure 10.14 regions labelled (2) and (3) reveal a non-uniform image contrast.

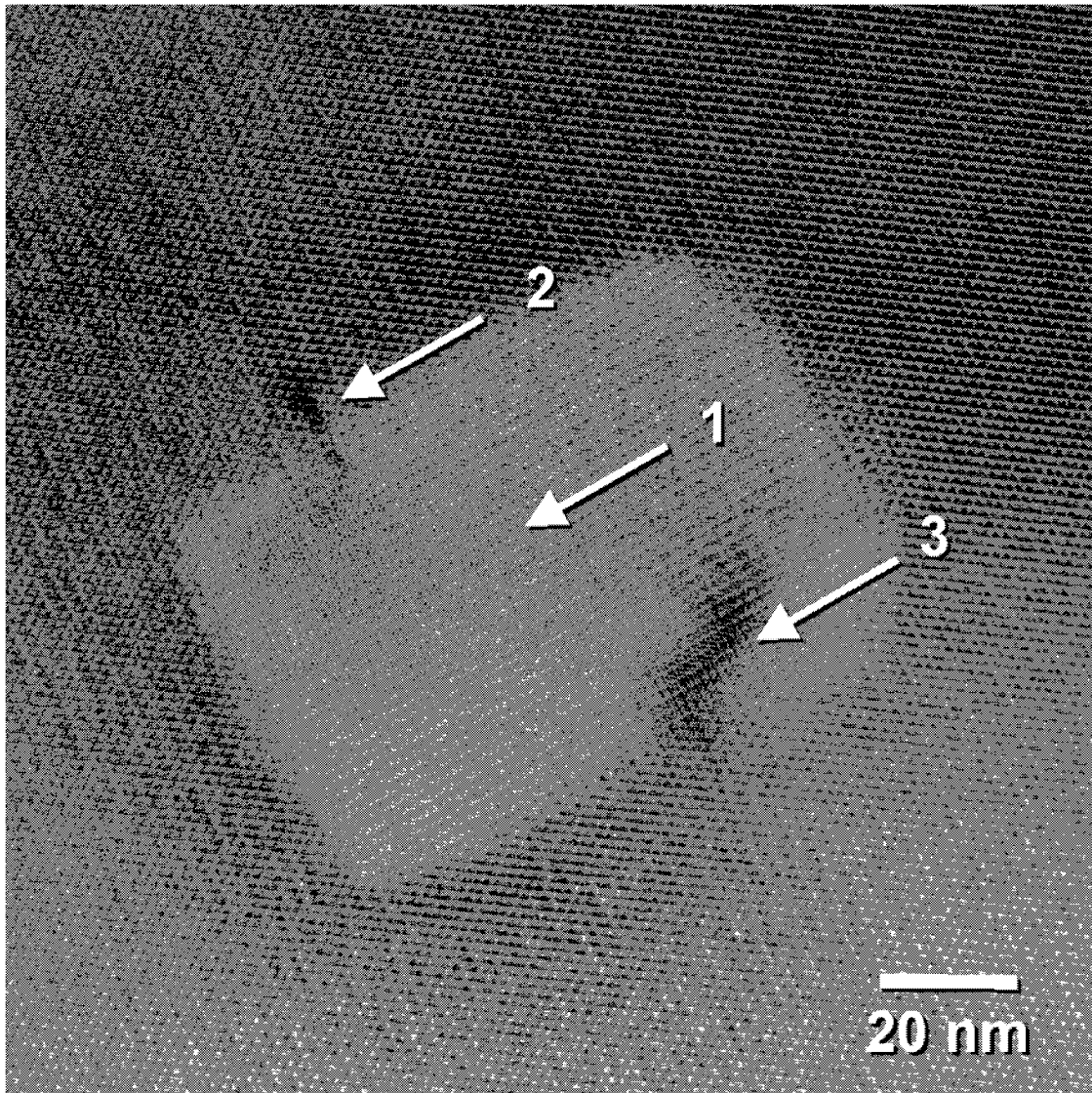


Figure 10.14: Lattice fringe picture of a defect in c_2 -Al-Pd-Fe (see text). The optical axis is oriented along the $[\bar{1}, 1, 0]$ -direction of the sample.

Figure 10.15 a and b show Fourier-filtered images of these regions using Fourier components corresponding to a $(0, 0, 2)$ reciprocal-lattice vector. In both cases inserted half planes are found, which terminate at the interface between defect and bulk. A Burgers circuit around region (2) in Figure 10.14 reveals a Burgers-vector component in the image plane of $\vec{b}_{(\bar{1},1,0)} = \frac{a_0}{2} [0, 0, \bar{1}]$. The opposite Burgers-vector component, $\vec{b}_{(\bar{1},1,0)} = \frac{a_0}{2} [0, 0, 1]$, is found for region (3). A Burgers circuit around the whole defect, therefore, reveals no closure failure, i.e. the resulting Burgers-vector component in the image plane is zero.

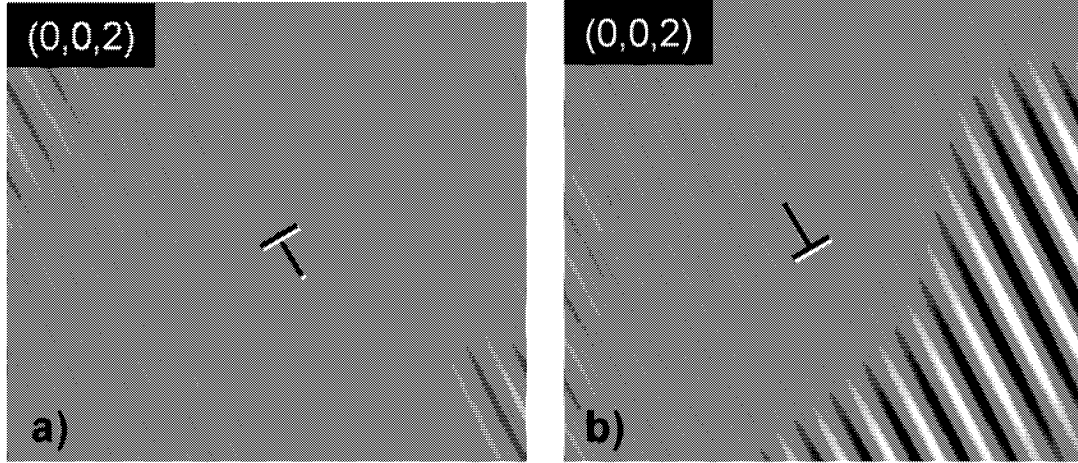


Figure 10.15: Enlarged Fourier-filtered image of the sample region (2) (a) and (3) (b) in Figure 10.14 using Fourier components corresponding to a $(0, 0, 2)$ -reciprocal-lattice vector.

Figure 10.16 shows a lattice fringe picture of another defect imaged along the $[\bar{1}, 1, 0]$ -direction of the sample. The overall length of the defect is about 45 nm. The lower part (1) is a planar defect, which shows the same lattice fringe shift as the planar defect in Figure 10.9. The lattice fringe shift of π can easily be observed if the picture is looked at under a grazing angle along the directions indicated by black arrows. The region labelled (2) shows the same power spectrum corresponding to a BCC-structure as observed before. Figure 10.17 a and b show Fourier-filtered images of the sample regions (3) and (4) in Figure 10.16 using Fourier components corresponding to a $(2, 2, 0)$ -reciprocal-lattice vector. In both cases a Burgers-vector component of $\vec{b}_{(\bar{1},1,0)} = \frac{a_0}{4} [1, 1, 0]$ was found in the image plane. Hence, the Burgers

vector of the whole defect is $\vec{b}_{(\bar{1},1,0)} = \frac{a_0}{2} [1, 1, 0]$, i.e. $|\vec{b}_{(\bar{1},1,0)}| = 10.97 \text{ \AA}$.

A local chemical composition analysis of defects was performed using EDX analysis. In nine cases the composition was measured at the end of planar defects, i.e. in the region where the BCC-phase is located in Figure 10.9. An average composition of $\text{Al}_{51.2} \text{Pd}_{41.4} \text{Fe}_{7.4}$ was found. The composition in the bulk, i.e. in the c₂-phase far away from the defect was also determined in five cases, yielding an average composition of $\text{Al}_{51.8} \text{Pd}_{41.6} \text{Fe}_{6.6}$.

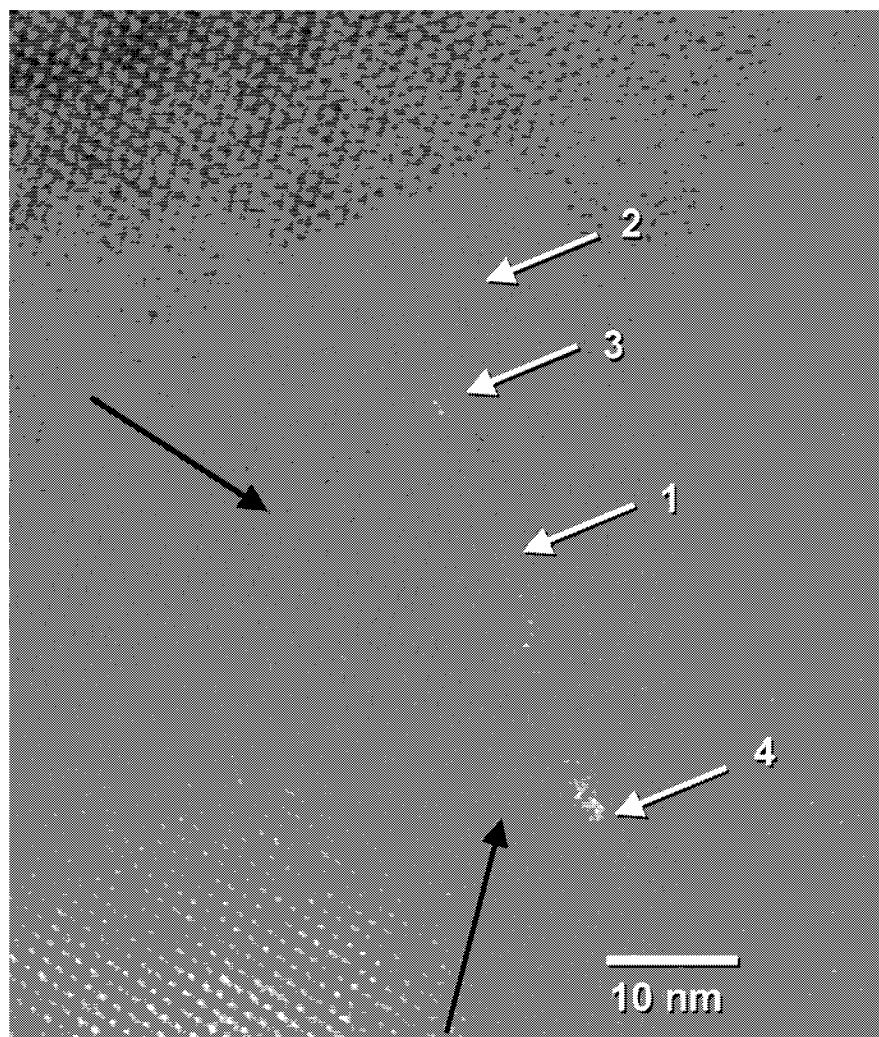


Figure 10.16: Lattice fringe picture of a defect containing a planar fault (1) in edge-on orientation. The optical axis is oriented along the $[\bar{1}, 1, 0]$ -direction of the sample. A lattice fringe shift at the planar defect (1) can be observed if the picture is looked at under a grazing angle along the directions indicated by black arrows.

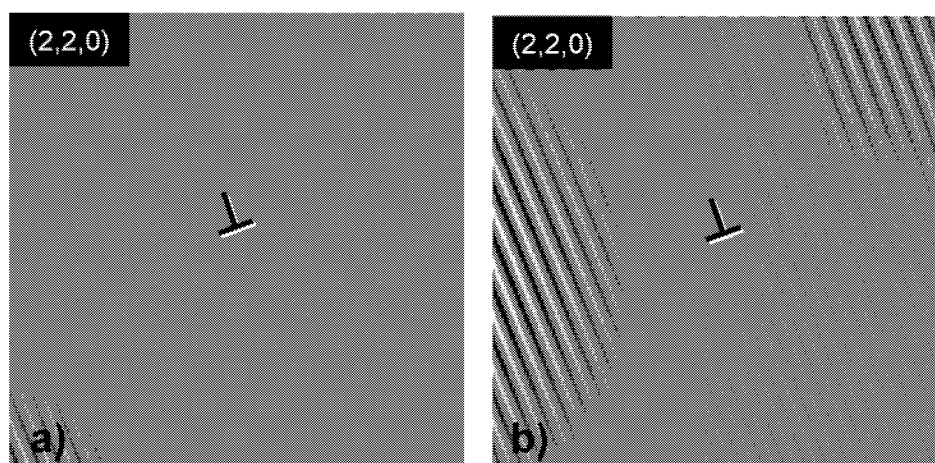


Figure 10.17: Enlarged Fourier-filtered image of the sample region (3) (a) and (4) (b) in Figure 10.16 using Fourier components corresponding to a $(2, 2, 0)$ reciprocal-lattice vector.

10.4 Discussion

Microstructural investigations showed the presence of defects in c_2 -Al-Pd-Fe samples that were subjected to plastic deformation. The defects observed contain planar faults which are terminated by a dislocation-like line contrast. A detailed microstructural study of these defects was performed using a lattice fringe analysis and subsequent image processing. Imaged along the $[\bar{1}, 1, 0]$ -direction, the defect in Figure 10.9 exhibits two dislocations with a large Burgers-vector component in the image plane of $\vec{b}_{(\bar{1},1,0)} = \frac{a_0}{2}[0, 0, \bar{1}]$, i.e. $|\vec{b}_{(\bar{1},1,0)}| = 7.76$ Å. The presence of a dislocation with a Burgers vector as high as this is surprising, since the elastic energy of a such a dislocation is high (Appendix D).

Planar defects

In an ordered FCC-structure the Burgers vector $\vec{b} = \frac{a_0}{2}[0, 0, \bar{1}]$ corresponds to a superpartial dislocation, trailing an antiphase boundary. Hence, the planar defect (3) in Figure 10.9 can be interpreted as an antiphase boundary between partial dislocations. A Burgers circuit around both dislocations exhibits a Burgers vector which is equal to the lattice parameter of 15.52 Å. Figure 10.18 demonstrates this more explicitly on a schematic projection of the unit cell of Al-Pd-Fe along the $[\bar{1}, 1, 0]$ -direction. The black and the white circles represent the different cluster filling motifs, i.e. the rhombic and pentagon dodecahedron, respectively. In the present work two different Burgers vectors of partial dislocations perpendicular to the $[\bar{1}, 1, 0]$ -direction were observed. They are indicated as arrows in Figure 10.18. Both Burgers vectors connect centres of different cluster filling motifs. Therefore, the planar defects, observed in Figure 10.9 and 10.16, can be interpreted as antiphase boundaries on a cluster scale. Accordingly, a shift along the antiphase boundary of half a lattice parameter can be observed on the Fourier-filtered image in Figure 10.13.

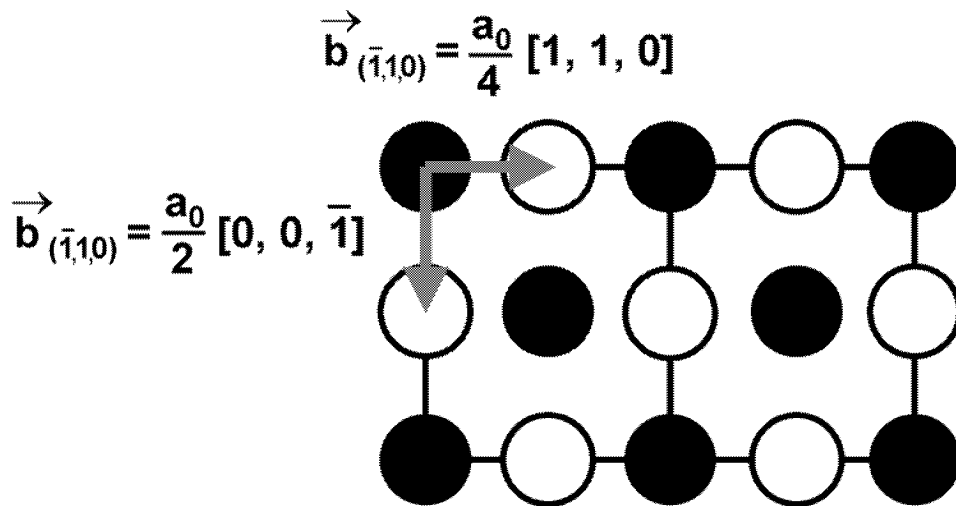


Figure 10.18: Projection of the unit cell of c_2 -AlPdFe along the $[\bar{1}, 1, 0]$ -direction. The black and the white circles represent the different cluster filling motifs. Dislocation Burgers vectors marked by arrows were experimentally observed in the present work.

Fourier analysis of the image regions (1) and (2) in Figure 10.9 revealed a power spectrum with a peak distribution corresponding to a BCC-structure rather than a FCC-structure. Since, in the Al-Pd-Fe alloy system a BCC-structure (the c_1 -phase) exists, the observation of a BCC-phase may be interpreted as a precipitation of c_1 -phase at the dislocation line. Therefore a determination of the local chemical composition using EDX was performed at the location of the defects and in the bulk c_2 -phase. The absolute error of measurement of standardless EDX is high which can be seen in the difference of the absolute values of the composition measurement in the c_2 -phase and in the ingot composition of $\text{Al}_{61} \text{Pd}_{34} \text{Fe}_4$ (Grushko 2000). A comparison of the measured average compositional differences between the defect and the bulk structure yields Al: -0.6 %, Pd: -0.2 %, Fe: +0.8 %. The compositional difference between the c_1 - and c_2 -phase is Al: +5 %, Pd: -21 %, Fe: +16 % (Edler 1997). Hence, no significant compositional change between the bulk c_2 -phase and the defect structure is present. Hence, the BCC-structure cannot be interpreted as a simple precipitation of c_1 -phase at the dislocation line.

Figure 10.19 shows a scheme of the defect imaged in Figure 10.9. The BCC-regions are located below the partial dislocation, in such a way that the inserted halfplane is situated in the BCC-region. Assuming that the BCC-phase in the defect structure possesses the same lattice parameter as the equilibrium c_1 -phase, i.e. 1 % smaller than the lattice parameter of the c_2 -phase, the elastic energy around the dislocation is released. Therefore evidence is furnished that the presence of the local BCC-phase at the dislocation core is an essential part of a mechanism to accommodate the dislocation with a large Burgers vector in the c_2 -structure.

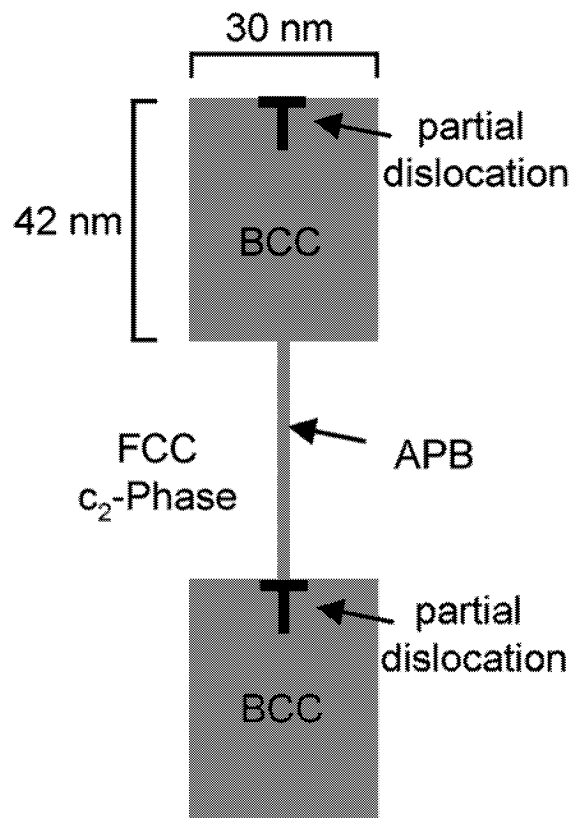


Figure 10.19: Scheme of the defect imaged in Figure 10.9.

The basic principle which is applied to reduce the elastic energy of the defect structure is shown in Figure 10.20 in a simple sketch. Figure 10.20 shows two arrangements of black tiles, which contain a dislocation-like defect. A Burgers circuit can be performed around the structure which reveals a closure failure of one tile in the direction indicated by arrows. The core region in the structure shown in Figure 10.20 a is filled with grey tiles, which are about 10 % smaller than the black tiles. At the interface (2) six black and grey tiles are confronted. The gaps between the grey tiles are wider than the gaps between black tiles. At the interface (1) five black and six grey tiles are confronted. Now the gaps between the black tiles are wider than the gaps between the grey tiles. An optimised size ratio between black and grey tiles can be calculated at which the mismatch is equally distributed to both interfaces (1 and 2) and the gaps in horizontal direction are least dilated⁴. Figure 10.20 b shows a dislocation-like defect with the same Burgers vector in a structure only consisting of black tiles. At the core of the dislocation-like defect the dilatation of the gaps is high. The simple tiling example given in Figure 10.20 can be interpreted in analogy to the defects observed in the present work. The black and grey tiles represent the unit-cells of the c_2 - and the c_1 -phase, respectively. The gaps between the tiles represent the local straining.

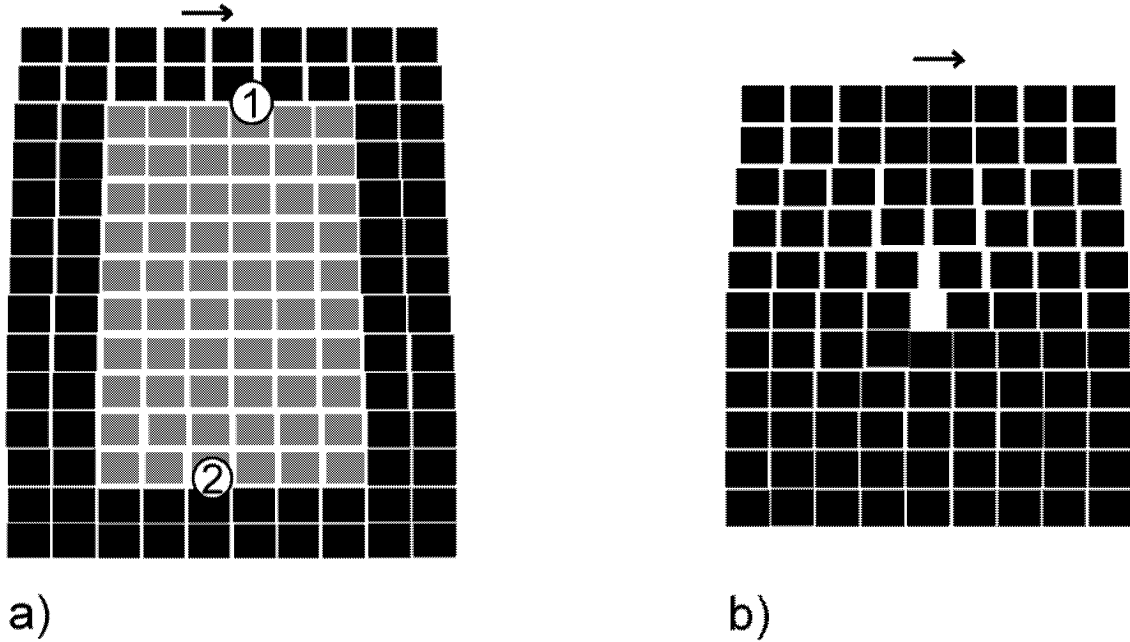


Figure 10.20: Arrangements of black tiles, which contain dislocation-like defects. The arrow indicates the closure failure of a Burgers circuit around the defect structure. (a) The core region is filled with grey tiles, which are smaller than the black tiles. The strain of the dislocation is equally distributed to both interfaces (1 and 2). (b) Defect structure of one single type of tiles.

Figure 10.21 shows the calculated hydrostatic pressure around an edge dislocation in an isotropic medium (Landau and Lifshitz 1989). The bright region below and the dark region above the dislocation core denote regions of positive and negative hydrostatic pressure, respectively. Since no compositional change was found in the defect region, it is supposed

⁴ In the present example the optimal size ratio between black and grey tiles can be calculated according to $6 a_b - 6 a_g = 6 a_g - 5 a_b$, i.e. $a_b / a_g = 12/11$, where a_b and a_g is the horizontal edge length of the black and grey tile, respectively.

that the local BCC-phase is stabilized by the high hydrostatic pressure below the dislocation core, indicated as boxed region in Figure 10.21.

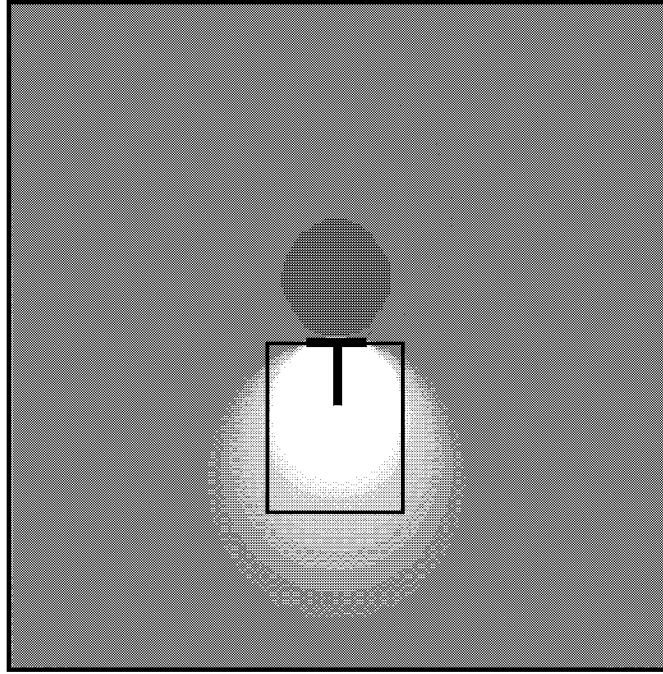


Figure 10.21: Calculated hydrostatic pressure around an edge dislocation in an isotropic medium. The bright and dark region denote regions of positive and negative hydrostatic pressure, respectively.

The elastic energy

As demonstrated in Figure 10.20 the introduction of a phase possessing a different lattice constant than the bulk phase at a dislocation may reduce the local strain. It has been argued that the BCC phase found in the defect structure of the defect shown in Figure 10.9 possesses a smaller lattice parameter than the c₂-bulk phase. In the present subsection, a first quantitative estimation of the reduction of the elastic energy is given.

In terms of elastic energy, the introduction of a phase with a smaller lattice parameter in a region of high hydrostatic pressure is favourable. To estimate the reduction of the elastic energy by such a mechanism, consider the elastic energy of a $\frac{a_0}{2}[0,0,\bar{1}]$ -partial dislocation inserted directly into the c₂-structure (denoted “FCC” in Figure 10.22 a). This arrangement is compared to the elastic energy of the same dislocation accompanied by the BCC-phase (Figure 10.22 b). For reason of simplicity, the antiphase boundary is not taken into account in the following consideration. The width of the defect at the interface between FCC and BCC where the dislocation is present is about 30 nm, which is about 19 lattice parameters of the c₂-phase. Assuming that the lattice parameter of the BCC-phase is the same as the equilibrium lattice parameter of the c₁-phase, the lattice mismatch at the interface is $19.5 \times 15.38 \text{ \AA} - 19 \times 15.52 \text{ \AA} = 5.03 \text{ \AA}$. According to Appendix D the elastic energy is proportional to the square of the Burgers vector. Hence, the elastic energy in the direct vicinity of the BCC-phase is

reduced by a factor of $\frac{7.76^2}{5.03^2} \approx 2.4$. However, the estimation of the reduction of the total elastic energy due to the introduction of the BCC-phase is difficult and prone to errors, e.g. because of the complex geometry of the defects.

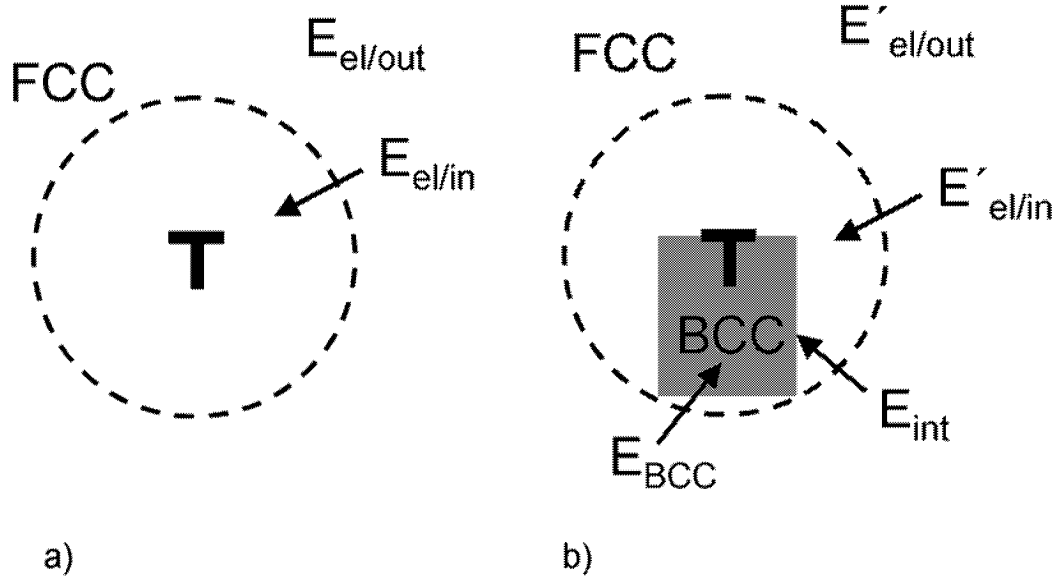


Figure 10.22: Scheme of a dislocation (a) inserted directly into the c₂-structure and (b) accompanied by the BCC-phase like it was observed in Figure 10.9. $E_{el/in}$, $E'_{el/in}$, $E_{el/out}$ and $E'_{el/out}$ denote the elastic energies inside and outside the dashed circles, respectively. E_{BCC} and E_{int} denote the BCC-phase formation energy and the interfacial energy between the c₂- and the BCC-phase, respectively.

Generally, the elastic energy of the defect can be divided into two parts: the elastic energy in the direct vicinity of the BCC-phase (denoted $E'_{el/in}$ in Figure 10.22 b) and the far-field elastic energy, which is not subjected to the influence of the BCC-phase (denoted $E'_{el/out}$).

Analogously, the elastic energy is divided for a hypothetical $\frac{a_0}{2}[0,0,\bar{1}]$ -partial dislocation in the c₂-matrix (Figure 10.22 a). The elastic energies inside and outside the circle are denoted $E_{el/in}$ and $E_{el/out}$, respectively. The elastic energies $E_{el/out}$ and $E'_{el/out}$ are supposed to be approximately equal, because in both cases a Burgers circuit around the circle results in the same Burgers vector. According to Appendix D the elastic energy in a specific region around a dislocation is proportional to $\ln \frac{R_0}{r_0}$, where r_0 and R_0 denote the inner and outer radius of the

region. For the calculation of $E_{el/out}$ (Figure 10.22 a) r_0 is equal to about 50 nm, i.e. the edge length of the BCC-phase, and R_0 is the outer cut-off radius which may be of the size of 500 nm, i.e. the average defect distance (cf. Figures 10.7). For the calculation of the elastic energy $E_{el/in}$, the outer radius R_0 can be estimated as 50 nm and the inner radius r_0 is the core radius of the partial dislocation in the c₂-matrix, which is equal to the Burgers vector modulus: $r_0 = 7.76 \text{ \AA}$. The ratio between the elastic energies inside and outside of the circle

indicated in Figure 10.22 a is the estimated as $\frac{E_{el/in}}{E_{el/out}} = \frac{\ln \frac{50}{0.776}}{\ln \frac{500}{50}} \approx 1.8$. Although this is just a

rough estimation, two conclusions can be drawn. Firstly, the elastic energy inside a region, which is directly affected by the introduction of the BCC-phase, represents a contribution to the total elastic energy, which is higher or at least of the same size as the elastic energy outside this region. Secondly, the elastic energy inside the region indicated by a circle in Figure 10.22 is distinctly lowered by the introduction of the BCC-phase.

The decrease of elastic energy due to the introduction of the BCC-phase has to over-compensate the formation energy of the BCC-phase (E_{BCC}), which is the difference in free energy between the c₁- and c₂-phase at the equilibrium composition of the c₂-phase. Furthermore the interface energy between both phases (E_{int}) has to be accounted for. The interface energy depends on the orientation of the interface. The rectangular shapes of the defects shown in Figures 10.9, 10.14 and 10.16 indicate that low-indexed interfaces of the FCC- and BCC-phase are preferred. Hence, the formation of the BCC-phase is energetically favourable if $E_{el/in} > E'_{el/in} + E_{BCC} + E_{int}$. The increase of the defect-structure size is accompanied by an increase of the energy $E_{BCC} + E_{int}$. If l represents the basic length unit of the defect, e.g. its diameter, the formation energy of the BCC-phase scales with l^2 and the interface energy with l . On the other hand, the increase of the defect-structure size is accompanied by a decrease of the elastic energy in the region of the BCC-phase. The decrease of the elastic energy $E_{el/in} - E'_{el/in}$ scales with $(\ln l)$. Hence, an equilibrium defect configuration exists which corresponds to the minimum of $E'_{el/in} - E_{el/in} + E_{BCC} + E_{int}$ with variation of the shape and size of the defect. The defect structure is large if e.g. the Burgers vector is large, the shear modulus is high and the formation energy of the BCC-phase and the interface energy are low.

The defects in Figures 10.9 and 10.14 possess the same Burgers-vector modulus. The length of the defects along the $[1, 1, 0]$ -direction is equal to about 40 nm, the width of the defects along the $[0, 0, 1]$ -direction is 30 nm in Figure 10.9 and 57 nm in Figure 10.14, containing two partial dislocations with Burgers vectors along the $[0, 0, 1]$ -direction. It is supposed that the rectangular shape of the defect imaged in Figure 10.14 almost corresponds to an equilibrium configuration. The defect shown in Figure 10.16 possesses a smaller Burgers-vector modulus than the defects in Figures 10.9 and 10.14. The size of the BCC region indicated by (2) in Figure 10.16 is much smaller than those in Figures 10.9 and 10.16. This observation supports the interpretation that the size of the BCC region formed is correlated with the Burgers vector, i.e. with the elastic energy of the dislocation.

Hollow-core dislocations

Hollow-core dislocations are energetically stable defect structures possessing large Burgers vectors. In 1953, Verma reported the first observation of a dislocation with a 15 Å Burgers vector possessing a hollow core in silicon carbide (Verma 1953). In a pioneering work, Frank (1950) predicted that dislocations in crystals with large unit cells of the order of 10 Å or more may possess an equilibrium state with an empty dislocation core. The change in energy per unit dislocation length associated with forming a hollow core with zero long-range strain field in an isotropic continuous medium is (Frank 1950)

$$\Delta E = 2\pi R\gamma - \frac{Gb^2}{4\pi} \ln\left(\frac{R}{r_0}\right), \quad (10.1)$$

where R is the hollow-core radius, γ the surface energy of the material, G the shear modulus, b the Burgers vector modulus and r_0 the nonlinear elastic core radius. The hollow-core radius R is in equilibrium when $\partial(\Delta E)/\partial R = 0$, hence

$$R = \frac{\mu b^2}{8\pi^2 \gamma}. \quad (10.2)$$

However, hollow cores are not necessarily cylindrical in shape. The shape of the cores can contain facets as for the case of YBa₂Cu₃O₇ (Chisholm 1989, Hawley 1991) which can be attributed to anisotropic elasticity and orientation dependent surface energy (Hirth 1994). Dislocations possessing hollow cores and large Burgers vectors were found in numerous materials as silicon carbide (Verma 1953, Amelinckx and Strumane 1960, Knippenberg 1963, Sunagawa 1981, Hobgood 1994) copper indium sulfide (van Enkevord 1982), pyrite (Baronnet 1976), gallium nitride (Qian 1995 a, b), garnets (Takasu 1974) or YBa₂Cu₃O₇ (Chisholm 1989, Hawley 1991).

A comparison of the defects observed in the present work with hollow-core dislocations shows some similarities. Firstly, hollow-core dislocations and the defects observed in the present work possess large Burgers vectors. Large elastic strain at the dislocation core is prevented, in generic terms, by the modification of the structure around the dislocation core. For hollow dislocations this is achieved by taking out material from a core region, while for the defects observed in the present work, a phase, possessing a different lattice parameter, is inserted at the dislocation core. Secondly, for hollow-core dislocations, the equilibrium between the decrease of elastic energy and the increase of the surface energy, which may be orientation-dependent, determines the diameter of the hollow cores. A relation exists between the Burgers-vector modulus and the diameter of the hollow core (Equation (10.2)). For the defects observed in the present work an equilibrium configuration is supposed from the decrease of elastic energy and the energy increase due to the formation of the BCC-phase. This equilibrium configuration also depends on the orientation dependence of the surface or interface energies, hence the size is not solely determined by the elastic strain. In the present work two different Burgers-vector moduli were found. For the defects observed so far, a correlation between Burgers-vector modulus and defect size exists.

Dislocation mobility

According to the present results it can be concluded that defects possessing large Burgers vectors are introduced into the c₂-structure as a consequence of plastic deformation. This defects are split superpartial dislocations connected by antiphase boundaries. However, no direct evidence exists that these defects support plastic deformation by their movement. Particularly the question whether the BCC-phase at the dislocation core is able to move along with the dislocation is still open.

Figure 10.23 shows a defect in c₂-Al-Pd-Fe possessing similar characteristics as the defect shown in Figure 10.9. The bright region (1) corresponds to a BCC-structure, a Burgers circuit reveals a vector of $\vec{b}_{(\bar{1},1,0)} = \frac{a_0}{2} [0, 0, \bar{1}]$ and an antiphase boundary (2) is created. However, the shapes of the defects are distinctly different. The defect in Figure 10.23 is drop-shaped and possesses a rather convoluted boundary to the surrounding FCC-phase. The dislocation line (3) is rather curved and deviates from the $[\bar{1}, 1, 0]$ -direction found for the sessile dislocation in Figure 10.9. It is therefore suggested that Figure 10.23 shows a dislocation frozen in during

its movement. Further investigations, particularly in-situ tensile test on c_2 -Al-Pd-Fe, will be carried out in order to show if these defects support plastic deformation by their movement.

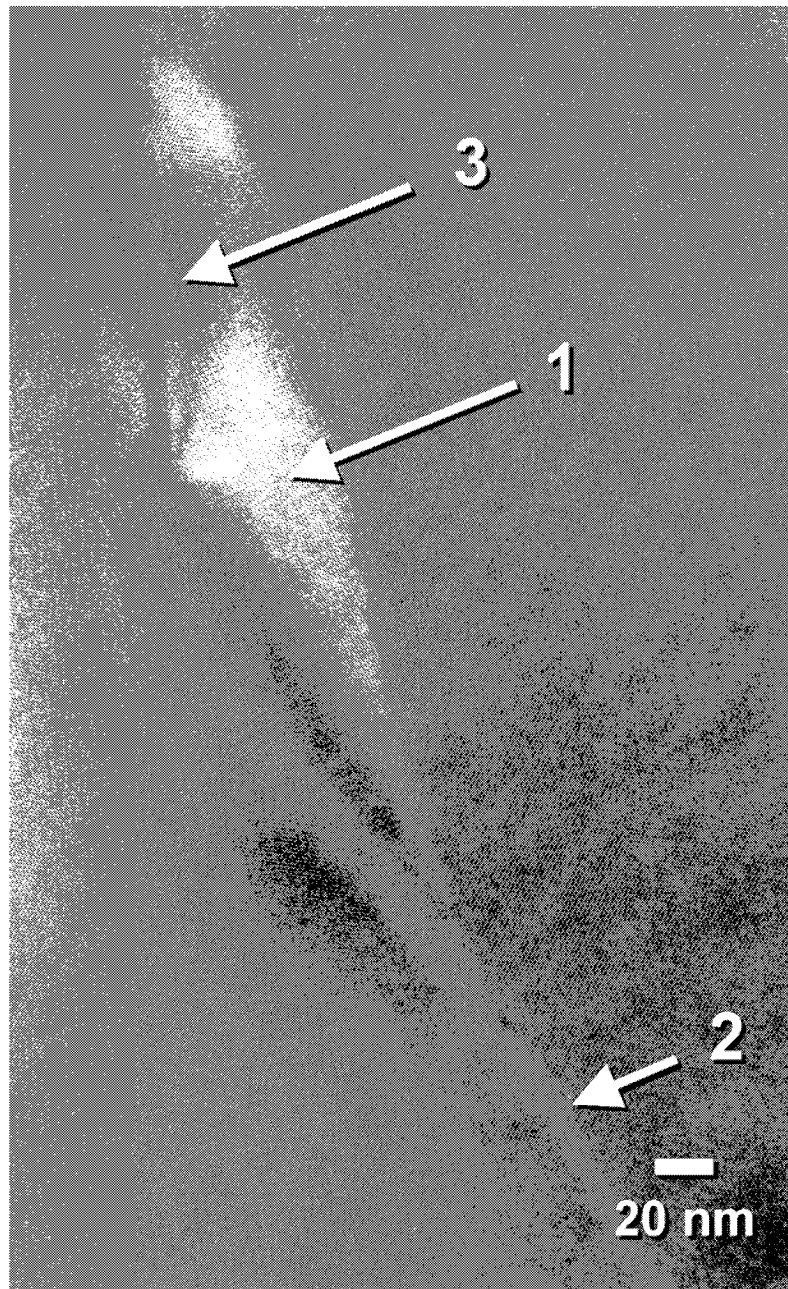


Figure 10.23: Lattice fringe picture of a defect oriented with the optical axis along the $[\bar{1}, 1, 0]$ -direction of the sample.

11. Generalizing discussion: Defects in SCAPs

The basic principles of elastic-energy reduction of dislocation-like defects in ξ' -Al-Pd-Mn and c_2 -Al-Pd-Fe are closely related. In both materials a second phase possessing a different lattice constant than the bulk phase is introduced at the dislocation core. Figure 11.1 a and b illustrate the appearance of second phases at the dislocation-cores in ξ' -Al-Pd-Mn and c_2 -Al-Pd-Fe, respectively. Figure 11.1 a is a simplified sketch of the phase boundary at a metadislocation according to Figure 9.1. The grey region, attached at the right-hand side of the metadislocation, corresponds to inserted phason halfplanes, i.e. a local area of ψ -Al-Pd-Mn phase. The unit cells of the ψ - and the ξ' -phase are shown as rectangles in Figure 11.1 a. The Burgers vector can, as demonstrated in Chapter 9, be determined calculating the lattice mismatch at the (1, 0, 0)-interface between the ψ - and the ξ' -phase.

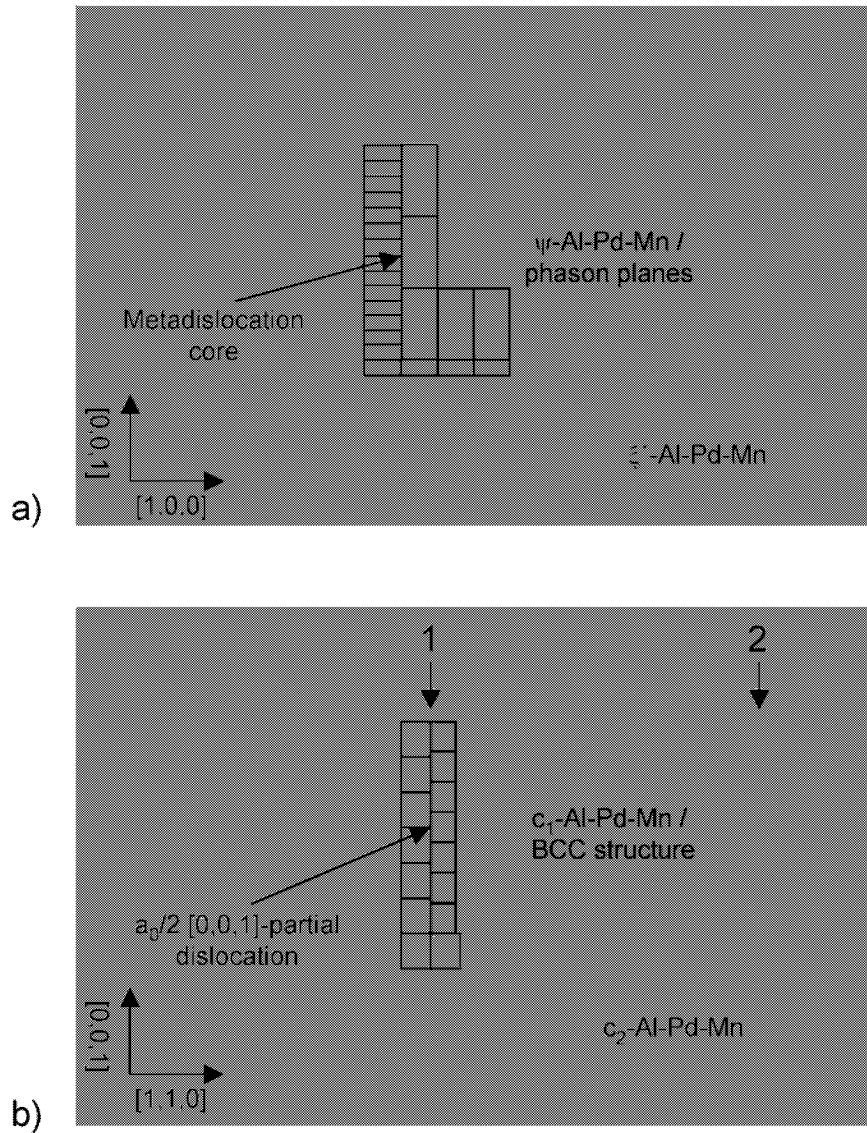


Figure 11.1: Appearance of second phases (dark grey) at dislocation-like defects in (a) ξ' -Al-Pd-Mn and (b) c_2 -Al-Pd-Fe, respectively.

The grey region in Figure 11.1 b corresponds to the BCC-phase in the defect structure that was observed in the present work in c_2 -Al-Pd-Fe. Evidence was furnished that the BCC-structure, like the c_1 -phase, possesses a lattice constant smaller than that of the c_2 -phase. The projection of the unit cells of both phases along the $[\bar{1}, 1, 0]$ -direction are shown as rectangles. For the reason of clarity, the appearance of an antiphase boundary was neglected. In this sense, the unit cells of the fundamental rather than the superstructure lattice are displayed. Furthermore, the size difference between both unit cells is exaggerated. The strain at the (1, 1, 0)-interface between the c_2 - and the BCC-phase at the dislocation core (1), is released by the different lattice constants of both phases. As in ξ' -Al-Pd-Mn, the Burgers vector can be determined as the lattice mismatch at the interface between two phases possessing different lattice parameters. It was shown that the length of the (1, 1, 0)-interface corresponds to approximately 19 lattice constants. Hence the lattice mismatch at the interface is $19.5 \times 15.38 \text{ \AA} - 19 \times 15.52 \text{ \AA} = 5.03 \text{ \AA}$. On the other hand, the lattice mismatch at the (1, 1, 0)-interface (2) is $19.5 \times 15.38 \text{ \AA} - 19.5 \times 15.52 \text{ \AA} = 2.73 \text{ \AA}$. Hence, the Burgers-vector magnitude (7.76 Å) of one partial-dislocation-like defect (e.g. (4) in Figure 10.9) is divided into two parts of 5.03 and 2.73 Å, located at both (1, 1, 0)-interfaces of the defect.

However, Figure 11.1 shows that the defects observed in c_2 -Al-Pd-Fe possess fundamentally different topological properties than single metadislocations. Defects in c_2 -Al-Pd-Fe are limited in size. A Burgers circuit can be performed around these defects entirely in the c_2 -phase which reveals a Burgers vector equal to the c_2 -phase lattice parameter of 15.52 Å. In ξ' -Al-Pd-Mn, phason planes terminate at metadislocations or at the crystal surface, respectively. A single metadislocation is a defect structure of “unlimited size” in the sense that the phason planes terminate at the boundary of the crystal.

In Chapter 9.3 of the present work the properties of metadislocation networks were studied theoretically. The metadislocation networks discussed possess a limited size in the sense that all phason planes terminate at metadislocation cores. Figure 11.2 shows a scheme of a 6,2/4,4-metadislocation network. The metadislocation network is embedded into the ξ' -phase. The size of the defect is limited to the central area of Figure 11.2. Around this area a Burgers circuit can be performed entirely in the ξ' -phase. It has been show that metadislocation networks can be constructed which are perfect dislocations in the ξ' -phase. The Burgers vector modulus is equal to the $c_{\xi'}$ lattice parameter of the ξ' -phase (12.56 Å). Although the Burgers vector modulus of such metadislocation networks is large, the local strain at each metadislocation core is small. In the present example the Burgers vector moduli of the individual metadislocations are 1.83, 4.80, 2.96, and 2.96 Å.

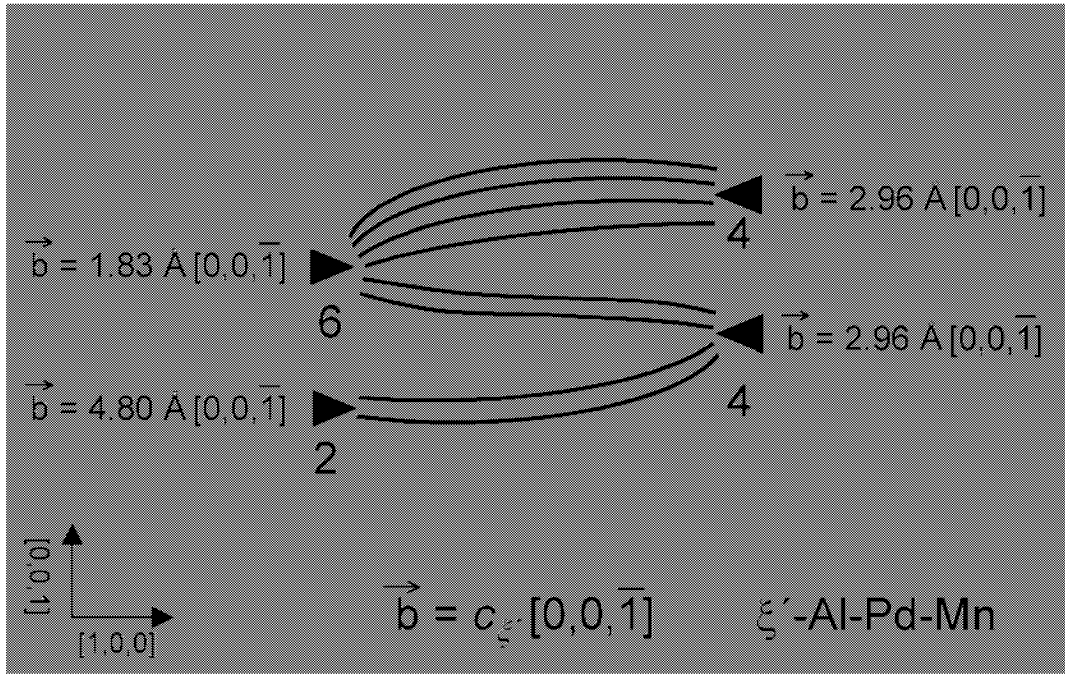


Figure 11.2: Scheme of a 6,2/4,4-metadislocation network embedded into the ξ' -phase. Metadislocation cores and phason planes are indicated as triangles and as black lines, respectively.

Summary

In the present work, the plasticity of quasicrystals, metallic glasses and structurally complex alloy phases was investigated. The concepts of plasticity for simple crystalline materials cannot be applied to these materials without substantial modification.

Plastic deformation experiments were performed on icosahedral Zn-Mg-Dy single quasicrystals. Stress-strain curves were recorded and the thermodynamic activation parameters of the deformation process were determined by means of incremental tests. The absolute values of the activation volume of icosahedral Zn-Mg-Dy as well as its stress dependence were shown to be comparable to those of icosahedral Al-Pd-Mn. A microstructural investigation by means of transmission electron microscopy (TEM) was performed on plastically deformed and undeformed material. The observation of an increase of the dislocation density by three orders of magnitude during plastic deformation provides direct evidence that the plastic deformation process is mediated by a dislocation mechanism. It was shown that the appearance of work softening is accompanied by the decrease of the dislocation density at high strains, a behaviour, which was observed in icosahedral Al-Pd-Mn as well. Hence, the fundamental plastic deformation properties of Zn-Mg-Dy and Al-Pd-Mn are similar. Planar defects like antiphase boundaries, stacking faults and phason defects, which are a quasicrystal-specific defect type, were observed and characterized in icosahedral Zn-Mg-Dy. The presence of antiphase boundaries provides a deeper insight into the mechanism of plastic deformation motion, since they allow for an independent determination of the planes of dislocation motion. Hence, the mode of dislocation motion and the orientation of planes with respect to the compression direction could be unambiguously determined for the first time. Plastic deformation was shown to be mainly performed by dislocation glide but climb processes occur as well. Differences of the modes of plastic deformation and the appearance of planar defects in icosahedral Zn-Mg-Dy and Al-Pd-Mn were discussed with the background of different diffusion dynamics in both materials.

A constitutive model approach describing the plasticity of icosahedral quasicrystals (Feuerbacher *et al.* 2001a) was applied to a wide range of experimental deformation parameters for icosahedral Al-Pd-Mn in the present work. The appearance of an additional hardening regime after the lower yield stress at high strain rates and the appearance of a constant flow stress level in low-strain-rate experiments was observed for the first time. This behaviour could be comprehensively explained in the framework of the constitutive model. It was shown that the evolution dynamics of the dislocation density and order parameter vary according to the temperature and strain rate. This leads to an expansion of the hardening regime at high strain rates and/or low temperature. At low strain rates and/or high temperatures, a structural steady state may be achieved, which leads to constant flow-stress levels. It can be concluded that the constitutive model successfully describes the plastic deformation behaviour of Zn-Mg-Dy as well as that of Al-Pd-Mn. In both materials plastic deformation depends on the interaction of dislocation storage and recovery and the strain driven disordering and diffusion driven reordering of the material.

In some respects the macroscopic plastic deformation behaviour of quasicrystals resembles that of metallic glasses. The plastic deformation behaviour of Pd-Ni-Cu-P bulk metallic glass was studied in creep experiments at three different temperatures and in a wide range of creep stresses. Creep experiments at constant true stress were performed for the first time and the transition between steady-state creep and accelerating creep was studied. Based on the free volume description (Cohen and Turnbull 1959, Spaepen 1981) a constitutive model was

developed, which comprehensively describes the salient features of metallic-glass plasticity for a wide range of experimental parameters. The evolution of creep rates is computed with respect to the change of free volume, reflecting the amount of disorder accumulated in the metallic glass structure. Metallic glasses as well as quasicrystals possess no translational symmetry but a high degree of structural order. Although the mechanisms of plastic deformation are different, the introduction of *disorder* upon plastic deformation is the decisive microstructural parameter in both materials which determines the plastic deformation behaviour and leads to work softening.

Structurally complex alloy phases are materials which possess large unit cells containing between about a hundred to some thousand atoms. The investigation of the mechanism of plastic deformation mechanisms of these materials is a challenging topic which already led to the discovery of a novel mechanism of plastic deformation in the orthorhombic ξ' -Al-Pd-Mn phase (Klein *et al.* 1999) based on so-called metadislocations. In the present work networks of metadislocations were investigated theoretically. It was for the first time shown that metadislocation networks can be formed, which represent perfect dislocations in the ξ' -phase. Although the Burgers vector modulus of such metadislocation networks is high (12.56 Å), the local strain at each metadislocation core is low. Therewith, metadislocation networks provide a novel mechanism for plastic deformation of SCAPs on the basis of localized structural defects.

For the first time the plasticity of c_2 -Al-Pd-Fe, another structurally complex phase, was investigated. The structure of this phase is representative for a number of structurally complex cubic phases and is referred to as an approximant of a metastable face-centred-icosahedral phase (Sugiyama *et al.* 2000, Shibuya *et al.* 2000). New types of defects, which are present in the structure after plastic deformation, were found and studied in detail by means of TEM. The defects consist of dislocations, possessing large Burgers-vector moduli of e.g. 15.52 Å, which is equal to the lattice constant. Structural modifications at the cores of the dislocations by introduction of a second phase were observed. Evidence was furnished that these structural modifications lower the elastic energy of the dislocations. A metastable equilibrium size and shape of these defect structures was discussed and compared to experimental observations. Furthermore, planar defects were observed, which were shown to be antiphase boundaries. The defect structures, observed in c_2 -Al-Pd-Fe in the present work were compared to defect structures in the orthorhombic ξ' -Al-Pd-Mn phase. It was shown that the basic concepts of dislocation-like defects in both structurally complex phases show clear similarities.

Appendix A

Ordered and disordered structures

In the following subsection the basic concepts of fundamental and superstructure lattices are introduced. Figure A.1 a shows a simple cubic lattice where all lattice positions are occupied by the same type of atom (grey spheres). The lattice parameter of the unit cell is a_0 . Figure A.1 b shows a similar lattice, but the lattice positions are alternately occupied by two different atomic species (white and black spheres). The lattice is chemically ordered. The atoms of a single species (for example the black spheres) build up a face centred lattice. The lattice parameter of the unit cell is $2a_0$. If the structure factor of both atomic species is different the diffraction pattern of this structure obeys the extinction conditions of a face centred lattice. The diffraction pattern along a $[1, \bar{1}, 0]$ -direction is shown in Figure A.2 b. The structure in Figure A.1 a can also be interpreted as disordered structure where two different atomic species are randomly distributed on the lattice sites. Then a grey sphere represents an atom, which is an atom of both species with 50 % likeliness. The transition between the structures shown in Figure A.1 a and b can be interpreted as disorder-order transition. The diffraction pattern of the structure in Figure A.1 a shows the extinction conditions of a simple cubic structure. However, for the sake of comparison between both structures the diffraction pattern is indexed with reference to a lattice parameter of $2a_0$. Therefore, the diffraction pattern is indexed only with even numbers. The simple cubic lattice (lattice parameter a_0) in the present example is referred to as fundamental lattice and the corresponding diffraction spots (black circles, indexed with even numbers) are referred to as fundamental spots. The face centred lattice (lattice parameter $2a_0$) is referred to as superlattice. The additional spots (grey circles, indexed with odd numbers) in Figure A.2 b are referred to as superstructure spots.

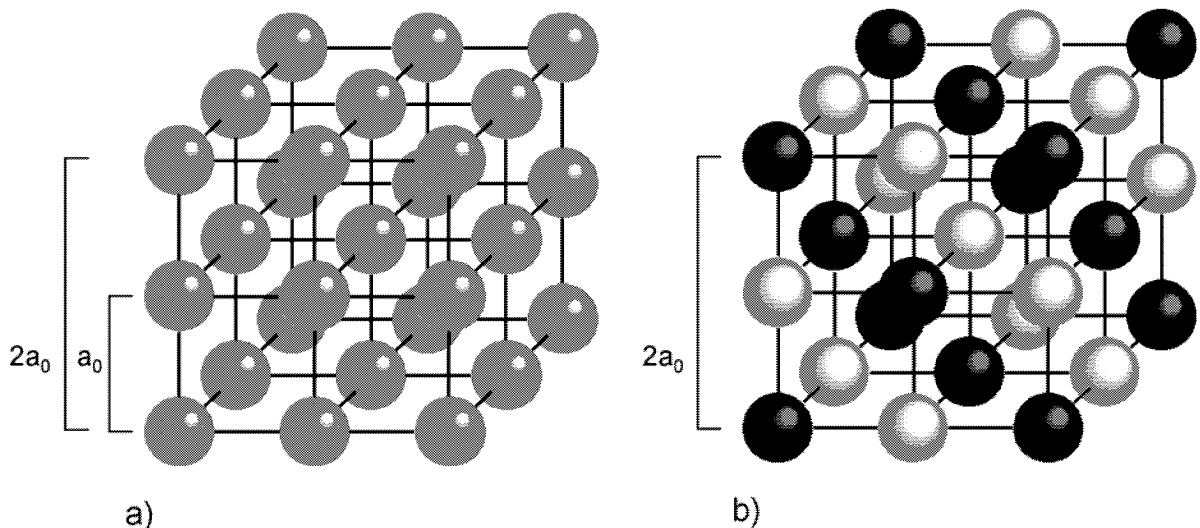


Figure A.1: Three dimensional crystal structure (a) occupancy of (b) six vectors are aligned along six five-fold directions.

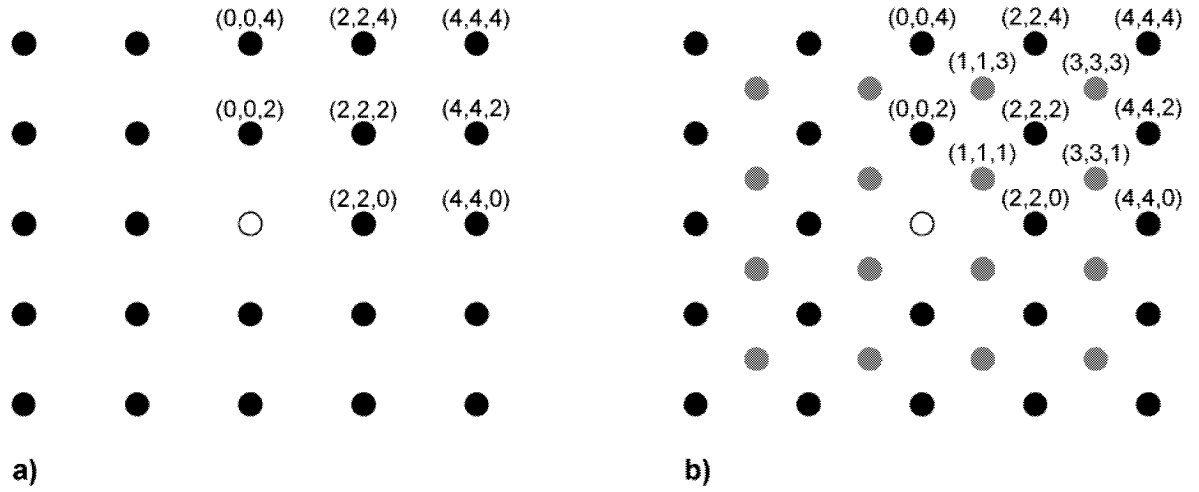


Figure A.2: Diffraction pattern along the $[1, \bar{1}, 0]$ -direction of the structures shown in Figure A.1. Reflections of both diffraction patterns (filled circles) are indexed referring to a lattice parameter $2a_0$. Fundamental spots (black circles) and superstructure spots (grey circles) are differentiated. The spot corresponding to the direct beam is marked as open circle.

Appendix B

Uniaxial testing machine

In the present work all plastic deformation experiments were performed using a modified Zwick Z050 uniaxial testing machine under compression. The essential parts of the testing machine are drafted in Figure B.1. The sample (1), which has usually a size of approximately $5 \times 2 \times 2 \text{ mm}^3$, is situated between two ceramic anvils (2). The upper anvil is connected to a moveable crossbar via a compression rod (3), the lower compression rod (3) is connected to a 10 kN load cell (4). The strain was measured directly at the sample by a linear inductive differential transducer at an accuracy of $\pm 10 \text{ nm}$ (5). A cylindrical furnace (6) equipped with an active temperature-gradient control was used to keep the sample region uniformly at the temperature of the experiment. The deformation temperature is controlled directly at the sample (7), two additional thermocouples in the upper and lower anvil (8) control the temperature gradient over the sample. The plastic deformation experiment is computer controlled, deformation data such as load, strain and time are recorded continuously during the experiment with a maximum scan frequency of 50 Hz. Plastic deformation experiments can be performed as constant-strain-rate experiments and creep experiments, i.e. constant stress experiments. In addition, incremental tests like strain-rate changes, stress-relaxation experiments and temperature changes can be performed. Furthermore, plastic deformation experiments can be controlled to constant true strain rate or constant true stress. The details on the modes of plastic deformation tests are given in the particular chapters of the present work.

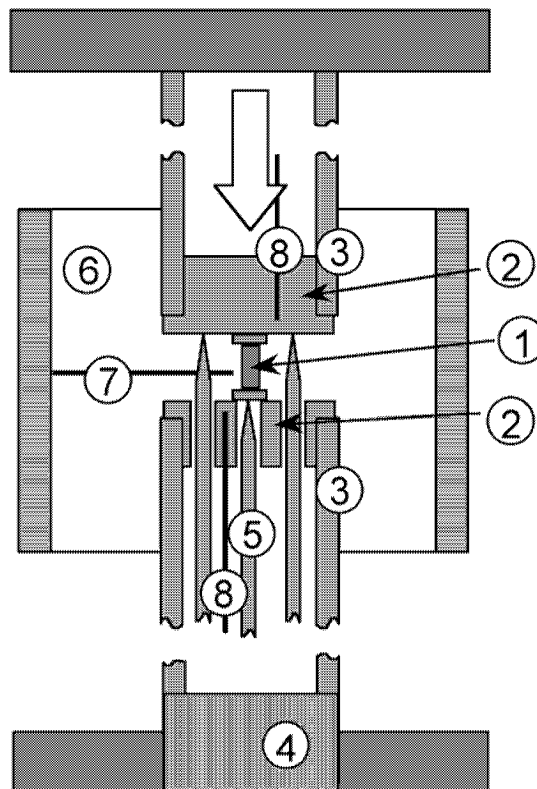


Figure B.1: Essential parts of the Zwick Z050 testing machine (see text).

Appendix C

Imaging in a transmission electron microscope

The elastic scattering of electrons by a lattice is the major contrast forming process for the imaging of crystals in the transmission electron microscope. A wave scattered by a crystal possesses constructive interference if the Bragg condition

$$2d \sin \theta = n\lambda \quad n \in \overline{\mathbb{Z}} \quad (\text{C.1})$$

is fulfilled, where d is the distance of the lattice planes, λ is the wavelength of the incoming electron beam, and θ is the angle between the incident and the diffracted wave. The incident and the diffracted beam can be characterized by their wave vectors $\vec{k}_0$ and $\vec{k}_g$, respectively. If an incident electron beam is scattered by a crystal, constructive interference is achieved when $\Delta\vec{k} = \vec{k}_g - \vec{k}_0$ equals a lattice vector $\vec{g}$ of the reciprocal lattice, i.e.

$$\Delta\vec{k} = \vec{g}. \quad (\text{C.2})$$

If the electron beam is scattered elastically, then $|\vec{k}_g| = |\vec{k}_0|$ is fulfilled and Equation (C.2) can be visualized via the Ewald construction. The wave vector $\vec{k}_0$ is embedded into the reciprocal lattice in such a way that the arrowhead points at the origin of the reciprocal lattice. Around the origin of the wave vector $\vec{k}_0$ the Ewald sphere is drawn with a radius of $|\vec{k}_0|$. If the Ewald sphere cuts a reciprocal lattice point, constructive interference takes place in the radial direction $\vec{k}_g$ to the reciprocal lattice point.

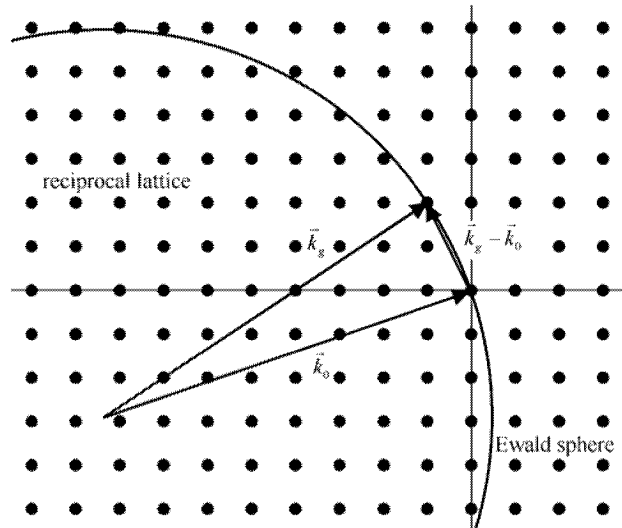


Figure C.1: Ewald construction: $\vec{k}_0$ and $\vec{k}_g$ are the wave vectors of the incident and the diffracted beam.

Reciprocal lattice points are “points” in an ideal crystal with infinite extension. However, a TEM sample is thin along the direction of the incident beam. Hence, the reciprocal lattice points are extended to “rods” in the direction corresponding to the sample normal. Therefore, in a thin sample diffraction spots are visible even if $\Delta\vec{k} = \vec{g}$ is only approximately fulfilled. The difference $\vec{s} = \Delta\vec{k} - \vec{g}$ is called “excitation error” (Figure C.2). If the excitation error is small, i.e. $\vec{s} \approx 0$, the intensity of the diffracted beam is high (dynamic excitation condition). On the other hand, if the excitation error is large, the intensity of the diffracted beam is low (kinematic excitation condition). Sample bending and lattice strain leads to fluctuations of $\vec{s}$, which results in intensity fluctuations of the electron wave. This principle is used for the imaging of the strain fields of dislocations.

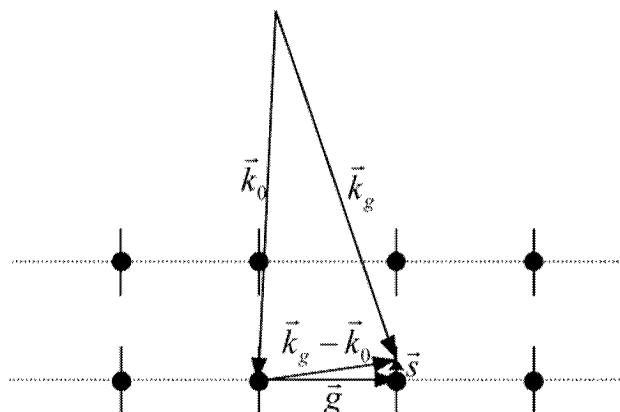


Figure C.2: Extended Ewald construction for the scattering at thin samples. The reciprocal lattice points are extended to “rods” in the direction of the sample normal. $\vec{k}_0$ and $\vec{k}_g$ are the wave vectors of the incident and the scattered beam. $\vec{s}$ is the excitation error.

Due to the high energy of the incident electrons (200 - 400 keV) the Ewald sphere has a small curvature. If the incident electron beam is parallel to a low indexed direction of the lattice many reciprocal lattice points are cut by the Ewald sphere. This scattering condition is called Laue case, and is used to take lattice fringe images in the present work. Due to lens aberrations a lattice-fringe image is not a direct image of the structure, but it gives lattice-spacing information corresponding to the diffraction spots that were selected for imaging.

If the sample is oriented in a way that only the direct beam and one diffracted beam are excited this diffraction condition is called two-beam case. Using now an objective aperture in the microscope the direct beam or the diffracted beam can be selected. An image using the direct beam is called bright-field image. If the Bragg condition is fulfilled in the strain field of the dislocation but not in the surrounding area, the dislocation line can be observed as dark line on a bright background. An image using the diffracted beam is called dark-field image. Here the dislocation line can be observed as bright line on a dark background.

The quantitative investigation of dislocation strain fields in crystals can be performed using two-beam images. The dislocation contrast is extinct if the reciprocal lattice vector $\vec{g}$ is perpendicular to the strain field $\vec{u}$, i.e. $\vec{g} \cdot \vec{u} = 0$ (cf. Williams and Carter 1996). If the strain field can be described using a Burgers vector $\vec{b}$, the dislocation contrast is extinct if

$$\vec{g} \vec{b} = 0. \quad (\text{C.3})$$

This relation, however, can only be applied in some special cases (Hirsch *et al.* 1977), e.g. for pure edge dislocations ($\vec{b}$ is perpendicular to the line direction of the dislocation) or for pure screw dislocations ($\vec{b}$ is parallel to the line direction of the dislocation).

The relation (C.3) can not directly be applied to quasicrystals. Due to the additional perpendicular-space Burgers-vector components modified extinction conditions apply. For icosahedral quasicrystals

$$\vec{G}\vec{B} = \vec{g}_{\parallel}\vec{b}_{\parallel} + \vec{g}_{\perp}\vec{b}_{\perp} = 0 \quad (\text{C.4})$$

holds (Wollgarten *et al.* 1991), where $\vec{G}$ is a six-dimensional reciprocal lattice vector possessing parallel- and perpendicular-space components $\vec{g}_{\parallel}$ and $\vec{g}_{\perp}$, respectively. The extinction condition can be fulfilled if

$$\vec{g}_{\parallel}\vec{b}_{\parallel} = \vec{g}_{\perp}\vec{b}_{\perp} = 0 \quad (\text{C.5})$$

or if

$$\vec{g}_{\parallel}\vec{b}_{\parallel} = -\vec{g}_{\perp}\vec{b}_{\perp} \neq 0. \quad (\text{C.6})$$

The first case is referred to as “strong extinction condition” (SEC). Experimentally, if condition (C.5) is fulfilled, the dislocation contrast vanishes for all reflections corresponding to reciprocal lattice vectors perpendicular to $\vec{b}_{\parallel}$, i.e. for all reflections of the corresponding systematic row. Equation (C.6) provides an additional condition only occurring in quasiperiodic lattices. It is referred to as “weak extinction condition” (WEC). Experimentally one finds an extinction for only one reflection of a systematic row for which Equation (C.6) is fulfilled, while the dislocation is visible for the others. The observation of two independent SECs allows for the determination of the direction of the Burgers vector in physical space.

Appendix D

Elastic energy of a dislocation

The elastic energy of a dislocation can be evaluated using isotropic elastic theory. The elastic energy of an edge dislocation is given by (cf. Gottstein 1998)

$$E_{el} = L \frac{Gb^2}{4\pi(1-\nu)} \ln \frac{R_0}{r_0}, \quad (D.1)$$

where L is the length of the dislocation line, G is the shear modulus, ν the Poisson ratio, and R_0 and r_0 denote the outer and inner cut-off radius of the dislocation strain field, respectively. The elastic energy is thus proportional to the square of the Burgers vector. Equation (D.1) excludes the elastic energy inside the radius r_0 , i.e. the energy of the dislocation core. Inside the dislocation core Hook's law can no longer be applied due to large strains. The energy within the core can be estimated proposing the shear stress reaches the theoretical limit $\tau_{th} = G/2\pi$. The energy of the core is

$$E_{core} = L \frac{Gb^2}{4\pi(1-\nu)}. \quad (D.2)$$

Equation (8.1) and (8.2) can be combined to the total energy of an edge dislocation

$$E_{el} + E_{core} = L \frac{Gb^2}{4\pi(1-\nu)} \left(\ln \frac{R_0}{r_0} + 1 \right). \quad (D.3)$$

Correspondingly, the total energy of a screw dislocation is given by (cf. Gottstein 1998)

$$E_{el} + E_{core} = L \frac{Gb^2}{4\pi} \left(\ln \frac{R_0}{r_0} + 1 \right). \quad (D.4)$$

In either case the elastic energy is proportional to the square of the Burgers vector modulus.

Appendix E

Fourier Filtering

The purpose of Fourier filtering is to attain structural information, which is associated with a narrow range of spatial frequencies from an image, e.g. a lattice fringe electron micrograph. In the present work, these spatial frequencies are associated with reciprocal lattice vectors. The Fourier transform of the image intensity is

$$I(\vec{r}) = \sum_{\vec{g}} I(\vec{g}) e^{2\pi i \vec{g} \cdot \vec{r}}, \quad (\text{E.1})$$

with the image coordinate $\vec{r}$, the reciprocal coordinate $\vec{g}$, and the coefficient of the Fourier transformation

$$I(\vec{g}) = \frac{1}{A} \int_A I(\vec{r}) e^{-2\pi i \vec{g} \cdot \vec{r}} d\vec{r}, \quad (\text{E.2})$$

with the integration over the area of the image plane A . Since $I(\vec{r})$ is a scalar field of real numbers, $I(\vec{g})$ possesses the Friedel symmetry

$$I(\vec{g}) = I^*(-\vec{g}). \quad (\text{E.3})$$

Structural information is selected by a top-hat function $a(\vec{g})$ by multiplication of the Fourier transform of the image intensity with the mask

$$I'(\vec{g}) = I(\vec{g}) \cdot a(\vec{g}), \quad (\text{E.4})$$

and by back transformation into the real space

$$I'(\vec{r}) = \sum_{\vec{g}} a(\vec{g}) \cdot I(\vec{g}) e^{2\pi i \vec{g} \cdot \vec{r}}. \quad (\text{E.5})$$

The mask possesses a value of 1 in a close range around a lattice vector $\vec{g}'$ and, under consideration of the Friedel symmetry, the corresponding negative vector $-\vec{g}'$. For other values $a(\vec{g})$ is equal to zero.

For practical applications the image intensity is present in a digitised form. In this case a discrete Fourier transformation (DFT) is performed:

$$I(\vec{g}) = \frac{1}{A} \sum_k I(\vec{r}_k) e^{-2\pi i \vec{g} \cdot \vec{r}_k} \Delta\vec{r} \quad (\text{E.6})$$

where $\Delta\vec{r}$ is the area of an image element and $\vec{r}_k$ is the discrete image coordinate. To display the complex expression $I(\vec{g})$ usually the so-called power spectrum $|I(\vec{g})|^2$ is used.

References

- Alamgir, F.M., Jain, H., Williams, D.B., Hug, G., Schwarz, R.B., and Jin, O., (2001) *Mat. Res. Soc. Symp. Proc.* **644**, L2.4.1.
- Amelinckx, S., and Strumane, G., (1960) *Silicon Carbide: a High Temperature Semiconductor*, Pergamon, Oxford, 162.
- Amelinckx, S., (1969) Dislocations in ordered alloys - superdislocations, in *Dislocations in Crystals Vol. 2* (Ed. F.R.N. Nabarro), North Holland, 231.
- Argon, A.S., (1979) *Acta Met.* **27**, 47.
- Argon, A.S., and Kuo, H.Y., (1980) *J. Non-Cryst. Solids* **37**, 241.
- Audier, M., Durand-Charre, M., and de Boissieu, M., (1993) *Phil. Mag. B* **68**, 607.
- Badhuri, S.B., and Sekhar, J.A., (1987) *Nature* **37**, 609.
- Balanetsky, S., Grushko, B., Kowalska-Strzeciwillk, E., Velikanova, T.Y., and Urban, K., (2003), to be published.
- Baronnet, A., (1976) thesis, University of Aix-Marseille.
- Bartsch, M., and Messerschmidt, U., (1997) *Mat. Sci. Eng. A* **233**, 103.
- Bartsch, M., Geyer, B., Häussler, D., Feuerbacher, M., Urban, K., and Messerschmidt, U., (2000) *Mat. Sci. Eng. A* **294-296**, 761.
- Basinski, S.J., and Basinski, Z.S., (1979) Plastic deformation and work hardening, in *Dislocations in Metallurgy Vol. 4* (Ed. F.R.N. Nabarro), North Holland, 261.
- Bennett, C.H., Chaudhari, P., Moruzzi, V., and Steinhard, P., (1979) *Phil. Mag. A* **40**, 485.
- Bergman, G., Waugh, J.L.T., and Pauling, L., (1957) *Acta Cryst.* **10**, 254.
- Bernal, J.D., (1960) *Nature* **185**, 68.
- Bernal, J.D., (1964) *Proc. R. Soc. A* **280**, 299.
- Berry, B.S., and Pritchett, W.C., (1973) *J. Appl. Phys.* **44**, 3122.
- Bohsung, J., and Trebin, H.R., (1989) *Introduction to the Mathematics of Quasicrystals*, Ed. Jaric M.V., Academic Press, London, 183.
- Boudard, M., de Boissieu, M., Janot, C., Dubois, J.M., and Dong, C., (1991) *Phil. Mag. Lett.* **64**, 197.
- Boudard, M., de Boissieu, M., Janot, C., Heger, G., Beli, C., Nissen, H.U., Vincent, H., Ibberson, R., Audier, M., and Dubois, J.M., (1992) *J. Phys. Cond. Matt.* **4**, 10149.
- Boudard, M., Bourgeat-Lami, E., de Boissieu, M., Janot, C., Durand-Charre, M., Klein, H., Audier, M., and Hennion, B., (1995) *Phil. Mag. Lett.* **71**, 11.

- Boudard, M., Klein, H., De Boissieu, M., Audier, M., and Vincent, H., (1996) *Phil. Mag. A* **74**, 939.
- Bresson, L. and Gratias, D., (1993) *J.Non-Cryst. Solids* **153 & 154**, 468.
- Cahn, J. W., Shechtman, D., and Gratias, D., (1986) *J. Mater. Res.* **1**, 13.
- Caillard, D., Vanderschaeve, G., Bresson, L., and Gratias, D., (2000) *Phil. Mag. A* **80**, 237.
- Caillard, D., and Feuerbacher, M., (2002a) private communication.
- Caillard, D., Morniroli, J.P., Vanderschaeve, G., Bresson, L., and Gratias, D., (2002b) *Eur. Phys. J AP* **20**, 3.
- Canfield, P.C., and Fisk, Z., (1992) *Phil. Mag.B* **65**, 1117.
- Cargill, G.S., (1970) *J. Appl. Phys.* **41**, 12.
- Chaudhari, P., Levi, A., and Steinhard, P., (1979) *Phys. Rev. Lett.* **43**, 1517.
- Chen, H.S., and Chuang, S.Y., (1975) *J. Electr. Mater.* **4**, 783.
- Chen, H.S., Kortan, A.R., and Parsey jr., J.M., (1987) *Phys. Rev. B* **36**, 7681.
- Chisholm, M.F., and Smith, D.A., (1989) *Phil. Mag. A* **59**, 181.
- Cohen, M., and Turnbull, D., (1959) *J. Chem. Phys.* **31**, 1164.
- de Boissieu, M., Stephens, P., Janot, C., Chapman, D.L., and Audier, M., (1994) *J. Cond. Matt.* **6**, 10725.
- de Hey, A. S., Sietsma, J., and van den Beukel, A., (1998) *Acta Mater.* **46**, 5873.
- Devaud-Rzepski, J., A. Quivy, Y. Calvayrac, M. Cornier-Quiquandon, and D. Gratias, (1989) *Phil. Mag. B* **60**, 855.
- Dong, C., Dubois, J.M., de Boissieu, M., Boudard, M., and Janot, C., (1991) *J. Mater. Res.* **6**, 2637.
- Duine, P.A., Sietsma, J., and van den Beukel, A., (1992) *Acta metall. mater.* **40**, 743.
- Ebalard, S., and Spaepen, F., (1989) *J. Mater. Res.* **4**, No.1, 39.
- Ebert, P., Feuerbacher, M., Tamura, N., Wollgarten, M., and Urban, K., (1996) *Phys. Rev. Lett.* **77**, 3827.
- Edagawa, K., Suzuki, T., and Takeuchi, S., (1997) *Proc. 6th Int. Conf. on Quasicrystals*, Eds Takeuchi, S., Fujiwara, T., World Scientific, Singapore, 517.
- Edler, F. J., (1997) thesis, ETH Zürich.
- Edler, F. J., Gramlich, V., and Steurer, W., (1998) *J. Alloys & Comp.* **269**, 7.
- Elser, V., (1985) *Phys. Rev. B* **32**, 4892.
- Estermann, M.A., Haibach, T., Steurer, W., and Kek, S., (1997) *Proc. Int. Conf. on Aperiodic Crystals. Aperiodic '97*, World Scientific, Singapore, 433.

- Estrin, Y., (1996) Unified Constitutive Laws of Plastic Deformation, (Eds. A. Krausz and K. Krausz), Academic press, p.69.
- Evans, A.G., and Rawlings, R.D., (1969) *Phys. Stat. Sol.* **34**, 9.
- Feuerbacher, M., Baufeld, B., Rosenfeld, R., Bartsch, M., Hanke, G., Beyss, M., Wollgarten, M., Messerschmidt, U., and Urban, K., (1995) *Phil. Mag. Lett.* **71**, 91.
- Feuerbacher, M., Weller, M., Diehl, J., and Urban, K., (1996a) *Phil. Mag. Lett.* **74**, 81.
- Feuerbacher, M., (1996b) thesis, RWTH-Aachen.
- Feuerbacher, M., Metzmacher, C., Wollgarten, M., Baufeld, B., Bartsch, M., Messerschmidt, U., and Urban, K., (1997a) *Mat. Sci. & Eng. A* **233**, 103.
- Feuerbacher, M., Metzmacher, C., Wollgarten, M., Urban, K., Baufeld, B., Bartsch, M., and Messerschmidt, U., (1997b) *Mat. Sci. & Eng. A* **226-228**, 943.
- Feuerbacher, M., Schall, P., Estrin, Y., and Brechet, Y., (2000) unpublished.
- Feuerbacher, M., Schall, P., Estrin, Y., and Brechet, Y., (2001a) *Phil. Mag. Lett.* **81**, 473.
- Feuerbacher, M., Klein, H., and Urban, K., (2001b) *Phil. Mag. Lett.* **81**, 639.
- Feuerbacher, M., (2002) unpublished.
- Feuerbacher, M., (2003a) private communication.
- Feuerbacher, M., Urban, K., (2003b) Plastic Behaviour of Quasicrystalline Materials. In Quasicrystals - Structure and Physical Properties (Ed., H.-R. Trebin) VCH Wiley.
- Feuerbacher, M., Mompiau, F., Caillard, D., (2003c) *Phys. Rev. Lett.*, in press.
- Fisher, I.R., Islam, Z., Panchula, A.F., Cheon, K.O., Kramer, M.J., Canfield, P.C., and Goldman, A.I., 1998, *Phil. Mag. B* **77**, 1601.
- Franz, V., Feuerbacher, M., Wollgarten, M., and Urban, K., (1999) *Phil. Mag. Lett.* **79**, 333.
- Frost, H.J., (1982) *Acta. Met.* **30**, 889.
- Galler, R., (2003) private communication.
- Geyer, B., Bartsch, M., Feuerbacher, M., Urban, K., and Messerschmidt, U., (2000) *Phil. Mag. A* **80**, 1151.
- Gilman, J.J., (1973) *J. Appl. Phys.* **44**, 675.
- Gödecke, T., Lück, R., (1995) *Z. Metallk.* **86**, 109.
- Gottstein, G., (1998) *Physikalische Grundlagen der Materialkunde*, Springer, Berlin.
- Grin, Y., Peters, K., Burkhardt, U., Gotzmann, K., and Ellner, M., (1997) *Z. Kristall.* **212**, 439.
- Grushko, B., Yureshko, M., and Tamura, N., (1999) *J. Alloys & Comp.* **290**, 164.
- Grushko, B., (2000) private communication.

- Guo, J.Q., Abe, E., and Tsai, A.P., (2000) *Phys. Rev. B* **62**, R14605.
- Guo, J.Q., and Tsai, A.P., (2002) *Phil. Mag. Lett.* **82**, 349.
- Ham, R.K., and Sharpe, N.G., (1961) *Phil. Mag.* **6**, 1193.
- Hawley, M., Raistrick, I.D., Beery, J.G., and Hulton, R.J., (1991) *Science* **25**, 1587.
- He, Y., Schwarz, R.B., and Archuleta, J.I., (1996) *Appl. Phys. Lett.* **69**, 1861.
- Heggen, M., Feuerbacher, M., Schall, P., Klein, H., Fisher, I.R., Canfield, P.C., and Urban, K., (2000a) *Phil. Mag. Lett.* **80**, 129.
- Heggen, M., Feuerbacher, M., Schall, P., Klein, H., Fisher, I.R., Canfield, P.C., and Urban, K., (2000b) *Mat. Sci. & Eng. A* **294-296**, 781.
- Heggen, M., Feuerbacher, M., Schall, P., and Urban, K., (2001) *Phys. Rev. B* **64**, 014202.
- Heggen, M., Feuerbacher, M., Lange, T., and Urban, K., (2002) *J. Alloys & Comp.* **342**, 333.
- Heggen, M., Spaepen, F., and Feuerbacher, M., (2003), in press.
- Hirsch, P.B., Howie, A., Nicholson, R.B., Pashley, D.W., Whelan, M.J., (1977) *Electron Microscopy of thin Crystals*, Krieger: Malabar.
- Hirth, J.P., and Lothe, J., (1982) *Theory of dislocations*, Wiley, New York, 384.
- Hirth, J.P., Srolovitz, D.J., (1994) *Phil. Mag. A* **69**, 341.
- Hobgood, H.M., Barrett, D.L., McHugh, J.P., Clarke, R.C., Sriram, S., Burk, A.A., Gregg, J., Brandt, C.D., Hopkins, R.H., and Choyke, W.J., (1994) *J. Crystal Growth* **137**, 181.
- Holzer, J.C., and Kelton, K.F., (1991) *Acta Metall. Mater.* **39**, 1833.
- Inoue, A., Bizen, Y., and Masumoto, T., (1988) *Metall. Trans. A* **19**, 383.
- Inoue, A., Zhang, T., Nishiyama, N., Ohba, K., and Masumoto, T., (1993) *Mater. Trans. JIM* **34**, 1234.
- Ishimasa, T., and Shimizu, T., (2000a) *Mat. Sci. & Eng. A* **294-296**, 232.
- Ishimasa, T., and Shimizu, T., (2000b) *Jpn. J. Appl. Phys.* **39**, 1235.
- Janot, C., (1994) *Quasicrystals*, 2nd Edition, Clarendon Press, Oxford.
- Janot, C., (1996a) *Europhys. News* **27**, 2, 60.
- Janot, C., (1996b) *Phys. Rev. B* **53**, 181.
- Kabutoya, E., Edagawa, K., Tamura, R., Takeuchi, S., Guo, J.Q., and Tsai, A. P., (2002) *Phil. Mag. A* **82**, 369.
- Kafolt, D., Nanao, S., Egami, T., Wong, K.M., and Poon, S.J., (1986) *Phys. Rev. Lett.* **57**, 114.
- Kang, S.S., and Dubois, J.M., (1992) *Phil. Mag.A* **66**, 151.
- Kato, H., Inoue, A., and Chen, H.S., (2001) *Appl. Phys. Lett.* **79**, 4515.

- Krausz, A.S., and Eyring, H., (1975) Deformation Kinetics, Wiley, New York.
- Klein, H., Audier, M., Boudard, M., de Boissieu, M., (1996) *Phil. Mag. A* **73**, 309.
- Klein, H., (1997) thesis, Grenoble.
- Klein, H., (1998) unpublished.
- Klein, H., Feuerbacher, M., Schall, P., and Urban, K., (1999) *Phys. Rev. Lett.* **82**, 3468.
- Kléman, M., (1988) in Quasicrystalline Materials, Eds. Janot, C., Dubois, J.M., World Scientific, Singapore, 628.
- Knippenberg, W.F., (1963) *Philips Res. Rept.* **18**, 161.
- Kocks, U.F., (1976a) *J. Eng. Mater. Technol.* **98**, 76.
- Kocks, U.F., Argon, A.S., and Ashby, M.F., (1976b) Thermodynamics and Kinetics of Slip, Pergamon Press.
- Köster, U., Liu, W., Liebertz, H., and Michel, M., (1993) *J.Non-Cryst. Solids* **153&154**, 446.
- Köster U., Meinhardt, J., Roos, S., and Liebertz, H., (1996) *Appl. Phys. Lett.* **69**, 179.
- Landau, L.D., and Lifshitz, E.M., (1989) Lehrbuch der Theoretischen Physik, Bd. 7 Elastizitätstheorie, Akademie Verlag, Berlin, pp 139.
- Langsdorf, A., Ritter, F., and Assmus, W., (1997) *Phil. Mag. Lett.* **75**, 381.
- Langsdorf, A., and Assmus, W., (1998) *J. Cryst. Growth.* **192**, 152.
- Leroux, C., Loiseau, A., Cadeville, M.C., Broddin, D., and van Tendeloo, G., (1990) *J. Phys. Condens. Matter.* **2**, 3479.
- Li, J.C.M., (1976) Metallic Glasses, American Society for Metals, 224.
- Lifshitz, M., and Slyozhov, J., (1961) *J. Phys. Chem. Solids* **19**, 35.
- Lillie, H. R., (1933) *J. Am. Ceram. Soc.* **16**, 619.
- Lu, I. R., Görler, G. P., Fecht, H. J., and Willnecker, R., (2000) *J.Non-Cryst. Solids* **274**, 294.
- Luo, Z., Zhang, S., Tang, Y., and Zhao, D., 1993, *Scripta metall.* **28**, 1513.
- Mahne, S., and Steurer, W., (1996) *Zeitschr. Krist.* **211**, 17.
- Matsubara, E., Waseda, Y., Tsai, A.P., Inoue, A., and Masumoto, T., (1988) *Z. Naturforsch.* **43**, 505.
- Mecking, H., and Kocks, U.F., (1981) *Acta Metall.* **28**, 1865.
- Mehrer, H., (2003) in: Quasicrystals - Structure and Physical Properties (Ed., H.-R. Trebin) VCH Wiley.
- Messerschmidt, U., Bartsch, M., Feuerbacher, M., Geyer, B., and Urban, K., (1999) *Phil. Mag. A* **79**, 2123.

References

- Messerschmidt, U., Bartsch, M., Geyer, B., Feuerbacher, M., and Urban, K., (2000) *Phil. Mag. A* **80**, 1165.
- Messerschmidt, U., Petukhov, B.V., Bartsch, M., Dietzsch, Ch., Geyer, B., Häussler, D., Ledig, L., Feuerbacher, M., Schall, P. and Urban, K., (2001) *Mat. Sci. & Eng. A* **319-321**, 107.
- Mikulla, R., Roth, J., and Trebin, H.R., (1995) *Phil. Mag. B* **71**, 981.
- Monokanov, V.V., Chebotnikov, V.N., (1990) *J.Non-Cryst. Solids* **117-118**, 789.
- Murata, T., Kimura, H., and Masumoto, T., (1976) *Scripta Met.* **10**, 705.
- Murata, T., Masumoto, T., and Sakai, M., (1978) *Proc. 3rd Int. Conf. on Rapidly Quenched Metals*, The Materials Society, London.
- Niikura, A., Tsai, A. P., Inoue, A., and Masumoto, T., (1994a), *Phil. Mag. Lett.* **69**, 351.
- Niikura, A., Tsai, A. P., Inoue, A., and Masumoto, T., (1994b), *Jpn. J. Appl. Phys. Part 1* **33**, 1538.
- Pauling, L., (1955) *Am. Sci.* **43**, 285.
- Peker, A., and Johnson, W.L., (1993) *Appl. Phys. Lett.* **63**, 2342.
- Poirier, J.P., (1985) *Creep of Crystals*, Cambridge University Press, New York.
- Poon, S.J., Drehman, A.J., and Lawless, K.R., (1985) *Phys. Rev. Lett.* **55**, 2324.
- Qian, W., Rohrer, G.S., Skowronski, M., Doverspike, K., Rowland, L.B., and Gaskill, D.K., (1995a) *Appl. Phys. Lett.* **76**, 2284.
- Qian, W., Skowronski, M., Doverspike, K., Rowland, L.B., and Gaskill, D.K., (1995b) *J. Crystal Growth* **151**, 396.
- Rasmussen, D.R., McKernan, S., and Carter, C.B., (1991) *Phys. Rev. Lett.* **66**, 2629.
- Roberts, G. J., and Roberts, J. P., (1965) *Proc. 7th Int. Conf. on Glass*, 31.
- Rodewald, M., Langsdorf, A., Assmus, W., and Fuess, H., (1997) *Proc. 6th Int. Conf. on Quasicrystals*, Tokyo, (Singapore: World Scientific), 51.
- Rosenfeld, R., Feuerbacher, M., Baufeld, B., Bartsch, M., Wollgarten, M., Hanke, G., Beyss, M. Messerschmidt, U. and Urban, K., (1995) *Phil. Mag. Lett.* **72**, 375.
- Samson, S., (1949) *Acta. Chem. Scand.* **3**, 809.
- Sato, T.J., Takakura, H., and Tsai, A.P., (1998) *Jpn. J. Appl. Phys.* **37**, 663.
- Schall, P., Feuerbacher, M., Bartsch, M.; Messerschmidt, U., and Urban, K., (1999) *Phil. Mag. Lett.*, **79**, 785.
- Sevillano, J.G, (1993) *Plastic Deformation and Fracture of Materials* (Eds. R.W. Cahn, P. Haasen, and E.J Kramer), Mat Sci. Tech. 6, VCH, Weinheim, 19.
- Shechtman, D., Blech, I., Gratias, D., and Cahn, J.W., (1984) *Phys. Rev. Lett.* **53**, 1951.

- Shibuya, T., Asao, T., Tamura, M., Tamura, R., and Takeuchi, S., (2000) *Mat. Sci. Eng. A* **294-296**, 61.
- Socular, J.E.S., Lubensky, T.C., Steinhard, P.J., (1986) *Phys. Rev. B* **34**, 3345.
- Sordelet, D.J., Rozhkova, E., Besser, M.F., and Kramer, M.J., (2002) *App. Phys. Lett.* **80**, 4735.
- Spaepen, F., and Turnbull, D., (1974) *Scr. Met.* **8**, 563.
- Spaepen, F., (1975) *Acta Met.* **23**, 615.
- Spaepen, F., (1977) *Acta Met.* **25**, 407.
- Spaepen, F., (1981) Defects in amorphous metals, Les Houches Lectures XXXV on Physics of Defects (Amsterdam: North Holland Press), 133.
- Spaepen, F., (1994) *Mat. Sci. Eng. A* **179-180**, 81.
- Steif, P.S., Spaepen, F., and Hutchinson, J.W., (1982) *Acta Met.* **30**, 447.
- Sugiyama, K., Hiraga, K., and Saito, K., (2000) *Mat. Sci. Eng. A* **294-296**, 345.
- Sunagawa, I., and Bennema, P., (1981) *J. Crystal Growth* **53**, 490.
- Takasu, S., and Shimanuki, S., (1974) *J. Crystal Growth* **24/25**, 641.
- Takeuchi, S., (1991) *Jpn. J. Appl. Phys.* **10**, 561.
- Takeuchi, S., Shinoda, K., Yoshida, T., and Kakegawa, T., (1998) *Proc. 6th Int. Conf. on Quasicrystals*, Tokyo (Singapore: World Scientific), 541.
- Takeuchi, S., Tamura, R., Kabutoya, E., and Edagawa, K., (2002) *Phil. Mag. A* **82**, 379.
- Tamura, N., (1997) *Phil. Mag. A* **76**, 337.
- Tanaka, K., (1996) *Phil. Mag. A* **73**, 1715.
- Taub, A.I., and Spaepen, F., (1980) *Acta. Met.* **28**, 1781.
- Taub, A.I., and Spaepen, F., (1981) *J. Mat. Science* **16**, 3087.
- Taylor, D. W., (1948) *Fundamentals of Soil Mechanics*, Wiley.
- Tsai, A.P., Inoue, A., and Masumoto, T., (1987) *Jap. J. Appl. Phys.* **26**, L1505.
- Tsai, A.P., Inoue, A., Bizen, Y., and Masumoto, T., (1989) *Acta. Metall.* **37**, 1443.
- Tsai, A.P., Inoue, A., Yokoyama, Y., and Masumoto, T., (1990) *Mater. Trans. JIM* **31**, 98.
- Tsai, A.P., Niikura, A., Inue, A., Masumoto, T., Nishida, Y., Tsuda, K., and Tamaka, M., (1994) *Phil. Mag. Lett.* **70**, 169.
- Tsai, A.P., (1999) in: *Physical Properties of Quasicrystal* (Ed: Z.M. Stadnik), Springer, Berlin.
- Tsai, A.P., Guo, J.Q., Abe, E., Takakura, H., and Sato, T.J., (2000) *Nature* **408**, 537.

- Tsao, S.S., and Spaepen, F., (1985) *Acta. Met.* **33**, 881.
- Underwood, E. E., (1970) *Quantitative Stereology*, Reading, Mass.: Addison-Wesley.
- Urban, K., and Feuerbacher, M., (2003) *J. Non-Cryst. Solids*, in press.
- van den Beukel, A., and Sietsma, J., (1990) *Acta metall. mater.* **38**, 383.
- van Enkevort, W.J.P., and Binsma, H., (1982) *J. Crystal Growth* **56**, 612.
- Vandervael, J.J., (1992) *Phys. Rev. B* **46**, 501.
- Verma, A.R., (1953) *Crystal Growth and Dislocations*, Butterworths, London.
- Villars, P., and Calvert, L.D., (1986) *Pearson's Handbook of Crystallographic Data for Intermetallic Phases*, American Society of Metals, Metals Park, Ohio.
- Wagner, C., (1961) *Z. Elektrochem.* **65**, 243.
- Wang, R., Feuerbacher, M., Yang, W., and Urban, K., (1998) *Phil. Mag. A* **78**, 273.
- Williams, D.B., and Carter, C.B., (1996) *Transmission Electron Microscopy: A Textbook for Materials Science*, Plenum Press, New York.
- Witvrouw, A., and Spaepen, F., (1993) *J. Appl. Phys.* **74**, 7154.
- Wollgarten, M., Gratias, D., Zhang, Z., and Urban, K., (1991) *Phil. Mag. A* **64**, 819.
- Wollgarten, M., Beyss, M., Urban, K., Liebertz, H., and Köster, U., (1993) *Phys. Rev. Lett.*, **71**, 549.
- Wollgarten, M., Bartsch, M., Messerschmidt, U., Feuerbacher, M., Rosenfeld, R., Beyss, M., and Urban, K., (1995) *Phil. Mag. Lett.* **71**, 99.
- Wollgarten, M., Franz, V., Feuerbacher, M., Urban, K., (2002) in: *Quasicrystals, An Introduction to Structure, Physical Properties and Applications* (Eds. Suck, J.B., Schreiber, M., Häussler, P.) Springer, Berlin.
- Yang, W., Feuerbacher, M., Tamura, N., Ding, D., Wang, R., and Urban, K., (1998) *Phil. Mag. A* **77**, 1481.
- Yokoyama, Y., Miura, T., Tsai, A.P., Inoue, A., and Masumoto, T., (1992) *Mater. Trans. JIM* **33**, 97.

Danksagung

Bei Professor Dr. K. Urban möchte ich mich herzlich für die Möglichkeit bedanken, diese Arbeit an seinem Institut anzufertigen. Weiterhin danke ich ihm für seine Unterstützung und für Rat und Hinweise, die zum Gelingen dieser Arbeit beigetragen haben.

Dr. M. Feuerbacher danke ich herzlich für die Betreuung dieser Arbeit und für die schöne gemeinsame Zeit im Institut. Durch seine motivierende Unterstützung, fachlichen Anregungen und zahlreichen hilfreichen Diskussionen ist diese Arbeit überhaupt nur möglich geworden. Weiterhin möchte ich ihm für das Korrekturlesen danken.

Dr. P. Schall zeigte fortwährendes Interesse an dieser Arbeit und war stets offen für Diskussionen. Für seine Anteilnahme und viele hilfreiche Gespräche möchte ich mich herzlich bei ihm bedanken. Herrn Dipl.-Phys. T. Lange schulde ich Dank für die gute Zusammenarbeit bei der Untersuchung von Antiphasengrenzen in Zn-Mg-Dy-Quasikristallen. Allen Mitarbeitern und ehemaligen Mitarbeitern der Arbeitsgruppe „Quasikristalle“ danke ich herzlich für die Unterstützung und für die schöne gemeinsame Zeit.

Besonders bedanken möchte ich mich bei Professor Dr. F. Spaepen, der als Humboldt-Preisträger mehrfach im Institut für Mikrostrukturforschung war. In Zusammenarbeit mit ihm wurde die Plastizität metallischer Gläser untersucht. Ohne seine enorme Wissens- und Erfahrungsvermittlung, seine Geduld und Hilfe wäre diese Arbeit nicht möglich gewesen.

Danken möchte ich weiterhin Dipl.-Ing. M. Beyss und Dipl.-Ing. C. Thomas für die gute Zusammenarbeit und die Unterstützung bei der Weiterentwicklung der Quasikristallzucht. Dr. B. Grushko und Dipl.-Phys. S. Balanetsky danke ich für viele anregende Diskussionen zum Al-Pd-Fe-Phasendiagramm und für die Herstellung von c_2 -Al-Pd-Fe-Proben. Für die Überlassung von Pd-Ni-Cu-P-Proben bedanke ich mich bei Dr. J. Schroers (Californian Institute of Technology) und Professor Dr. D. M. Herlach (Deutsches Zentrum für Luft- und Raumfahrt).

Ein großer Dank gilt Herrn Dipl.-Ing. W. Pieper für die schnelle Bewältigung von technischen Problemen aller Art und die Instandhaltung der Elektronenmikroskope. Weiterhin möchte ich mich bei Frau I. Rische-Radloff, Frau G. Wassenhofen und Frau D. Meertens bedanken.

Ich bedanke mich herzlich bei allen Mitgliedern des Instituts für Mikrostrukturforschung für die geleistete Unterstützung und für eine angenehme Arbeitsatmosphäre. Besonders hervorheben möchte ich Dr. B. Jahnen, Dipl.-Phys. N. Hüging und Dr. M. Lentzen, die mir in vielerlei Hinsicht zur Seite standen.

Ein ganz besonderer Dank gilt den wichtigsten Menschen in meinem Privatleben, meiner Frau Sylvia und meinen Eltern.

Forschungszentrum Jülich
in der Helmholtz-Gemeinschaft



Jül-4099
November 2003
ISSN 0944-2952