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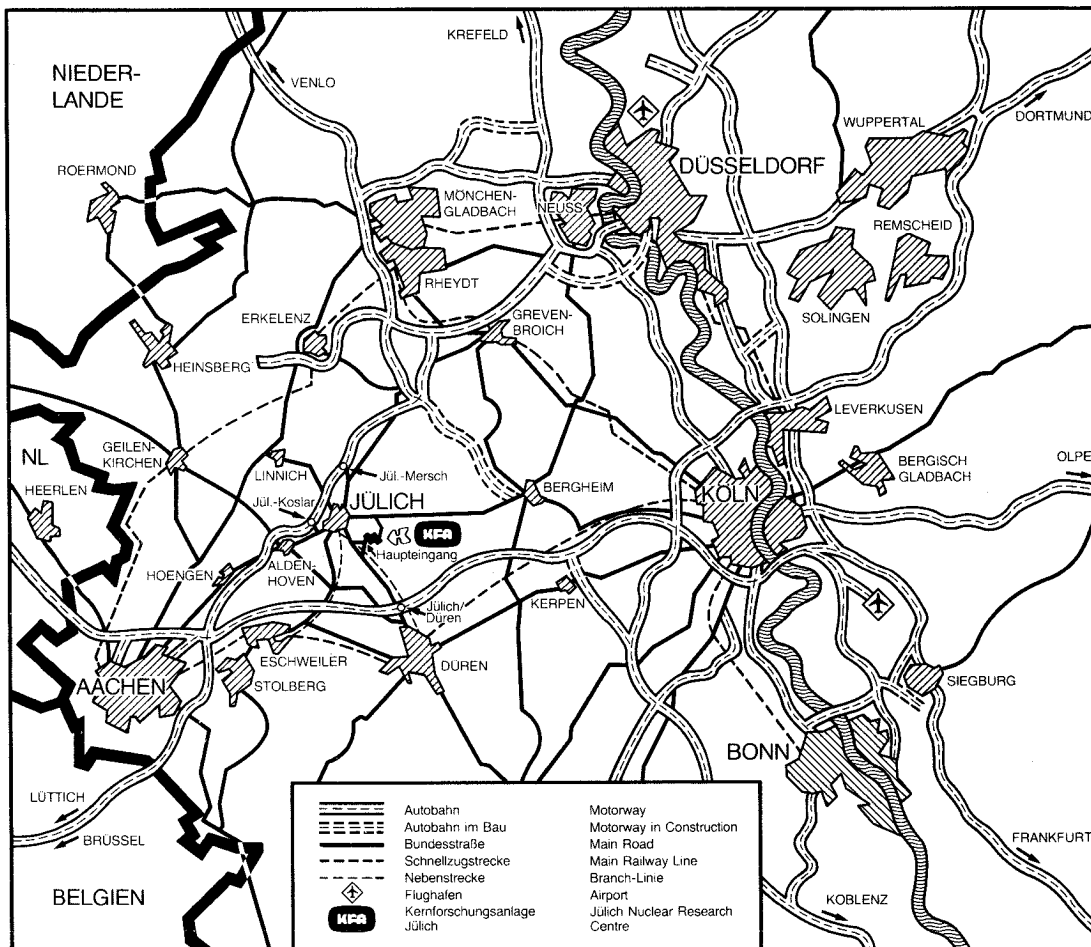
Institut für Festkörperforschung

**Low Temperature Calorimetry and
Transmission Electron Microscopy
of Helium Bubbles in Cu**

von

E. Syskakis

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Low Temperature Calorimetry and Transmission Electron Microscopy of Helium Bubbles in Cu

von

E. Syskakis

D 82 (Diss. T. H. Aachen)

Abstract.

Helium has been introduced into 100 μm thick pure Cu specimens by implantation of α -particles at $T = 300$ K. Post-implantation annealing of the specimens at high temperatures caused helium to precipitate into bubbles. We have measured the low-temperature heat capacity of helium confined in bubbles of average radius of less than 100 $\text{\AA}$. The size of the bubbles was obtained by transmission electron microscope investigations.

We have observed that helium liquifies at low temperatures and undergoes the transition to the superfluid state in bubbles of average radius larger than 35 $\text{\AA}$. Strong modification of superfluidity of helium in bubbles has been observed. It is attributed to the effective confinement of helium in such microscopic bubbles. The temperature of the transition to the superfluid state is discussed in terms of the Ginzburg-Pitaevskii-Mamaladze mean field model. To calculate thermodynamic parameters of helium in bubbles we have used an EOS for "superdense" helium in bubbles, whose prediction is found to be in good agreement to our calorimetric observations.

The confining geometry of bubbles is new and possesses unique features for investigations of confined helium. It provides the possibility to study properties of extremely small, spherical, completely isolated Bose "particles" consisting of 10^4 helium atoms each. Furthermore, as we show, it can be known with better accuracy than formerly investigated confining geometries.

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1. INTRODUCTION.

The study of the properties of liquid and solid helium continues to be a fascinating and fertile area of low temperature research. Helium, (we concentrate on the isotope ^4He) liquifies at 4.2 K under normal pressure and remains liquid under its vapor pressure to absolute zero. Solidification of helium requires a minimum pressure of about 25 bar. At 2.172 K liquid helium undergoes a phase transition to the famous superfluid state thereby exhibiting several unusual properties which underline the importance of quantum effects. There is a great number of detailed and precise experimental investigations concerning static and dynamic properties of the bulk condensed phases of helium.

The behaviour of helium at low temperatures is strongly modified in the regime with specimen dimensions ranging between thin films and $10^3 \text{ \AA}$ spheres.

Fundamentally important for experimental investigations in this regime is the interaction of helium atoms with substrates and the fact that the superfluid order parameter vanishes at the confining walls. Of further importance is the ability of helium to form films on various substrates and penetrate microscopic channels (superfluidity) in porous materials.

Helium systems with finite dimensions exhibit modified thermodynamic behaviour in comparison to the bulk, the degree of modification depending on a characteristic dimension of the specimen. The length scale is set by an intrinsic length. Reduced dimensionality effects are expected when the confining size becomes comparable with the thermal phonon wavelength or with the coherence length of the superfluid state.

Size effect investigations have been performed in various confi-

ning geometries, i.e. films, cylindrical channels and the intergranular space in fine powders. They have concentrated mostly on the superfluid transition in these systems. Qualitatively the superfluid behaviour of confined helium is today sufficiently well understood. But many investigations have failed in providing data which could test theoretical predictions. The main reason for that was insufficient knowledge and irregularities of the confining geometries.

On the other hand helium is a unique system for such studies because of its purity and structural perfection. For these reasons, the superfluid transition allowed the most detailed investigation of critical phenomena up to date.

For the theorist, finite size effects are of considerable interest in that they can provide a test for the validity of the scaling and universality concepts in finite size systems.

Helium, as coolant or refrigerant, has contributed crucially to the development of cryogenic technology and all applications related to low or very low temperatures. In addition, at high temperatures the properties of helium in metals are studied today intensively in close relationship to the development of advanced alloys to be used in future nuclear devices, i.e., the fusion and fast breeder reactor or spallation neutron sources. The necessity and technological importance of these studies becomes obvious by the fact that helium atoms are generated by transmutation reactions (or introduced directly) in metals exposed to radiation and can then influence detrimentally their mechanical properties.

The energetics and kinetics of helium in metals is greatly influenced by atomistic properties, i.e. the fact that helium is a small, light, and chemically inert atom. It has an extremely low solubility in metals and therefore tends strongly to precipitate forming clusters and helium-filled cavities (bubbles).

Precipitated helium causes swelling and high temperature embrittlement of metals (bulk effects) or surface roughening and blistering. Especially helium-embrittlement /1/ is considered today as a severe life time limiting factor for the inner wall and blanket materials of a fusion reactor.

Recently, quantitative research has been initiated and directed towards systematic investigations of basic properties of helium in metals. Simulation techniques are used to introduce helium into metals and study atomistic properties such as solubility and diffusion as well as the evolution of the bubble population and the thermodynamic state of helium in bubbles. A qualitative conclusion drawn is that the density of helium in small bubbles can be very high, approaching metallic densities and being therefore much higher than the density of liquid or solid helium at low temperatures. Obviously, at such high densities the state of helium in bubbles cannot be described by ideal or Van der Waals gas laws. Experimental investigations indicate indeed very high densities in very small bubbles ($r = 20 \text{ \AA}$).

In this work, properties of helium in somewhat larger bubbles ($r = 25 \text{ \AA}$ to $100 \text{ \AA}$) in bulk Cu specimens have been investigated by means of heat capacity measurements at low temperatures. In parallel, the evolution of the bubble size and bubble population has been followed by transmission electron microscope investigations. In these bubbles the helium pressure is in the range of a few Kbar at room temperature. For these smaller-pressure bubbles, the helium condenses into a strongly confined solid or liquid state at pressures below 100 bar at low temperature. We were therefore able to investigate phase transitions of liquid and solid helium in the Kelvin range,

and in particular the superfluid transition of helium confined in all three dimensions inside the bubbles in our Cu specimens.

Because typical bubble radii in our studies were below $100 \text{ \AA}$ we observed typical finite-size behaviour.

The confining geometry of bubbles, introduced in this work for the first time in a detailed investigation, is qualitatively different from formerly investigated geometries. It is homogeneous in three dimensions (spherical bubbles) and the confining size can be known quite exactly by means of a direct and accurate measurement. A unique and attractive feature of the confining geometry of bubbles is that it creates an ensemble of extremely small Bose "particles" (10^4 atoms each !!) which are completely isolated from each other. This bubble-geometry can be developed into a very useful tool for investigating new aspects of the behaviour of confined systems.

2. PROPERTIES OF HELIUM IN METALS.

2.1. Solubility of helium in metals.

The equilibrium concentration of helium atoms dissolved in a metal at temperature T in a gas bath of pressure P can be easily derived by means of thermodynamic arguments as /2/

$$\bar{C}_{\text{He}} = h^3 (2 \pi m)^{-3/2} (k_B T)^{-5/2} P \exp(-\Delta H/k_B T) \exp(\Delta S/k_B) \quad (2.1)$$

in the limit $\bar{C}_{\text{He}} \ll 1$. In eq.(2.1) h is Planck's constant, k_B Boltzmann's constant, m the mass of the helium atom, ΔH the formation enthalpy of a helium atom in solution and ΔS the associated entropy change of the lattice estimated to be $\approx k_B$.

According to eq.(2.1) the concentration of helium in solution increases proportionally with pressure and also with temperature since the exponential temperature dependence dominates. The concentration of helium in solution depends on whether it will be dissolved as substitutional or interstitial atom in the metal matrix. Consideration of the solution enthalpies indicates that substitutional configuration is strongly favored for most simple metals.

The solubility of helium has been recently experimentally investigated in Ni /3/ and Au mono- and polycrystalline specimens /4/. It has been found that even for specimens charged at high pressures (several Kbar) and temperatures close to the melting temperatures of these metals, the concentration of dissolved helium was of the order of 10^{-3} appm.

Similarly low solubilities are expected for other metals and alloys. A direct consequence of such an extremely low solubility is that the supersaturated state will be reached very fast during, for example, a helium implantation and thereafter the helium will tend strongly to agglomerate forming clusters and bubbles.

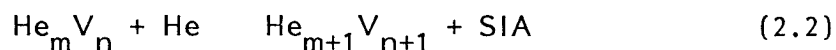
2.2. Nucleation and growth of helium bubbles in metals.

Introduction of helium atoms in a metallic lattice can proceed with or without simultaneous production of irradiation induced atomic defects.

Implantation of helium ions with energy above the threshold energy for radiation damage production introduces Frenkel-pairs. A small fraction of vacancies surviving recombination can be filled with helium atoms forming the first stable helium clusters (bubble nuclei). On the other hand in "helium filling" experiments, i.e. subthreshold implantation or helium production by nuclear decay of tritium, no damage is introduced in the lattice.

Nucleation and growth of bubbles depends on parameters like defect concentration, temperature, applied stress, microstructure etc. Different mechanisms have been discussed in the literature for the one or the other specific case /5,6/. In the following we will concentrate to nucleation and growth of bubbles as taking place during a low temperature implantation and during post-irradiation annealing of the specimen at high temperatures under zero external stress.

At temperatures below about $T_m/3$ (T_m is the melting temperature of the metal under consideration), nucleation and growth of bubbles /7/ is characterized by a low concentration of vacancies which are assumed to be immobile. Interstitial helium atoms (IHA's) and self interstitial atoms (SIA's) are mobile defects. SIA's migrate easier than IHA's. Vacancies capture IHA's and form clusters of the form $(He_m V)$. At a certain value of m trap-mutation takes place leading to formation of a $He_{m+1} V_2$ cluster. This process may repeat itself spontaneously according to the kinetic reaction



which increases the size of the cluster by roughly an atomic volume

per captured helium atom and produces SIA's. SIA's can then be trapped at lattice defects, annihilate clusters of the form He_mV with $m \leq 6$, diffuse to the surface or condense to form interstitial type dislocation loops. In this way the concentration of small clusters can be kept small while larger clusters can grow further. As a certain size is reached, corresponding to certain m and n in eq.(2.2), it becomes energetically favorable for an interstitial type dislocation loop to be emitted rather than a series of isolated interstitial atoms.

If the energy required for the emission of an isolated SIA is E_f , and the increase of the volume of the resulting cluster is taken to be one atomic volume, ω , then a threshold pressure of /8/

$$P = E_f / \omega \quad (2.3)$$

must be exceeded in the cluster in order for this mechanism to be operable. Inserting numerical values for E_f and ω for Cu, as an example, in eq.(2.3) the pressure is found to be of the order of 200 Kbar.

Similarly, growth by the interstitial loop punching mechanism requires a pressure approximately given by /8/:

$$P = (2\gamma + \mu b) / r_b \quad (2.4)$$

where γ is the specific surface energy of the metal, μ its shear modulus, b the length of Burger's vector of the emitted loop, and r_b the radius of the cluster (bubble).

These growth processes can take place already during a low temperature implantation after the concentration of helium in the specimen exceeds the solubility limit. They lead to relaxation of the pressure in small overpressurised bubbles by means of athermal processes (athermal growth). Growth of helium bubbles by loop punching has been observed in the TEM /9/.

In contrast to the low temperature nucleation and growth, at temperatures above $T_m/2$ the evolution of the precipitation is

greatly assisted by the presence of thermal vacancies which become abundant and are mobile. They can easily be absorbed at helium clusters. Stable bubble nuclei can grow by absorbing more vacancies and helium atoms. As the number of vacancies trapped in a bubble increases, the pressure of the helium gas in it is reduced until it will be balanced by the surface tension of the metal. For a spherical bubble of radius r_b , the pressure of helium at thermal equilibrium will be given by:

$$P_{eq.} = 2\gamma / r_b \quad (2.5)$$

where γ is the specific surface energy of the metal.

The energetics of the precipitation can be divided into two distinct stages /9/. In the first stage, involving small helium clusters, the interaction of the helium atoms with each other and with the host atoms plays an important role in determining the geometry and stability of the cluster. This stage is not directly observable; its energetics is analysed by atomistic calculations and computer simulation. Such studies show that small helium vacancy clusters are very stable. For example, it has been predicted /10/ that a single vacancy in Cu can accomodate up to six helium atoms.

As the number of helium atoms (and the number of vacancies) in a cluster increases the interaction of helium atoms with the metal atoms becomes of less and less importance and is limited to the atoms on the "surface" of the already large enough "cluster", which can be called bubble. Above a certain size the energetic state of the bubble can be characterized by its size and the state of helium in it, i.e. it can be described in terms of statistical mechanics.

Growth of nucleated helium bubbles can take place even in the absence of further helium supply. In contrast to nucleation it can be easily followed by means of TEM investigations. Thermally activated growth of helium bubbles is known to take place either by

migration and coalescence with other bubbles or by resolution of helium atoms in the metal matrix and coarsening.

2.2.1 Bubble migration and coalescence.

We examine a random migration of helium bubbles.

In order to move the center of a gas bubble in a metal, atoms of the metal have to be moved from one side of the bubble surface to another. This material transport can be achieved by surface diffusion of metal atoms, volume diffusion, or transport of evaporated metal atoms through the gas in the bubble. These processes are schematically shown in fig.(2.1a).

Coalescence of bubbles can be thought to take place in three steps. In the first step the bubbles touch each other and the total volume is conserved. The second step involves transport of material and transformation of the shape of the resulting bubble to a more regular one. In the third step the pressure of helium in the new bubble is relaxed to equilibrium by absorption of vacancies.

Theoretical analyses /11/ permit evaluation of the resulting (size-dependent) bubble-diffusion coefficient which can be used to calculate the time of coalescence and the resulting increase of the size of the bubbles. However, simple analytical expressions for the time dependence of both, the average bubble radius, $\bar{r}_b$, and the volume density of the bubbles, ρ_b , can be obtained only if ideal gas behaviour and spherical bubbles are assumed. In this case one obtains /11/:

$$\bar{r}_b \propto (D(T) M_{\text{He}} t)^{1/z} \quad (2.6a)$$

$$\rho_b \propto M_{\text{He}} (D(T) M_{\text{He}} t)^{-2/z} \quad (2.6b)$$

where M_{He} is the helium content in the specimen and $D(T)$ is the diffusion coefficient of metal atoms. For surface diffusion $z = 5$ and $D = D_s$ is the surface diffusion coefficient, for volume diffusion $z = 4$ and $D = D_{\text{sd}}$ is the self diffusion coefficient of the metal.

Finally, for vapor transport $z = 3$ and $D = D_g$ is the diffusion coefficient for transport of the metal atoms through the gas.

2.2.2. Gas resolution and coarsening (Ostwald ripening).

From eq.(2.1) and eq.(2.5) it can be seen that the concentration of helium in solution in the matrix around a bubble depends on the size of the bubble. Therefore, given a size distribution of bubbles in the specimen, helium-concentration gradients between bubbles of different sizes, see fig.(2.1b), will lead to permeation of helium from small to bigger bubbles. Thus, large bubbles can grow, while

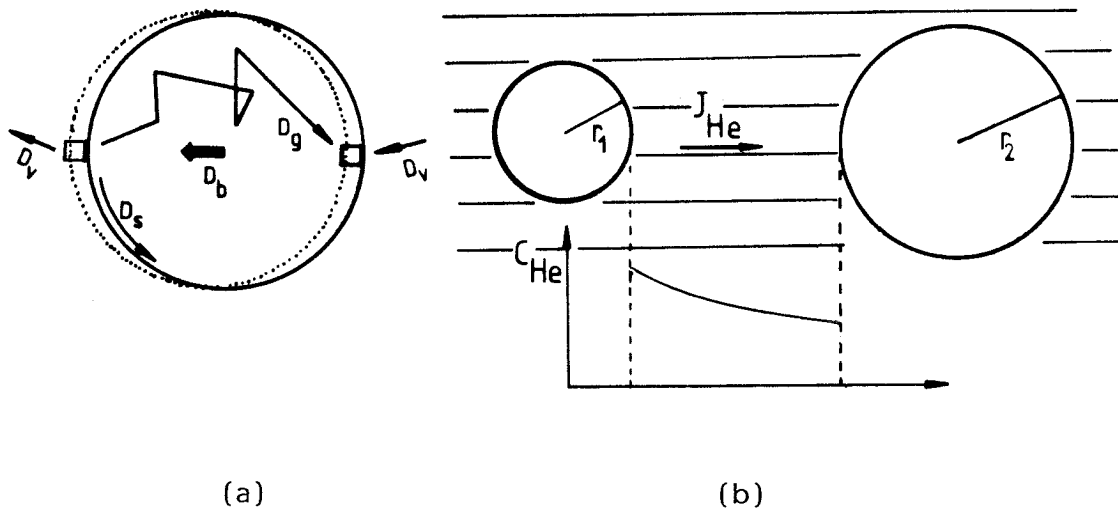


Fig.(2.1): Schematic view of transport processes:(a) Possible ways for transport of metal atoms resulting in movement of the center of a bubble. (b) Flow of helium atoms from small to larger bubbles.

smaller ones will shrink. Assuming again ideal gas behaviour and spherical bubbles the time dependence of the average bubble radius and volume density of the bubbles can be derived to be [12]:

$$\bar{r}_b \propto (D_{He} \bar{C}_{He} t)^{1/2} \quad (2.7a)$$

$$\rho_b \propto M_{He} (D_{He} \bar{C}_{He} t)^{-1} \quad (2.7b).$$

Thus, the time dependence of $\bar{r}_b$ and ρ_b in this mechanism is governed by the product of the average concentration of helium in solution, $\bar{C}_{He}$, and its diffusion coefficient through the lattice. From the analysis leading to eq.'s (2.7) it turns out that bubbles with radius larger than $\bar{r}_b$ will grow while smaller ones will shrink. According to the same analysis /13/ the radius r_m of the biggest bubbles of a given size distribution will be related to $\bar{r}_b$ as: $r_m = 2 \bar{r}_b$.

In summary, the mechanisms discussed above represent two distinct cases. Migration and coalescence attributes bubble-growth to the motion of bubbles and the variation of $\bar{r}_b$ and ρ_b is determined by material specific parameters (diffusion coefficient). In contrast, Ostwald ripening describes static bubbles and the growth in that case is determined by helium specific parameters, i.e., D_{He} , $\bar{C}_{He}$. As mentioned above, in both cases, the simplifying (but not necessarily realistic!) assumption of ideal gas behaviour is used. Modifications of the growth-laws due to non-ideal gas behaviour have been examined /14/. It is found that for small bubbles the exponents of growth will be larger, emerging finally to the values given in eq.(2.6) and eq.(2.7) as the bubbles become large.

2.3. Density and pressure of helium in bubbles in metals.

An important parameter for a better understanding of nucleation and growth of helium bubbles in metals is the density or pressure of helium in the bubbles. The pressure of helium in bubbles can be estimated by using eq.(2.4) or eq.(2.5) at low (i.e. $T < T_m/3$) and high temperatures, respectively. The size of the bubbles to be inserted in these equations is provided by TEM. Pressures estimated in this way are very high, usually of the order of several tens or hundreds of Kbars. Comparing these pressures with the melting

line of helium at high temperatures /15/ the existence of solid helium in small bubbles at moderate or even ambient temperatures is strongly evidenced. Obviously at such high pressures and temperatures below 10^4 K neither the ideal nor the Van der Waals gas equation of state are reliable approximations for the description of thermodynamic properties of helium in small bubbles.

2.3.1. Experimental determinations of the density of helium in small bubbles.

Several recent experimental investigations have determined directly the density of helium in small bubbles in metals.

Ultraviolet Vacuum Absorption (UVA) /16/ as a first start and subsequently a more systematic investigation by means of Electron Energy Loss Spectroscopy (EELS) /17/ have been used to determine the (maximum) density of helium in Al and Ni (EELS) and Al (UVA) specimens having thickness $\text{ca. } 10^3 \text{ \AA}$. The specimens were implanted at $T = 300 \text{ K}$ to different high helium doses and subsequently measured at $T = 300 \text{ K}$ as well as after isochronal annealing at higher temperatures.

The density-dependent property measured in these experiments was the displacement, ΔE , of the $1S_0 - 2P_1^1$ transition line of helium to higher energies relative to its value in the ideal gas state.

It has been related to the density of helium, n , in the bubbles as:

$$\Delta E = G n \quad (2.8)$$

where $G = \text{const.} = (24 \pm 5) 10^{-3} \text{ eV nm}^3$ deduced from the analysis of experimental data obtained by the EELS investigation. These experiments showed that the density of helium in bubbles of average radius less than $25 \text{ \AA}$ exceeded greatly the density of liquid helium at 4.2 K ($0.022 \text{ \AA}^{-3}$). In as-implanted Al foils it was

$0.14 \text{ \AA}^{-3}$ and decreased to $0.040 \text{ \AA}^{-3}$ after annealing them to $0.8 T_m$. Ni foils showed still higher densities of $0.2 \text{ \AA}^{-3}$, exceeding the density of liquid helium at 4 K by a factor of 10.

Similarly high densities were recently reported /18/ for bubbles of other rare gases (Ar, Xe, Kr) in Al thin foils measured with the EELS technique.

The density of helium in bubbles has been also determined by means of Small Angle Neutron Scattering (SANS) experiments /19/ performed on bulk Ni-isotope specimens homogeneously implanted at $T = 300 \text{ K}$ to 0.12% helium. It has been determined to be $ca. 0.080 \text{ \AA}^{-3}$ in bubbles of average radius of $12 \pm 1 \text{ \AA}$, after the specimens were annealed isochronally up to $T = 1023 \text{ K}$.

2.3.2. An equation of state for "superdense" helium.

In parallel to experimental investigations, an adequate equation of state (EOS) has been developed /20/ to relate the density to the pressure of helium for the high densities observed in small bubbles in metals. It can be written as:

$$Z(n, T) = P/(nk_B T) = 1 + B(T) n + C(T) n^2 + D(T) n^3 \quad (2.9)$$

where n is the particle density of helium and the coefficients $B(T)$, $C(T)$, and $D(T)$ have been obtained by interpolating properties of helium between the melt and the dilute state.

Pressure-density relationships calculated from an analytic expression of eq.(2.9) for different temperatures are shown in fig.(2.2). Fig.(2.2) includes also the radii of bubbles at thermal equilibrium (eq.(2.5)) corresponding to these pressures in Cu ($\gamma = 1.67 \text{ J/m}^2$). According to fig.(2.2) linear relationship between density and pressure, i.e. ideal gas behaviour, can be obtained for densities below about $5 \cdot 10^{-3} \text{ \AA}^{-3}$, corresponding to bubble radii (upper abscissa of fig.(2.2)) larger than $10^3 \text{ \AA}$. It can further be seen from

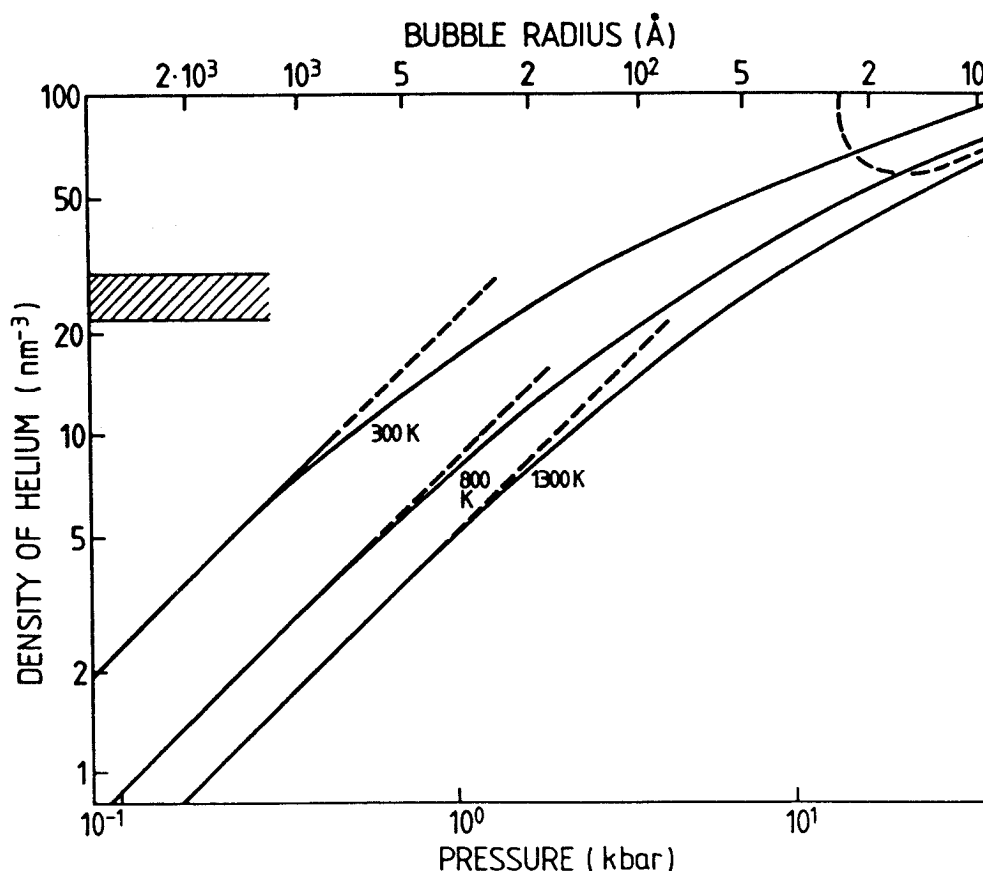


Fig.(2.2): Pressure density relationship at different temperatures according to an EOS for "superdense" helium. Ideal gas behaviour is predicted up to densities of $5 \cdot 10^{-3} \text{ \AA}^{-3}$ only. The hatched area indicates liquid helium densities. For more details see text.

fig.(2.2) that using the ideal gas law (dashed lines) would lead to severe overestimation of the density of helium in bubbles of radius below $100 \text{ \AA}$, as typically observed in metals.

The hatched area of fig.(2.2) corresponds to liquid helium densities at low temperatures between saturated liquid at 4.2 K , $n = 0.022 \text{ \AA}^{-3}$ and melting at 1.76 K , $n = 0.027 \text{ \AA}^{-3}$. Thus, according to fig.(2.2), liquid helium is expected to appear in bubbles of radius ca. $40 \text{ \AA}$, assuming they are at thermal equilibrium at $T = 10^3 \text{ K}$. Finally, the area enclosed by the dashed line on the upper right side of fig.(2.2) shows roughly the density-regime covered by experimental investigations described briefly in section 2.3.1.

3. ON THE PROPERTIES OF FINITE HELIUM SPECIMENS AT LOW TEMPERATURES.

In our introduction we have already mentioned that the low temperature properties of liquid helium appear considerably modified when small enough specimens are involved.

In the following section of this chapter we discuss briefly the geometries which have been used up to date to form and investigate finite helium specimens. This will help in understanding the differences between formerly used geometries and the new geometry of spherical helium bubbles which has been used in our investigations. To form a basis for interpretation of our observations we will proceed by discussing theoretical approaches developed for the description of finite size effects.

3.1. Confining geometries.

The modifications of the low temperature properties of liquid helium specimens having at least one dimension smaller than about $10^3 \text{ \AA}$ are known as "finite geometry effects" or simply "size effects". The formation of finite helium specimens employs substrates of different regularity and complexity. To first approximation their function is only to limit the spatial extension of the specimens, providing to the experimentalist the possibility to form and investigate an ensemble of small subsystems with typical dimensions of the order of a few tens of $\text{\AA}$ and lower.

Plane substrates and highly porous materials have been used as confining geometries. Taking as criterion the dimensionality of specimens formed in these confining geometries they can be ordered and presented as follows:

- a) Helium films on smooth or rough substrates (two dimensional).
- b) Helium in the pores of vycor glass or polycarbonate membranes (nuclepore filters). These substrates consist of cylindrical channels of infinite length (one dimensional). The case of vycor glass is somewhat "pathologic" (see below).
- b) Helium in the intergranular space of fine powders (zero dimensional).

Although investigations of the behaviour of confined helium have been performed also at temperatures far below 2 K /21/, investigations of the superfluid transition were and continue to be of central interest.

Various properties of confined helium around its transition to the superfluid state have been experimentally investigated in all the mentioned confining geometries. The main experimental results are qualitatively sufficiently well understood. They include the displacement of the λ -line (melting line) of confined helium to lower temperatures (higher pressures), respectively. This is shown qualitatively in fig.(3.1), dashed lines, for a constant (but arbitrary)-confining dimension. Fig.(3.1) includes for comparison the phase diagram of bulk helium (solid lines).

Quantitative interpretations of experimental data and comparisons with theoretical predictions (see section 3.2) are however scarce. The main reason for that is the difficulty to obtain a simple, regular and sufficiently well known confining geometry. A direct consequence of irregularity of the available confining geometries is the formation of inhomogeneous helium specimens which do not always reveal the true behaviour of confined helium.

Thus, for helium films difficulties arise from surface irregularities, from capillary condensation /22/ and possibly droplet formation /23/ which limit the regime of thicknesses of homogeneous films

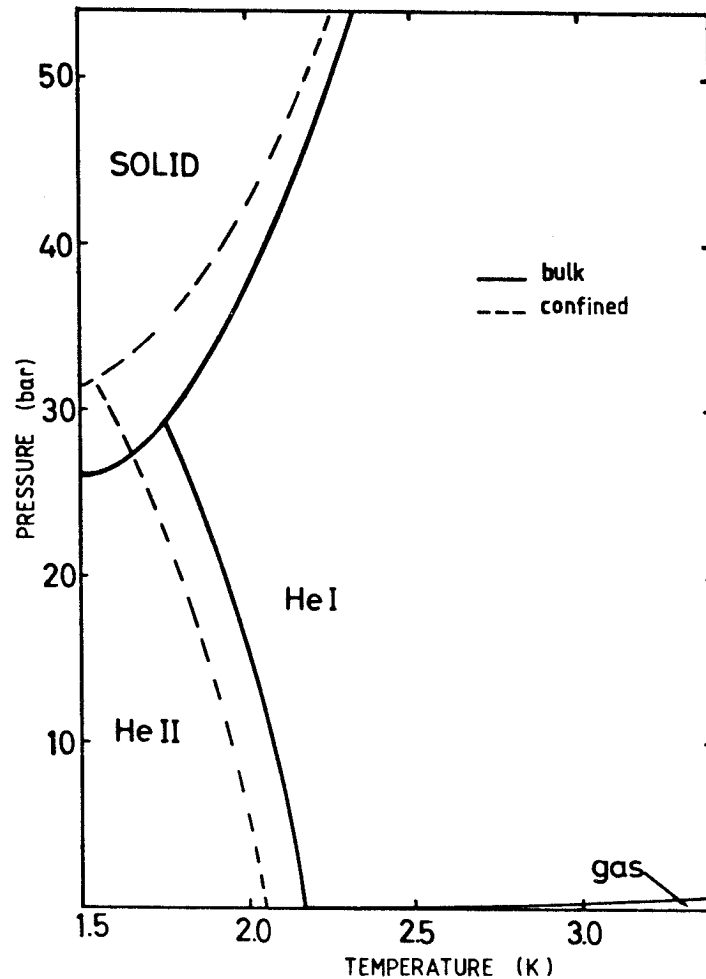


Fig.(3.1): Phase diagram of bulk (solid lines) and confined helium (dashed lines). The phase diagram of confined helium is shown qualitatively.

which can be obtained on real substrates.

With helium-filled pores the main problems are the irregularity of the pores and the complexity of the confining geometries. Both together make it often impossible to obtain detailed information on the size of the pores.

But the major disadvantage in this case might be the connectivity of the pores with each other. This can be clearly demonstrated in the case of vycor glass. The geometry of vycor glass is modeled as cylindrical channels with $70 \text{ \AA}$ diameter and is on the average

well known. It is a complex structure of interconnected channels forming a network in three dimensions. The multiple connectivity of vycor channels is reflected on the properties of helium confined in it as an apparent reduction of the effectivity of the confinement. Despite the $70 \text{ \AA}$ channels the behaviour of helium in vycor is three dimensional !!!

The geometry of nuclepore filters with channel radii above $150 \text{ \AA}$ is probably considerably more homogeneous and enabled quantitative information on the behaviour of confined helium in two dimensions /24/.

Independent of the particular confining geometry used, it is obvious that since one intends to study properties of helium depending on a characteristic dimension of the specimen (confining size), a very important step for correct interpretation of experimental data is the investigation of the confining size and geometry itself. Investigations in the past employed almost exclusively absorption techniques in combination with model assumptions to obtain an average effective confining dimension. The reliability of this procedure has been recently questioned even in the case of helium film studies /25/.

The need for a regular, considerably better known and zero dimensional confining geometry has been recognized early and emphasized several times in the past. According to /26/ "... a sort of dense aerosol spray of helium droplets about $100 \text{ \AA}$ in diameter would be ideal for some experiments". Such a confining geometry has been realised in the experiments discussed in chapter 5. of this work.

3.2. Theoretical considerations.

The description of finite size effects has been developed by modifying theoretical treatments of bulk superfluid helium. Therefore in order to describe finite size effects it is necessary to introduce briefly the corresponding description of the bulk liquid.

As in bulk helium, there are two temperature regions of principal interest for the behaviour of confined helium. The low temperature region, i.e. $T \lesssim 1.6$ K, and the region around the transition to the superfluid state. In the low temperature region the theory of elementary excitations can be used for the description of finite size effects /27/. In the neighborhood of the transition to the superfluid state, which is of our interest, concepts developed within the theory of critical phenomena can be tested in a precise way with the help of confined helium.

3.2.1. The Ginzburg-Pitaevskii-Mamaladze description.

This phenomenological approach /28/ is based on the Landau theory of second order phase transitions as it has been modified to be applicable for bulk superfluid helium. It is developed on the assumption that the free energy density of liquid helium around the transition can be expanded in powers of a macroscopic order parameter, $\Psi(r,T)$, which has been related to the particle density, n_s , of the ordered state (He II) as:

$$n_s = |\Psi(r,T)|^2 \quad (3.1)$$

In this treatment the order parameter satisfies at equilibrium a nonlinear differential equation which under certain assumptions can

be written as

$$\{h^2/2ma(T)\} \nabla^2 \Psi + a(T) \Psi - b(T) |\Psi|^2 \Psi = 0 \quad (3.2)$$

where: h = reduced Planck's constant, m = mass of the helium atom
and /29/: $a(T) = a_0(T_\lambda - T)^{4/3}$; $b(T) = b_0(T_\lambda - T)^{2/3}$ (3.3)

with a_0 , b_0 in general functions of the pressure.

Using these expressions one obtains for the coherence length, $\xi(T)$, which is the characteristic length of variation of the order parameter in eq.(3.2)

$$\xi(T) = \{h^2/2ma(T)\}^{1/2} = \xi_0 \{(T_\lambda - T)/T_\lambda\}^{-2/3} \quad (3.4)$$

with $\xi_0 = 2.8 \text{ \AA}$.

The solution of eq.(3.2) for bulk helium is straightforward and the superfluid density, n_s , can be written:

$$n_s = (a_0/b_0)(T_\lambda - T)^{2/3} \quad (3.5).$$

Turning now to the behaviour of helium confined in a small volume, with smallest dimension d , it can be expected that at the transition temperature, $T_\lambda(d)$, it will be:

$$\xi(T = T_\lambda(d)) \sim d \quad (3.6)$$

and therefore, on the basis of this rather crude argument, the dependence of the displacement of the superfluid transition, $\Delta T_\lambda(d)$, upon the size d , can be deduced with the help of eq.(3.4) above. One finds:

$$\Delta T_\lambda(d) = T_\lambda(\infty) - T_\lambda(d) = c d^{-3/2} \quad (3.7)$$

The constant c in the above expression is expected to depend on the details of the confining geometry and can be found by solving eq.(3.2) with appropriate boundary conditions. At the confining

walls where superfluidity vanishes one has $\Psi = 0$, (while a second boundary condition can be deduced from symmetry considerations). The condition $\Psi = 0$ at the walls can imply the existence of another length which is related to the order parameter. In simple terms, this "healing length" is a temperature dependent distance measuring how far from the walls the order parameter is influenced by them. According to the present understanding, the healing length must be proportional to the coherence length, and the proportionality constant be of order unity. For this reason we will not distinguish between them any more.

Given a solution $\Psi(r, T)$ of the problem (i.e. eq.(3.2)+boundary conditions) several thermodynamic properties of confined helium can be obtained. An analytical solution has been given for the plane-parallel-wall geometry (i.e. for example helium films) in terms of elliptic integrals /30/. A numerical evaluation of the average superfluid fraction of helium in cylindrical channels of infinite length has been also obtained /31/. In terms of these solutions the constant c in eq.(3.7) has been found to be:

$$c^2 = 0.89 \cdot 10^{-11} \text{ cm}^{3/2} \text{ K for films, (conf. dimension: } d^2 = \text{thickness}/2)$$

$$c^1 = 1.69 \cdot 10^{-11} \text{ cm}^{3/2} \text{ K for cylinders, (conf. dimension: } d^1 = \text{radius}).$$

Both solutions predict also that the fraction of helium participating in superfluidity in these systems, at a given temperature, depends on the confining dimension and is smaller than the corresponding bulk fraction. This behaviour is qualitatively shown in fig.(3.2) for two sizes d_1 and d_2 .

Further, the ratio of the average superfluid density of helium confined in the parallel wall geometry, to the superfluid density in the bulk, can be obtained from the analytical solution to vary

inversely proportional to the confining dimension, d , at large d /32/.

The same dependence can be found in terms of simple but somewhat crude arguments for other geometries.

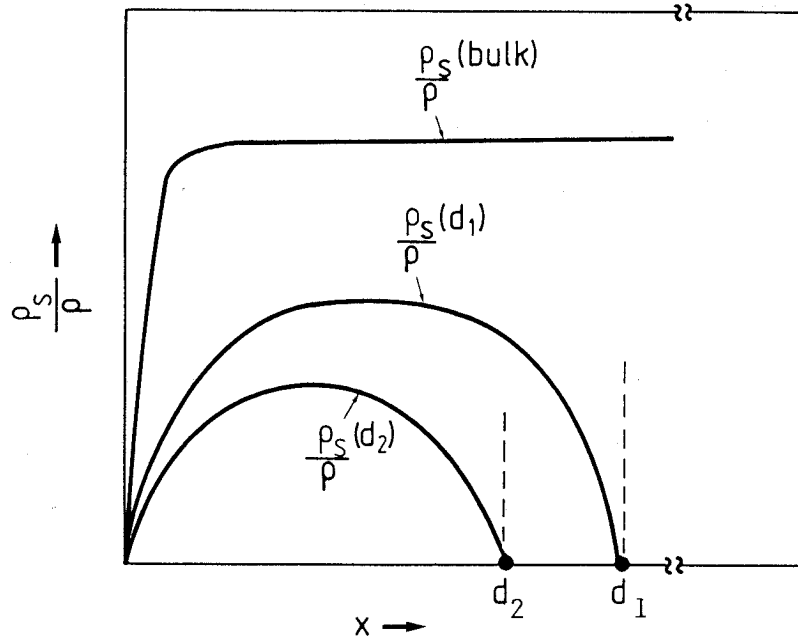


Fig.(3.2): Depression of the superfluid density below the bulk value for two confining sizes d_1 and d_2 ($d_1 > d_2$). The superfluid density is plotted as function of the distance from the confining walls.

For a spherical pore or a helium drop with radius R , it has been predicted /33/:

$$\Delta T_\lambda(R) = 2.53 \cdot 10^{-11} R^{-3/2} \text{ cm}^{3/2} \text{ K} \quad (3.7 \text{ a})$$

We have obtained the same expression by solving the linearized problem. It is satisfactory because the cubic term in eq.(3.2) is negligible close to the transition point. We should however remark that to obtain the temperature dependence of the superfluid frac-

tion, solution of the exact problem is necessary. To our knowledge such a solution is not available.

3.2.2. Critical behaviour of confined helium.

The superfluid transition of bulk helium has been used to test (and verify !) several predictions of the scaling theory of critical phenomena. The thermodynamic behaviour of helium near the transition to the superfluid state can be interpreted in terms of the critical behaviour near a continuous phase transition.

The central postulate in the theory of critical phenomena is the belief in the existence of an intrinsic temperature dependent length which determines the range of correlation of fluctuations of the order parameter and diverges at the transition in a characteristic manner. This correlation length, ξ , is not measurable in the case of liquid helium. It is usually written as:

$$\xi = \xi_0 t^{-\zeta}, \quad \text{with } t = 1 - T/T_\lambda \quad (3.8)$$

and $\xi_0 = 3 \text{ \AA}$.

The critical exponent ζ can be obtained by combining the scaling relationship $\nu = \zeta / 34$ with /35/:

$$\sigma \nu = 2 - \alpha$$

where $\sigma = 3$ is the dimensionality of the system and $\alpha = -0.020$ /36/ is the critical exponent for the growth of the specific heat in the very neighborhood of the transition, i.e.

$$C = \frac{A(P)}{\alpha} (t^{-\alpha} - 1) + B; \quad B = \text{const.} \quad (3.9)$$

For a finite helium specimen confined in a volume with smallest dimension d the correlation length cannot grow larger than d and

therefore the critical behaviour is modified. Extension of scaling arguments to finite size systems /37/ predict an altered behaviour.

It is expected, for instance, that the sharp peak of the specific heat of bulk helium at T_λ will be replaced by a rounded maximum at a temperature T_m lower than T_λ . The reduced shift in the transition temperature, $t_o = 1 - T_m/T_\lambda$, should be related to the confining dimension d as:

$$d = b t_o^{-1/\Lambda} \quad (3.10)$$

where $b = \text{const.}$ depending on the geometry.

The extent of rounding of the specific heat (i.e. the temperature region in which appreciable deviation from bulk behaviour can be seen) should also be varying with an exponent θ according to the relationship

$$d = e (\delta T/T_\lambda)^{-1/\theta}, \quad e = \text{const.} \quad (3.11).$$

Further, the maximum value reached by the specific heat, $C_{\max}$, should grow toward its magnitude in the bulk as

$$C_{\max} = A(P) \theta (1+\alpha) \ln d \quad (3.12)$$

where $A(P)$ is the amplitude of the dominant temperature dependent term of the specific heat in the bulk (see eq.(3.9)). Eq.(3.12) is exact in the limit $\alpha = 0$, that is, the specific heat in the bulk diverges logarithmically.

The new exponents Λ and θ which have been introduced for the description of the displacement of the superfluid transition and the growth of the specific heat of confined helium can be related to the correlation length exponent in the bulk by

$$\zeta = 1/\Lambda = 1/\theta \quad (3.13)$$

provided that the correlation length of confined helium is the proper scaling length and provided it has the same temperature dependence as in the bulk. Equation (3.13) is the final result to be

verified or disputed by experimental investigations. Higher order corrections to eq.(3.10) and eq.(3.12) have been also suggested /38/. It should be mentioned that in this description the contribution of surfaces is neglected. Further, eq.(3.10)-(3.12) hold for a particular temperature at which the transition to the superfluid state takes place.

Another very important prediction of the theory of critical phenomena concerns the influence of the pressure on the superfluid transition and is known as universality concept /39/. It can be formulated as follows: Near to the critical point, the correlation length of superfluidity, ξ , becomes much larger than interatomic distances. On the other hand, the asymptotic variation of thermodynamic properties near to the transition is expected to be dominated by fluctuations of typical size ξ . Therefore, the parameters characterising the transition should be determined by general properties of the system such as its dimensionality and the symmetry of the order parameter for the transition, i.e., they should be independent of the microscopic interactions.

According to the universality concept, the critical indices of the superfluid transition should not change by application of pressure. This statement has been verified for bulk helium by several experimental investigations /40/. The same statement can be also tested for confined helium specimens. This could be done with the help of eq.(3.10) and eq.(3.12) with t_0 similarly defined and by taking into account that $A = A(P)$ in eq.(3.12). At present there is only one experimental investigation /41/ which showed the validity of the universality concept for confined helium up to confining dimensions of $10^3 \text{ \AA}$.

4. EXPERIMENTAL.

4.1. Specimen preparation.

Pure Cu (ASARCO, 5N) has been chosen to be implanted since it is one of the metals which have small low temperature heat capacity. The specimens were discs with dimensions $7 \text{ mm } \varnothing \times \approx 100 \text{ } \mu\text{m}$, prepared from solution annealed foils and have been cut by spark erosion. They have been annealed at $T = 1100 \text{ K}$ for 2 h and subsequently implanted at $T = 300 \text{ K}$ with α -particles in the small cyclotron of the Kernforschungsanlage Jülich.

The apparatus used for these implantations is shown schematically in fig.(4.1). Aperture, beam stopper, energy degrader and specimen holder were the main parts of the implantation chamber which could be separated from the main vacuum of the cyclotron by a high vacuum valve. Each of these parts was electrically isolated from each other. Preparations and a typical implantation proceeded

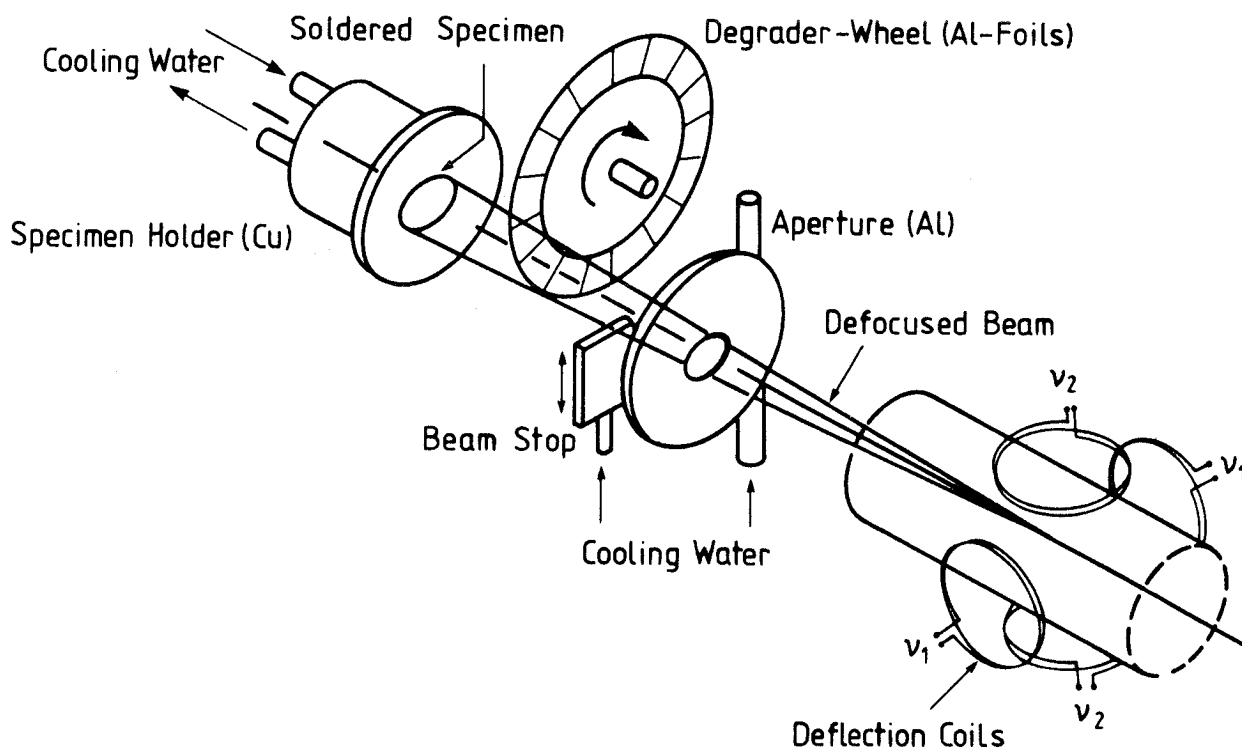


Fig.(4.1): The implantation apparatus (schematically shown).

as follows:

a) A specimen was soldered to the specimen holder (a massive Cu block) with indium, taking care to center it properly. The specimen holder was attached to the implantation chamber which was then be evacuated.

b) In order to avoid a substantial increase of the temperature of the specimen during implantation, the specimen holder (as well as beam stopper and aperture) were cooled continuously by circulating water.

c) Before the implantation started the vacuum of the implantation chamber was improved to 10^{-5} torr by pumping from the cyclotron side and the α -particle beam of energy 28 MeV was prepared. The beam was passed through the aperture (whose diameter was equal to that of the specimen) and maximized on the beam stopper. Lateral beam homogeneity was achieved by wobbling the beam in two perpendicular directions at a frequency of 100 Hz with the help of the deflection coils of fig.(4.1). Their excitation voltage was adjusted while observing the variation of the beam current on the beam stopper. After these adjustments the beam stopper could be opened allowing the beam to reach the specimen.

d) In order to achieve a homogeneous deposition of α -particles along the thickness of the specimen an energy degrader (see fig.4.1) was used to reduce the energy of the beam from its maximum to zero in 24 steps. It is made of Al foils (mounted along the circumference of a rotating wheel, see fig.4.1) of properly chosen thickness so that the average of the 24 individual deposition profiles be constant along the thickness of the specimen.

e) The implanted amount of helium was determined by integrating the beam current as it was measured on the specimen. Corrections for beam-broadening effects (introduced by the energy degrader)

and for secondary electron emission have not been applied, i.e. the "nominal" helium concentration is higher than the actually implanted concentration (see also 5.3).

After the implantation, the rest of indium and a few μm of Cu have been removed from the back surface of the specimens by standard metallurgical polishing.

In this way, two pairs of specimens have been implanted, one pair with 1200 appm and the second pair with 2600 appm helium/Cu. One member of each pair has been used for heat capacity measurements, while the second one was cut into 3 mm $\varnothing$ discs and used for TEM investigations.

The energy range of the available α -particles in Cu limited the thickness of our specimens, while the maximum permissible implantation rate (≈ 100 appm/h) lengthened appreciably the implantation time.

After the implantation our specimens have undergone an extensive annealing program at high temperatures: They have been annealed in a quartz tube which has been used exclusively for Cu. A turbomolecular pump provided vacuum conditions of $5 \cdot 10^{-7}$ mbar at the annealing temperature. The temperature of the furnace could be kept constant within ± 2 K and the overall temperature uncertainty should not be larger than ± 5 K. At the end of the annealing the quartz tube was cooled by air. In a few minutes its temperature decreased to below 400 K.

Both, calorimetry and microscopy specimens were annealed simultaneously.

4.2. Low temperature calorimetry.

The specimens prepared for our investigations were small in size, ca.30 mg, and had small low temperature heat capacity. In order to measure it with sufficient accuracy it was therefore necessary to modify a heat capacity apparatus and construct a specimen holder appropriate for small-specimen calorimetry.

4.2.1. The heat capacity apparatus.

The heat capacity apparatus used in this work has been described in detail elsewhere [42]. Our short description here will be limited to those parts of the apparatus which are essential in understanding its operation. A block diagram of the apparatus and its electronics is shown in fig.(4.2).

The heart of the apparatus is a Cu isothermal shield enclosing completely the space where the specimen holder can be mounted. It is made of high conductivity Cu (9 mole) in order to ensure isothermal conditions. Its temperature is close to the temperature of the specimen and protects the specimen from radiation. The isothermal shield together with the specimen holder constitute a typical low-temperature calorimeter.

A bifilar heater (manganin 0.1 mm $\varnothing$) and a temperature sensor (Allen Bradley 650 Ω) are properly attached on the isothermal shield enabling precise stabilisation of its temperature above the temperature of the liquid helium bath. The isothermal shield is fixed with four stainless steel rods on the top platform of a vacuum container which in turn is immersed into the helium bath in a conventional glass dewar. Thermal contact between ^4He bath and isothermal shield is provided by a bellow-type heat switch which is activated with pressurised helium gas.

For the measurement of the temperature of the isothermal shield a calibrated Ge resistor or a Pt resistor were used. Both were mounted on the isothermal shield in the following way: They have been wrapped in Au foils, a grease (Apiezon N) was added and then enclosed in properly machined Cu cages which were directly screwed to the isothermal shield.

All electrical leads (manganin 0.1 mm $\varnothing$) were thermally anchored once to the ^4He bath temperature and a second time on the isothermal shield. Each thermal anchoring involved several meters of wire wound on short Cu rods (5 mm $\varnothing$) and attached to it with GE varnish. The leads were also separated to "high" and "low" -current leads and were running down to the low temperature part of the apparatus in separate evacuated tubes in order to avoid cross-talk between them. Outside of the cryostat Lemo-coaxial cables were used

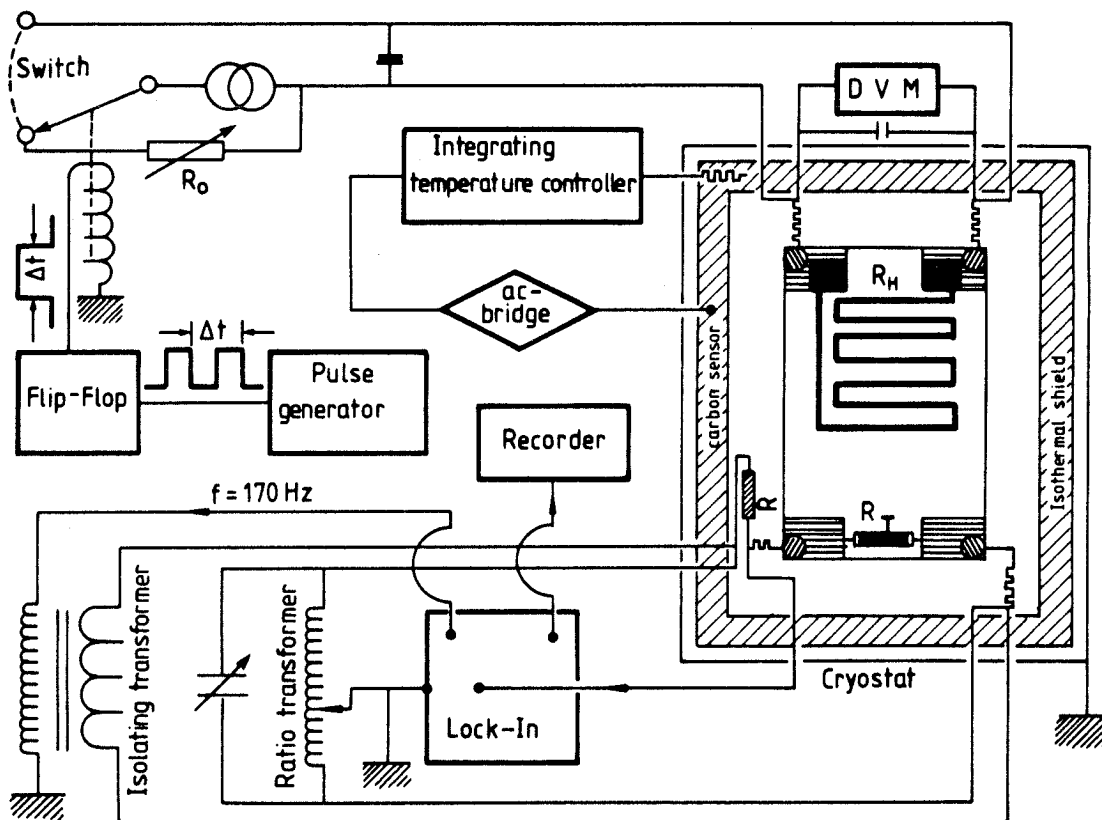


Fig.(4.2): The heat capacity apparatus (schematic drawing). For details see text.

and their shields were grounded together with the cryostat itself. Care has been also taken to protect the cryostat from mechanical vibrations induced through the pumping lines.

4.2.2. The calorimeter.

In the construction of a specimen holder appropriate for the measurement of the low temperature heat capacity of small specimens the following experimental requirements have to be taken into account:

- i) The heat capacity of the holder has to be kept as small as possible since it has to be subtracted from the measured heat capacity in order to obtain the heat capacity of the specimen. Thus, proper choice of materials and reduction of its size are desirable. Miniaturisation of the specimen holder is however practically limited by constructional and handling difficulties for hand-made specimen holders.
- ii) The materials chosen should be good thermal conductors at low temperatures. Moreover, sufficiently good thermal coupling between different parts of the specimen holder i.e. substrate, heater, thermometer and specimen is of importance.
- iii) Apart from good thermal properties and the requirement to have a sensitive thermometer a specimen holder should permit direct determination of its heat capacity and facilitate easy change of specimens.

Considering these requirements we proceed in the construction of our specimen holder as follows: We have used a small synthetic sapphire platform with dimensions of $12 \times 8 \times 0.08 \text{ mm}^3$ as substrate material /43/. Sapphire has been chosen because of its unique combination of small specific heat ($\Theta_D = 600 \text{ K}$ /44/) and high thermal conductivity (comparable to that of high purity Cu) at low

temperatures. Sapphire is also superior to metallic platforms since it is an almost undeformable and electrically insulating material.

Thin Au films were vacuum-deposited at the sapphire corners in order to provide oxide-free electrical contacts to the heater and an additional heat flow path to the thermometer. In our experience, metallic films stick considerably better on rough substrate surfaces. The surfaces of our sapphire were therefore not polished but roughened.

As heater a constantan film of meander shape with a few μm thickness has been evaporated onto the sapphire platform with the help of a Cu mask and with its ends overlapping the Au contacts. After a heat treatment at 900 K for 30 min the resistance of the constantan film was stable and high ($\approx 2.5 \text{ K } \Omega$) as required. The same heat treatment improved the sticking of the predeposited Au films.

For the construction of a small and sensitive thermometer for the measurement of the temperature of the specimen holder a carbon resistor (Allen Bradley 51Ω) has been selected. To reduce its heat capacity we removed its isolation by grinding the resistor carefully on an abrasive paper. The naked carbon element has been further machined into a parallelepiped with approximate dimensions of $0.2 \times 0.2 \times 3 \text{ mm}^3$ whose resistance was 300 at room temperature. Next, we deposited electrolytically a $15 \mu\text{m}$ Au film on the cross-sectional surfaces of the carbon element in a "Technigold 25" bath at 60°C . Au-plated $30 \mu\text{m } \varnothing$ Cu wires were then contacted to the cross sectional surfaces of the carbon element under a light microscope. As contacting material we used a silver epoxy (EPO-TEK 417 /45/). With some experience the mass of the silver epoxy could be kept small, ca. 0.1 mg per contact. The thermometer was then glued onto the sapphire platform by using a two-component thermally conducting epoxy containing Al_2O_3 powder (EPO-TEK 421 FL /45/).

It has been cured at 50°C for about 6 h. Contacting of the heater and carbon thermometer has been then completed by attaching to them and to the sapphire platform 3 mm long Cu wires, 30 μm $\varnothing$.

In this step by step procedure, sapphire platform and carbon thermometer have been weighted before and after each assembling stage. The total mass of the complete specimen holder was 31.5 mg and consisted of: 29.8 mg sapphire, 0.6 mg carbon, 0.4 mg Copper, 0.4 mg silver epoxy (EPO-TEK 417), 0.1 mg EPO-TEK 421 FL, and 0.1 mg Au.

In preliminary experiments our specimen holder was linked to the isothermal shield by means of various geometric arrangements and materials. We exploited the possibility to use 15 μm $\varnothing$ superconducting monofilaments ($T_c = 8.5$ K) prepared from a commercial NbTi superconducting wire. The Cu matrix of the wire had been removed by etching in HNO_3 except for short pieces at both ends to provide electrical contacts. All filaments but one were then cut and removed as carefully as possible. The specimen holder was supported in these runs in a similar way as that shown in fig.(4.3).

Sufficiently long thermal relaxation times of the calorimeter could be achieved in this way but only a poor reproducibility of heat capacity data could be obtained. This behaviour is not understood in detail. Irreproducibility of the data might have been caused by the fact that parts of the linking wires became resistive during application of heat pulses to the specimen holder and falsified our measurements.

By comparing thermal conductivity and specific heat data of suitable normal-conducting metallic alloys which have been used in sensitive low temperature calorimeters we found a Pt92%-W8% alloy to be most favorable for our purpose. This alloy has been used for

calorimetric investigations at temperatures below 1 K /46/, and it turns out that it fulfils our requirements also above 1 K, having smaller thermal conductivity and specific heat than constantan, manganin and NiCr alloys /47/.

The mounting shown in fig.(4.3) has been chosen and used throughout this work. In this arrangement the specimen holder is supported by four Pt-W wires, twisted in springs, with a thickness

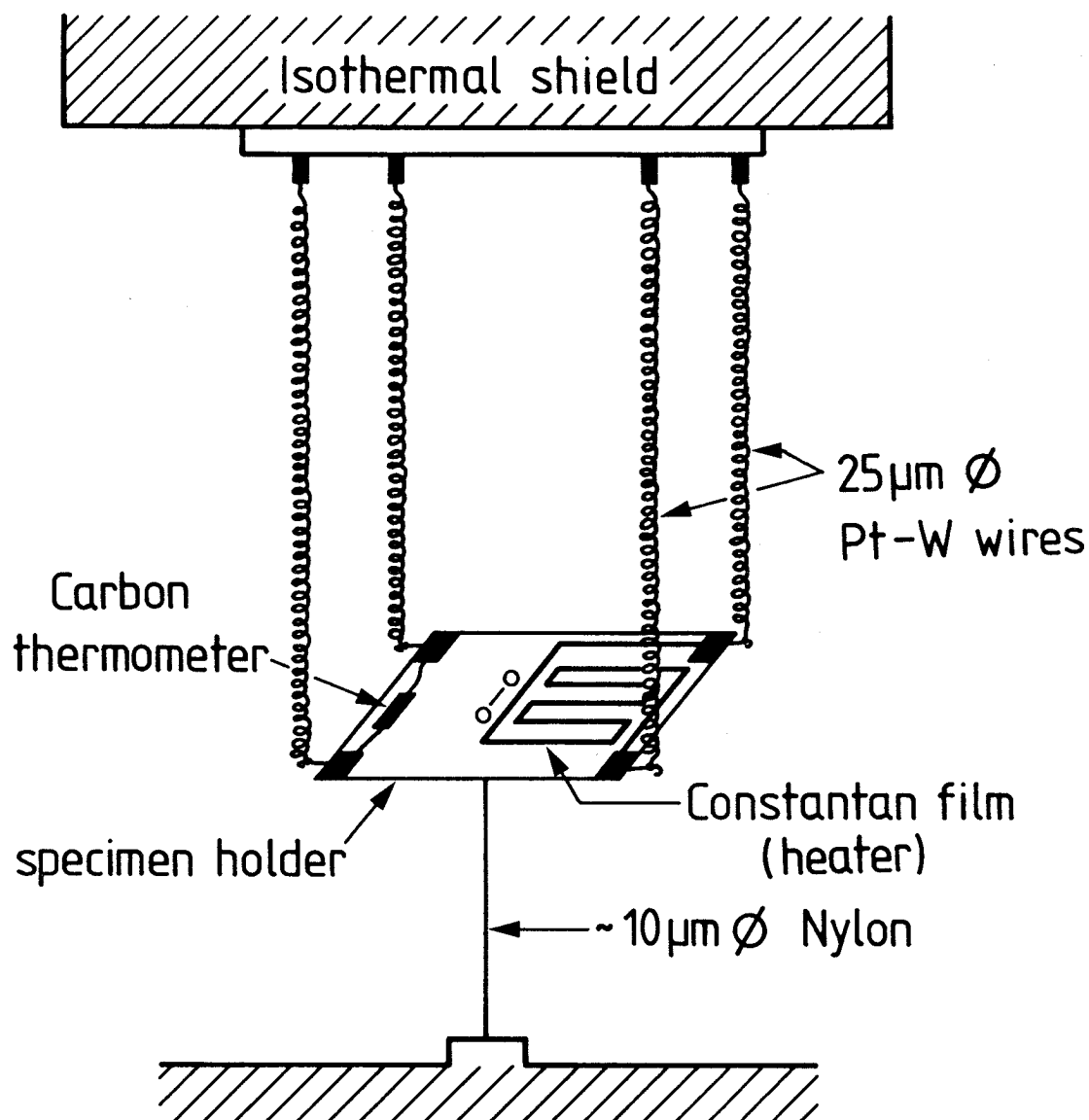


Fig.(4.3): Attachement of the specimen holder to the isothermal shield. The specimen holder is supported by four 25 μm $\varnothing$ Pt-W wires which provide also electrical and thermal linking.

of 25 μm $\emptyset$ and a length of 14 cm each. (The insulation of the Pt-W wires had been removed in formic acid).

They provide mechanical support and thermal linking of the specimen holder as well as electrical connection to the heater and thermometer. For additional mechanical support we attached a Nylon thread ($\approx 10 \mu\text{m}$ $\emptyset$) to the specimen holder and to the bottom of the isothermal shield. We have selected the four-lead arrangement of fig.(4.3) as offering the smallest possible heat leak and addenda enhancement without introducing further uncertainty to the heat capacity data. In this way the thermal isolation of our specimen holder was sufficient to provide us almost adiabatic conditions (see, for example fig.(4.4)). We could therefore measure the heat capacity of our 30 mg Cu specimens with the classical adiabatic technique, (see section 4.2.2).

Our specimens have been attached to the specimen holder with a grease, namely Apiezon N. Sufficiently good thermal contacts could be obtained by warming slightly the specimen holder after a specimen has been attached to it. Similarly, warming was necessary for the removal of the specimens without damaging the specimen holder.

Precise knowledge of the mass of grease was necessary since the heat capacity of a mg Apiezon N is comparable to that of our Cu specimens at around 4 K. We have explored the possibility for something better. However it seems that the specific heat of other suitable greases, e.g. silicon oil, Wakefield thermal compound etc. /48/, is larger or comparable to that of Apiezon N below about 10 K. We have therefore used Apiezon N and kept its mass less than 1 mg in all our experiments.

The calorimeter has been kept in vacuum except during changing

specimens (≈ 15 min). Cooling of the apparatus started after it had been evacuated at room temperature to 10^{-6} torr and proceeded without any exchange gas. The specimen holder followed the temperature of the isothermal shield with a time delay of 10 h. After both of them were at 4.2 K the cryostat was refilled with liquid helium and by pumping the helium bath the lowest temperature of 1.4 K could be reached in a few hours.

This cooling procedure, i.e. without exchange gas, resulted in quite long cooling times (≈ 60 h). It has been selected because:

- a) Even small amounts of absorbed exchange gas on the specimen holder could have erroneously influenced our heat capacity data.
- b) According to our experience reevacuation of the apparatus at low temperatures was insufficient within reasonable times.

Exchange gas, 10^{-3} torr of ^3He , has been admitted to the vacuum space of the apparatus in several runs for check purposes (temperature scale etc.) after the heat capacity data were taken.

4.2.3. Thermometry.

a) Standard thermometer.

The principal temperature scale for our measurements was provided by an encapsulated CR 2500 H Ge-resistor, calibrated by Cryo Cal Inc, Florida USA.

Its resistance was measured with the four point technique with a measuring current of 1.00 ± 0.01 μA . Its calibration curve has been repeatedly checked during the experiments by comparing it to the vapor pressure scale of ^4He (T_{58}) between 4.2 K and 1.8 K. During such a check ^3He gas has been admitted to the vacuum space of the apparatus to ensure for thermal equilibrium with the helium bath. The vapor pressure of ^4He was measured with a capacitive mano-

meter and steady state conditions were allowed to establish themselves after the pumping speed was regulated.

Small, random deviations have been observed, however lying always within those quoted by the supplier. This, together with the perfect reproducibility of the Ge-resistance upon thermal cycling provided confidence for the reliability of the supplier's calibration curve which has been used for the evaluation of our heat capacity data. It has been extended by us to 1.3 K, by using a polynomial representation given in the manual of the thermometer.

b) Secondary (carbon) thermometer.

The resistance of the carbon thermometer was measured with a home-made 5-lead resistance bridge /36/ operating at 170 Hz. As zero detector we have used a sensitive lock-in amplifier (PAR, 124 A) which also excited the bridge through an isolation transformer (PAR, AM 1). The resistance of the thermometer, R_T , was obtained by comparing it to a reference resistor, whose resistance ($R_{ref.} = 600 \Omega$) was temperature independent below 40 K. The bridge was balanced with a 7-digit decade ratio transformer (DEKATRAN DT72 A, ESI). Phase adjustment between the driving and reference signal of the lock-in amplifier was performed with a variable capacitor (General radio 1412-BC). Finally, the time variation of R_T was monitored with a chart-paper recorder (HP 7100B).

To calibrate the carbon thermometer, the temperature of the isothermal shield was stabilised at, say T , and thermal equilibrium was allowed to establish. In order to shorten the equilibration time we have usually carefully heated the colder part, and waited until thermal shifts disappeared at maximum lock-in amplifier sensitivity. Phase adjustment between the driving and reference signals of the bridge was then applied. At balance the resistance of the thermome-

ter was given by:

$$R_T = R_{\text{ref.}} s / (1-s) \quad (4.1)$$

with s the "bridge ratio" read on the ratio transformer.

After a set of pairs (R_T, T) scanning the whole temperature range of interest were obtained they have been fitted to a polynomial of the form

$$T^{-1} = \sum_{k=1}^{k=N} a_k (\log R_T - A)^k \quad \text{with } N \leq 6. \quad (4.2)$$

For the constant A ($\log R_T$ at high temperatures) the value 2.9 was used. Statistical deviations between the fitted temperature, T_f , and the measured temperature, T , were typically of the order of a few tenths of a percent. A new calibration curve has been taken for the carbon thermometer in each run and its reproducibility has been checked in several runs with the help of ^3He exchange gas. Calibrations of the same run were perfectly reproducible, while those of different runs deviated from each other at most by a few per cent.

In order to eliminate overheating of the specimen holder and thermometer and therefore be sure for the reliability of our secondary temperature scale we selected the power for the operation of the carbon thermometer as follows: The steady state resistance of the carbon thermometer has been plotted as a function of power dissipated in it at constant isothermal shield temperature and this procedure was repeated at several temperatures. In this way the maximum permissible power could be determined as function of temperature. The power for the operation of the thermometer, about 1 pW, has been chosen as a compromise between temperature resolution and overheating. The maximum overheating of the specimen holder did not exceed 5 mK.

The main noise introduced to the apparatus was electrical. Its most annoying component was a high frequency signal (10 MHz)

which had a characteristic time dependence (radio station?) becoming seriously large in the night. It could introduce a few percent scattering of the heat capacity data. For this reason measurements were avoided when it was present.

Further, although all electronic devices were plugged into the output of a voltage stabiliser (not shown in fig.(4.2), the calorimeter was also responding to electrical sparks produced when several apparatuses were switched on in the laboratory.

Finally, a few mK heating of the specimen holder was also systematically observed during refilling the cryostat with liquid helium. It might have been caused by mechanical vibrations.

The influence of all those kinds of noise could be minimized by waiting for the calorimeter to relax to its equilibrium temperature. They had only the effect of lengthening the measuring time. Under normal conditions (typical noise is shown in fig.(4.4) the temperature scale could be reproduced within 0.5% and a long-time temperature stability as high as 0.1% could be routinely obtained.

4.2.4. Measurement and evaluation of the heat capacity.

As already mentioned in section 4.2.2., we have measured the heat capacity of our specimens with the adiabatic heat pulse technique, i.e., the temperature of the specimen holder before (T_i) and after (T_f) the application of a heat pulse of energy Q_0 was accurately measured and the total heat capacity, C_t , was obtained from the well known expression

$$C_t(T_i+T_f/2) = Q_0/(T_f-T_i) \quad (4.3)$$

which is accurate provided that $T_f-T_i \ll T_i$.

To apply a heat pulse, a constant current, I , was applied to the specimen holder heating resistance, $R_H = 2450 \Omega$, for a known time

interval, t_h , and the voltage drop, U , was measured with the 4-point technique as indicated in fig.(4.2). The current was provided by a precision current source (Knick J 41) and the voltage was measured with a sensitive integrating microvoltmeter (Doric DS 100). An inductive switch was used to switch the current from a dummy load resistor, R_o , ($R_o = R_H$) to R_H . The pulse length was preset on a pulse generator which was operating the inductive switch. To avoid pick-up signals the current source and the voltmeter were short-circuited with small capacitors.

The energy of the heat pulse, $Q_o = I U t_h$, includes a small amount of heat, Q' , developed in the wires linking R_H to the isothermal shield. Approximately 1/2 of Q' ($= I^2 R_L t_h$), ($R_L = 325 \Omega$, the resistance of the linking wires), escapes directly to the isothermal shield and has to be subtracted from Q_o . To take into account this heat loss, a multiplicative correction factor, f , for the energy of the heat pulse has been estimated as:

$$f = 1 - (Q'/2Q_o) = 1 - (R_L/2(R_H + R_L)) = 1 - (325/5550) = 0.946 \quad (4.4).$$

The temperature rise following the application of a heat pulse was found by evaluating recorded resistance-time curves of the carbon thermometer such as that shown in fig.(4.4). Fig.(4.4) is the trace of the R_T resistance for a complete heat capacity measurement. The temperature and time scale included there as well as the data of this particular heat pulse were typical of our measurements on helium-implanted specimens. Fig.(4.4) can be explained briefly as follows: Before the application of the heat pulse the calorimeter is at thermal equilibrium with its environment. The thermometer bridge is then balanced exactly; let the reading of the balance potentiometer be s . After the baseline, $R_i(t)$, is established the bridge is manually set out of balance by a known change s_o for

a short time. This displaces the baseline by a distance Y on the recorder paper which is used to calibrate the output on the recorder. Application of the heat pulse follows at point A of fig.(4.4), causing decrease of R_T and therefore an out-of-balance signal, $R_f(t)$. Due to the small heat leak of our calorimeter to the isothermal shield this signal decays linearly for the recording time of interest.

Extrapolating the post-heating curve to the middle of the heating time and measuring the distances X and Y as indicated in fig.(4.4), the change of R_T caused by the heat pulse can be found and converted to a temperature difference $\Delta T = T_f(t_h/2) - T_i(t_h/2)$ with the help of eq.(4.2).

Evaluation of the heat capacity data from measurements of I , U , s , t_h , s_o , X , Y , and the coefficients of eq.(4.1) has been performed with

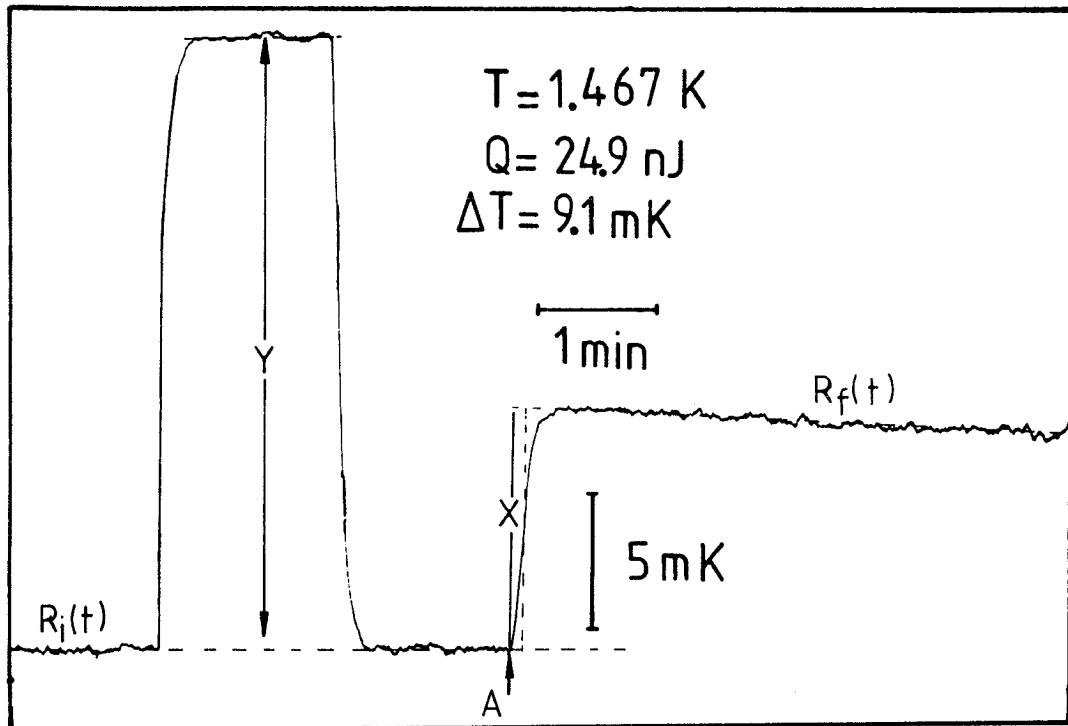


Fig.(4.4): A resistance-time curve for a complete heat capacity measurement. The heat pulse is applied at point A. Notice the slow relaxation of the calorimeter. This heat capacity measurement was taken with a specimen of $9 \cdot 10^{-6}$ mole Cu containing 170 nmole ^4He .

a 9830 HP desk computer plotter system.

The computer program contained polynomial representations of eq.(4.1), of the specific heat of Cu /49/ and the specific heat of Apiezon N grease /50/ as well as for the heat capacity of the empty specimen holder (see section 4.2.5).

For each run new values were introduced for the coefficients a_k of eq.(4.2), for the mass of the specimen and mass of Apiezon N grease.

The computer then evaluated and plotted:

- Temperature, T , and temperature difference, ΔT .
- Total heat capacity, $C_t = I U t_h f / \Delta T(t_h/2)$.
- Addenda, Cu and helium contributions to C_t .
- All heat capacities were also plotted as functions of temperature.

Higher order corrections have not been applied to the heat capacity data. The second order heat leak correction $(t_h/\tau)^2$ is negligible since we had always $(t_h/\tau) \ll 1$. The temperature differences, ΔT , were also kept sufficiently small, $\Delta T/T < 5\%$, and therefore curvature corrections to the heat capacity are also negligible.

4.2.5. Measurement of the heat capacity of the specimen holder.

We have extracted the heat capacity, C_{sh} , of our specimen holder by measuring the heat capacity of two pure Cu specimens between 1.5 K and 10 K. The specimens were annealed in vacuum ($5 \cdot 10^{-7}$ mbar) before measurement and had masses $m_1 = 27.3$ mg and $m_2 = 34.7$ mg, i.e. comparable to the mass of our implanted specimens.

The heat capacity of the specimen holder has been determined from the total measured heat capacities C_{1t} and C_{2t} , and the specific heat c_g and masses m_{1g} and m_{2g} of the Apiezon N grease, from the

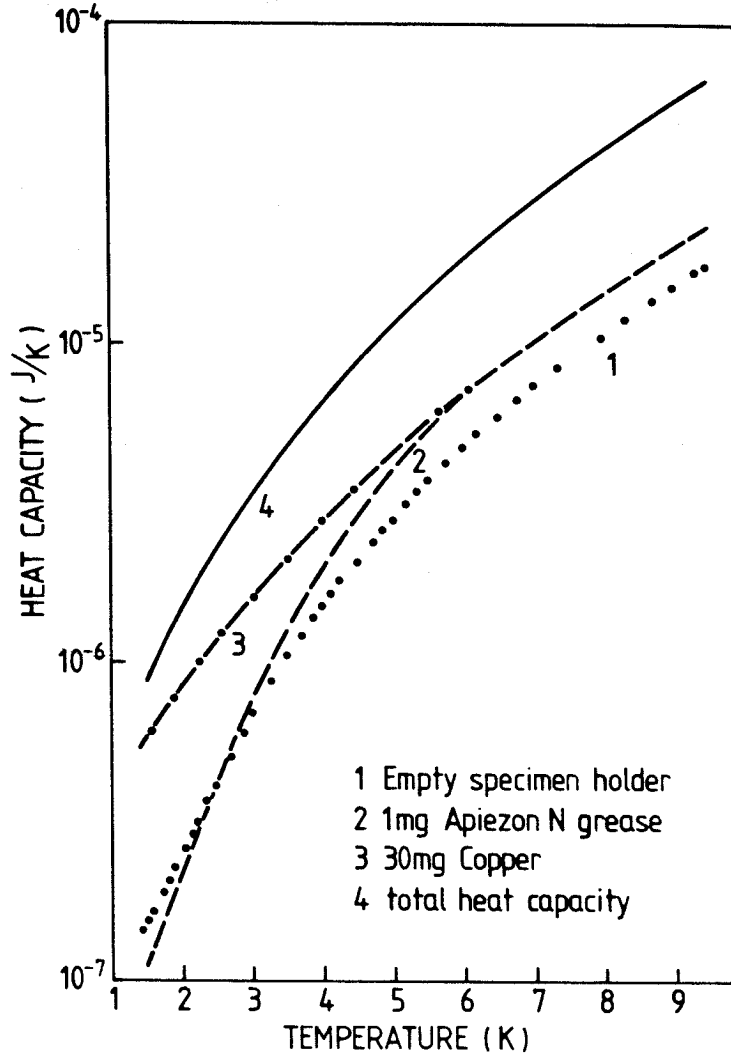


Fig.(4.5): Measured heat capacity of the empty specimen holder.
For comparison other data are also included in the figure.

expression

$$C_{sh} = ((C_{1t} - c_g m_{1g})m_1 - (C_{2t} - c_g m_{2g})m_2) / (m_1 - m_2) \quad (4.5)$$

Data obtained in this way have been plotted in fig.(4.5) which also includes for comparison purposes the total measured heat capacity, the heat capacity of 30 mg Cu and that of 1 mg Apiezon N grease. A set of selected points were then least-squares fitted to a polynomial of the form

$$\text{Log}(C_{sh}) = \sum_{l=0}^{l=5} b_l (\log T)^l \quad (4.6)$$

which has been used to subtract the addenda heat capacity in subsequent experiments.

The specific heat of Cu was then found by subtraction of C_{sh} and C_g from the total measured heat capacity and compared to literature data /50/. The largest deviations were amounting 4% and below about 4 K they were smaller than 2%.

It is worthwhile to mention that the total heat capacity measured in these experiments is essentially the background involved in the heat capacity measurements of the implanted specimens in which the total heat capacity was actually up to factor 15 larger than C_t of these experiments.

A further test of our calorimeter has been done by measuring its thermal coupling constant to the isothermal shield as a function of temperature. By means of the known geometry factor such data were then converted to thermal conductivity data for the Pt-W alloy and were found in good agreement with literature data /51/. Significant is also to mention that by evaluating recorded resistance-time curves we had an independent measurement of the total heat capacity involving only the slope of the post-heating curve. Heat capacity data obtained in this way showed in general more scattering and therefore were considered only as an additional verification of proper functioning of our calorimeter.

4.3 Electron microscope investigations.

The evolution of the bubble size and population has been followed by examining properly electropolished thin foils prepared from our specimens in a Transmission Electron Microscope (TEM) (Philips 300G) operating at 100 KeV. This enabled us to know the average size, size distribution, and volume density of the bubbles in our specimens as functions of the annealing parameters. A few specimens were also examined in a Scanning Electron Microscope (SEM) (Philips 500) operating at 25 KeV.

4.3.1. Preparation and examination of thin Cu foils.

For the TEM investigations thin foils transparent to the electron beam (thickness 300 nm) have been prepared from 3 mm Ø discs punched out from our specimens. They have been electrolytically thinned with the "jet" polishing technique /52/ in a commercial double jet apparatus. In this procedure polishing takes place at about equal rates simultaneously from both sides of the specimen and is interrupted automatically as the first tiny hole appears at the center of the polished area. The region around this hole is transparent to the electron beam.

The electrolytic bath used (500 ml dist. water, 250 ml methanol, 250 ml conc. H_3PO_4 , 50 ml propylalkohol, 5 gr urea, 2 ml "vogler's Sparbeize"), is known under the trade mark name D₂. The best results have been obtained with the polishing parameters : 1.5 A/cm², 7 V, 15°C. According to collected experience the electrolyte had to be often renewed, otherwise contamination developed during polishing. We found it very helpful to test each time the polishing conditions by means of unimplanted specimens.

Thinned specimens were cleaned in dist. water and alkohol, dried in air and examined directly in the TEM. (Thin Cu foils deteriorate

seriously in a few days by fast oxide formation. Keeping them in "vacuum" did not elongate their life time appreciably).

The specimens have been photographed in the TEM at zero tilting angle and for best visibility of the bubbles underfocused /53/ by a distance depending slightly on the mean size of the bubbles. Typical magnifications of the microscope were ranging between 130 to 60 ($\times 10^3$). From enlarged (usually $\times 3$) prints of the films the evaluation of the bubble size data proceeded at a particle size analyser (Zeiss TGA 10). There, a light spot emitted from an aperture of variable diameter was used to equalize the projection of each individual bubble on the print to the diameter of the aperture. That in turn was converted to actual bubble diameter with the help of a microprocessor, which also classified them into 16 different classes.

In this way more than 800 bubbles have been counted in each experiment. The evaluation described above yielded the average bubble radius, $\bar{r}_b$, as

$$\bar{r}_b = \sum(n_i r_i) / \sum n_i, \quad (4.7)$$

(n_i = fractional occupation of class i),

a histogram of the size distribution as well as the standard deviation of the normal distribution fitting the histogram at best.

4.3.2. Measurement of the thickness of thin Cu foils.

In order to be able to determine the volume density of the bubbles, the thickness of the transparent area under investigation must be known.

In principle, it is possible to use simple geometrical relationships to calculate the thickness of the foil, provided that its surfaces can be located. Crystallographic defects or contamination on the surfaces can be used as "marking points". In preliminary experiments we have exploited the possibility to produce such marking points in

a controlled way. We have tried to mark the surfaces of test specimens by depositing on them tiny crystallites ("islands") of heavier metallic elements, i.e. Au, Sb, Pb, Ag. Satisfactory results have been obtained by depositing slowly Ag on hot ($\approx 350^{\circ}\text{C}$) specimens. First observations on an implanted specimen indicated that the deposition temperature influenced the bubble population in the thinned foil, and therefore this technique had to be abandoned. However, a specimen with Ag "islands" on its surfaces was used to calibrate a TEM (TEM 400T, Philips 120 KeV) for Cu and perform the measurements with the X-ray fluorescence technique.

This new technique /54/ is based on the fact that the inelastic scattering of the electron beam in the specimen produces the characteristic X-ray radiation of the atomic species of the foil. The X-ray intensity is under certain conditions proportional to the thickness of the specimen as long as corrections due to reabsorption of X-rays can be neglected. This is found to be the case in the whole thickness range amenable to our microscope. The most important aspects of this new technique are its fastness and its high accuracy (better than $\pm 10\%$) which can be obtained if certain precautions are taken /54/.

In our microscope the X-ray intensity is measured by an energy dispersive X-ray spectrometer whose detector is positioned in the microscope.

With the thickness of the foil known, one calculates straightforwardly the photographed volume of the specimen, V . The volume density of the bubbles is then given by:

$$\rho_b = n_b / V ; \quad n_b = \text{number of bubbles in } V.$$

For the determination of n_b several places of the transparent area of each specimen have been photographed and their thickness was measured. The volume densities were then averaged.

5. RESULTS AND DISCUSSION.

In this chapter we will present and discuss in detail our observations concerning low temperature properties of helium confined in bubbles in Cu. We will begin with the presentation of the heat capacity results, whose main features will be pointed out and explained qualitatively. Then our TEM results will be presented and discussed. By combining the TEM and the heat capacity results we will then concentrate to the finite size behaviour of superfluid helium in bubbles. Finally, additional aspects of our observations will be discussed.

Our experimental procedure is shown schematically in fig.(5.1). In order to increase the size of the bubbles in our specimens we have annealed them at high temperatures. After each annealing step the heat capacity of our calorimetry specimen has been measured at low temperatures and a TEM-specimen was electropolished and examined in a TEM. Thus, the closed loop of fig.(5.1) has been followed several times for each calorimetry specimen annealed at different temperatures and/or for different annealing times.

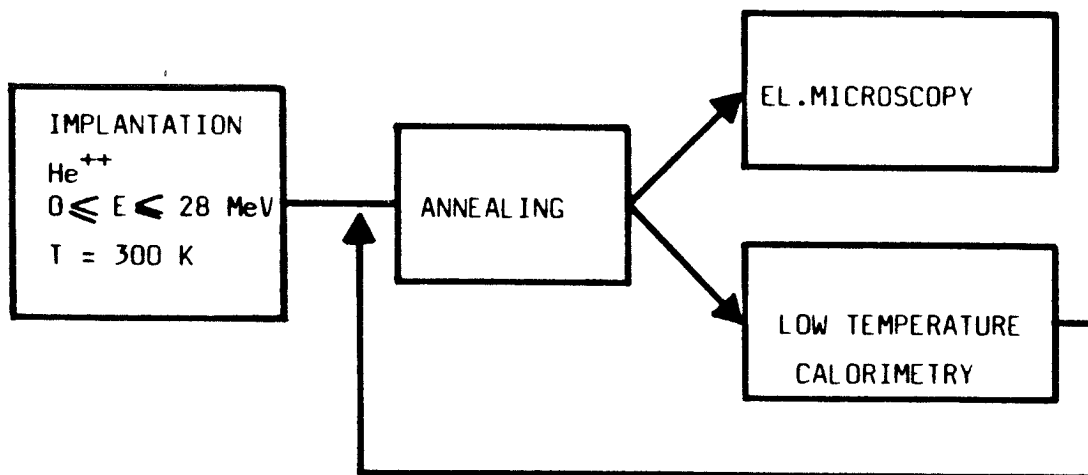


Fig.(5.1): Experimental procedure (schematic).

5.1. Heat capacity measurements.

The heat capacity of helium, C_{He} , was found by subtraction from the total measured heat capacity, C_t , the addenda heat capacity, C_{add} , consisting of the contribution of Cu, and that of the empty calorimeter and Apiezon N, i.e.

$$C_{\text{He}} = C_t - C_{\text{add}}. \quad (5.1).$$

The heat capacity of both calorimetry specimens has been measured between 1.5 K and 7 K directly after implantation. The measured heat capacity did not deviate by more than ± 3 % from that of the unimplanted specimens, indicating that the contribution of helium was negligibly small. A similar observation has been reported earlier for an Al specimen implanted with helium /55/.

Our observation indicates that directly after implantation the helium will be accommodated in our specimens primarily as small clusters. The tiny athermally grown bubbles which should exist in our specimens at this stage, should contain solid helium under high density and therefore not contribute significantly to the heat capacity at low temperatures.

After these measurements our specimens were subjected to different annealing programs, at annealing temperatures, T_a , $T_a > 0.6 T_m$ ($T_m = 1353$ K, melting temperature of Cu). For our convenience we shall present the heat capacity results separately for each specimen and distinguish the specimens by their nominal helium concentration.

5.1.1. Measurements of the heat capacity of the specimen implanted with 1200 appm helium.

This specimen was annealed isochronally (= constant annealing time, $t_a = 2$ h) under vacuum conditions ($P = 5 \cdot 10^{-7}$ mbar) at

annealing temperatures, T_a , ranging between 830 K and 1220 K.

The heat capacity measurements after $T_a = 830$ K and $T_a = 930$ K did not show any heat capacity anomaly at around 2 K. For the first of them the heat capacity contribution of helium was zero to within ± 3 %, while for the second one i.e. after $T_a = 930$ K, a small "excess" contribution to $C_{tot.}$ could be resolved. It is plotted in fig.(5.2).

Since already after the first annealing practically all helium should be in bubbles (see section 2.1), the result of the measurement after $T_a = 830$ K implies that the density of helium in the bubbles was still quite high i.e. it should be solid at low temperatures. Examining the magnitude of the "excess" heat capacity observed after $T_a = 930$ K, we find it to be a little larger than that which could be attributed to solid helium under realistic assumptions. The observed enhancement can be due to melting of helium in big bubbles in our specimen. There is however another possibility. We suggest that the heat capacity of solid helium confined in spheres with a radius of $25 \text{ \AA}$ might be enhanced relative to its bulk value, in analogy with the behaviour of metallic superconducting particles /56/ of comparable size. Enhanced heat capacity has also been observed /57/ for solid H_2 and D_2 confined in vycor glass.

Assuming all the observed enhancement in our case is due to the finite size of the bubbles, it would correspond to a decrease of the Debye temperature of solid helium in bubbles by ca.50%.

After the subsequent annealing steps from $T_a = 1030$ K to $T_a = 1220$ K the heat capacity of helium was clearly observable. Its main feature was first a bump below 2 K which developed progressively to a sharp and growing peak, thus becoming the dominant contribution of the total measured heat capacity. The heat capacity of helium is shown in fig.(5.2) as a function of temperature for all

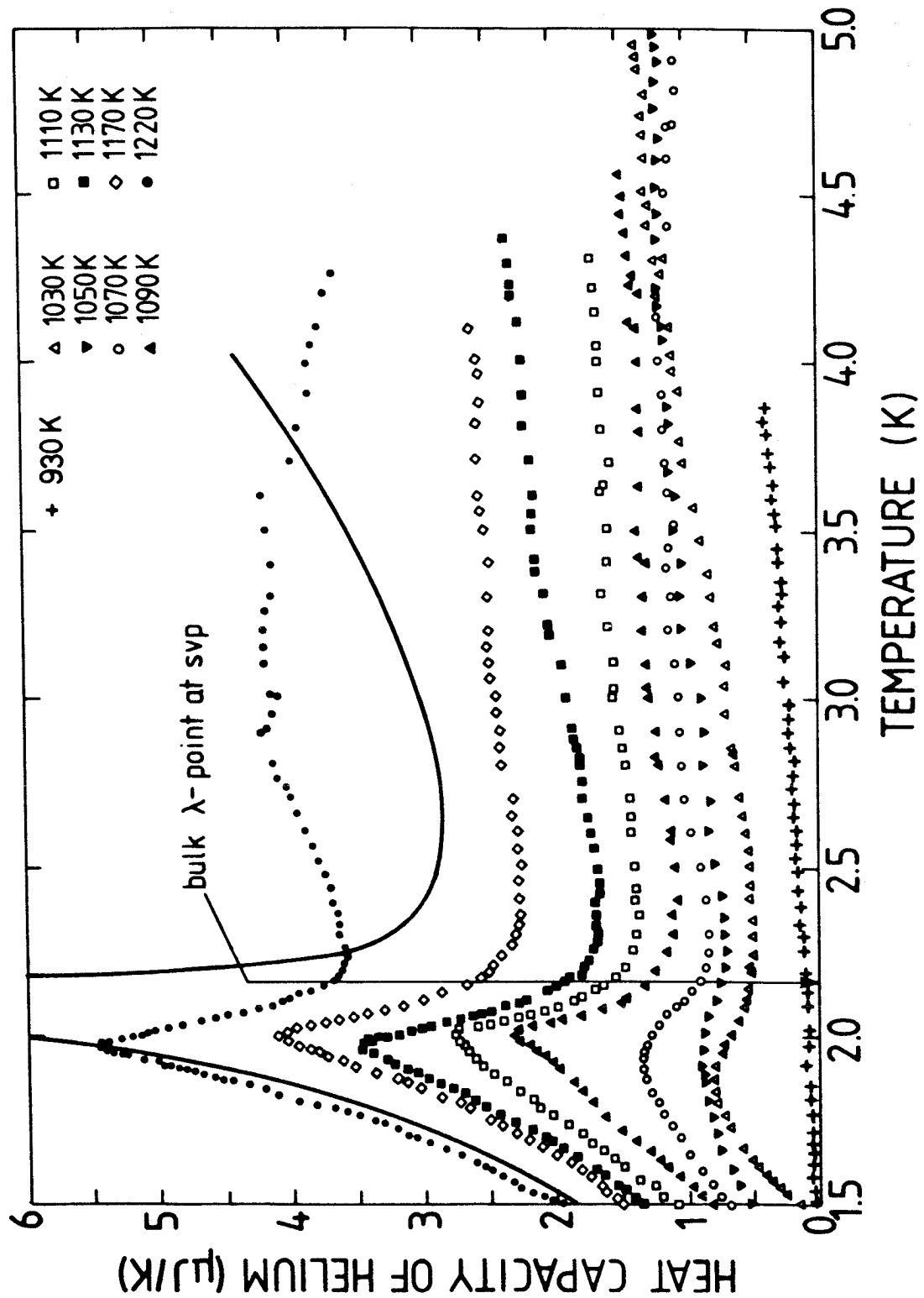


Fig.(5.2): Heat capacity of $1.19 \mu\text{g}$ helium confined in bubbles in Cu. The specimen has been annealed at the temperatures given in the figure. The continuous line shows the heat capacity of $1.19 \mu\text{g}$ of bulk helium at SVP.

measurements performed with the 1200 appm-specimen. Different symbols in fig.(5.2) correspond to different measurements after annealing at the temperatures given in fig.(5.2). Usually two sets of data were taken for each curve of fig.(5.2). They were reproducible to within 2 %. The absolute accuracy of these measurements is estimated to be better than 5 % below about 2.5 K, decreasing to about 10 % at around 5 K.

As it can be seen from fig.(5.2), for $T_a = 1030$ K a small and rounded heat capacity peak was present in the heat capacity of helium and had a maximum at $T_p = (1.83 \pm 0.04)$ K. This peak is attributed to the superfluid transition of helium under pressure in bubbles in our specimen. Thus, the annealing temperature of $T_a = 1030$ K was sufficient to produce bubbles big enough to contain helium at a density that could liquify at low temperatures. To understand why the heat capacity peak appears so small and rounded, we have to take into account that only a small fraction of the bubbles with an average radius of $37 \text{ \AA}$ (see sec.5.2.1) should contain liquid helium at this stage. In addition the confinement of helium in such microscopic spheres should modify its superfluid properties causing depression and rounding of the heat capacity peak due to superfluidity /58/. A contribution to the rounding of the peak should also be caused by the fact that there is a spectrum of liquid densities in bubbles (see sec.5.4).

In contrast to the depression of the peak, the heat capacity above 2 K appears enhanced compared to the magnitude of the peak. If we attempt, for example, to explain its magnitude in terms of the specific heat of bulk liquid helium under a pressure of 25 bar /59/ it turns out that 40 to 50 % of the helium mass in our specimen would be already in the liquid state in this temperature range.

Since this appears too high, we tend to believe that a significant contribution to the enhanced heat capacity above 2 K should come from the heat of melting of solid helium in small bubbles.

Upon further annealing the characteristic parameters of the heat capacity of helium in bubbles are changing. The heat capacity increased in the whole temperature range of measurements and the heat capacity peak grew faster and sharpened. The growth of the heat capacity will be discussed more extensively later. Qualitatively the growth of the heat capacity peak can be attributed to a progressive increase of the mass of liquid helium as well as to the fact that as the bubbles were growing, superfluid helium in it should "feel" less and less the influence of the confinement. This later fact should also be mainly responsible for the observed sharpening of the heat capacity peak.

Simultaneously, the maximum of the heat capacity has been observed to shift slightly but monotonously to higher temperatures for the measurements performed after T_a less than 1090 K. The heat capacity peak temperatures, T_p , have been summarized in table I, which also gives the displacement of T_p relative to $T_{\lambda \text{ SVP}} = 2.172$ K and includes the absolute height of the heat capacity at T_p . The uncertainty of T_p 's in table I have been subjectively estimated and are mainly due to the rounding of the heat capacity peaks.

The displacement of the maximum of the heat capacity to higher temperatures with increasing annealing temperature can be understood by taking into account that the bubbles are growing (see section 5.2). This means simultaneous decrease of both factors influencing the position of T_p on the temperature axis, i.e. the pressure of liquid helium in the bubbles and the influence of the

T_a (K)	T_a/T_m	T_p (K)	$(T_{\lambda SVP} - T_p)$ (K)	$C_{He}(T_p)$ ($\mu J/K$)	$C_{add.}$ ($\mu J/K$)
930	0.687	----	----	----	
1030	0.761	1.83 ± 0.04	0.34 ± 0.04	0.80	
1050	0.776	1.90 ± 0.04	0.27 ± 0.04	0.90	
1070	0.790	1.93 ± 0.04	0.24 ± 0.04	1.35	1.2
1090	0.805	1.99 ± 0.03	0.18 ± 0.03	2.35	
1110	0.820	2.01 ± 0.02	0.16 ± 0.02	2.75	
1130	0.835	1.96 ± 0.01	0.21 ± 0.01	3.35	
1170	0.864	2.00 ± 0.01	0.17 ± 0.01	4.10	
1220	0.901	1.97 ± 0.01	0.20 ± 0.01	5.45	

Table I: Annealing temperatures, T_a ; temperatures of the maximum of the heat capacity, T_p ; their displacement relative to $T_{\lambda SVP} = 2.172$ K and the value of the heat capacity of superfluid helium at T_p for the specimen of 1200 appm helium. For comparison the background heat capacity, $C_{add.}$, at 2 K is given. t_a was always 2 h.

confining geometry. However, after annealing the specimen at still higher temperatures, i.e., $T_a = 1090, 1110, 1130, 1170$, and 1220 K, the temperature of the heat capacity peak did not shift any more. It varied slightly but randomly from experiment to experiment (see table I). Averaging the peak temperatures for the last five measurements we obtain $\bar{T}_p = (1.99 \pm 0.01)$ K. This behaviour is somewhat surprising, especially in relationship to our TEM observations which showed that the average size of the bubbles was continuously increasing with T_a . This should result in pronounced changes of the thermodynamic state (density) of helium in the

bubbles which in turn would be expected to be reflected in the magnitude of the T_p 's. The observed approximate constancy of T_p in these last experiments suggests that the maximum of the heat capacity became insensitive in relationship to the increase of the average size of the bubbles and to the variation of the thermodynamic state of helium in it. A plausible explanation for this behaviour will be offered in section 5.5.2.

5.1.2. Heat capacity measurements of the specimen implanted with 2600 appm helium.

This specimen has been subjected to an isothermal vacuum annealing program i.e. T_a was constant. The temperature of annealing, $T_a = 1020$ K, has been chosen slightly lower than that which had produced the first appearance of superfluid helium in bubbles in our first series of measurements. The underlying idea was to look for the very first stage of the appearance of superfluid helium in bubbles, which could have been lost in our first series of measurements. The annealing times at this temperature, after which the heat capacity of the specimen was measured at low temperatures, were $t_a = 1, 10, 50$, and 250 h. The heat capacity of helium is shown in fig.(5.3) as a function of temperature. (Fig.(5.3) includes also a subsequent measurement of the same specimen, after $T_a = 1115$ K and $t_a = 1$ h). According to fig.(5.3), the heat capacity measurement at $T_a = 1020$ K and $t_a = 1$ h indicates that there has been only a very small fraction of bubbles in the specimen contributing to the superfluid heat capacity peak, which we associate with the biggest bubbles of the size distribution. The rest of helium, residing in smaller bubbles under higher density, is still probably solid at 2 K. Its heat of melting above 2 K is believed

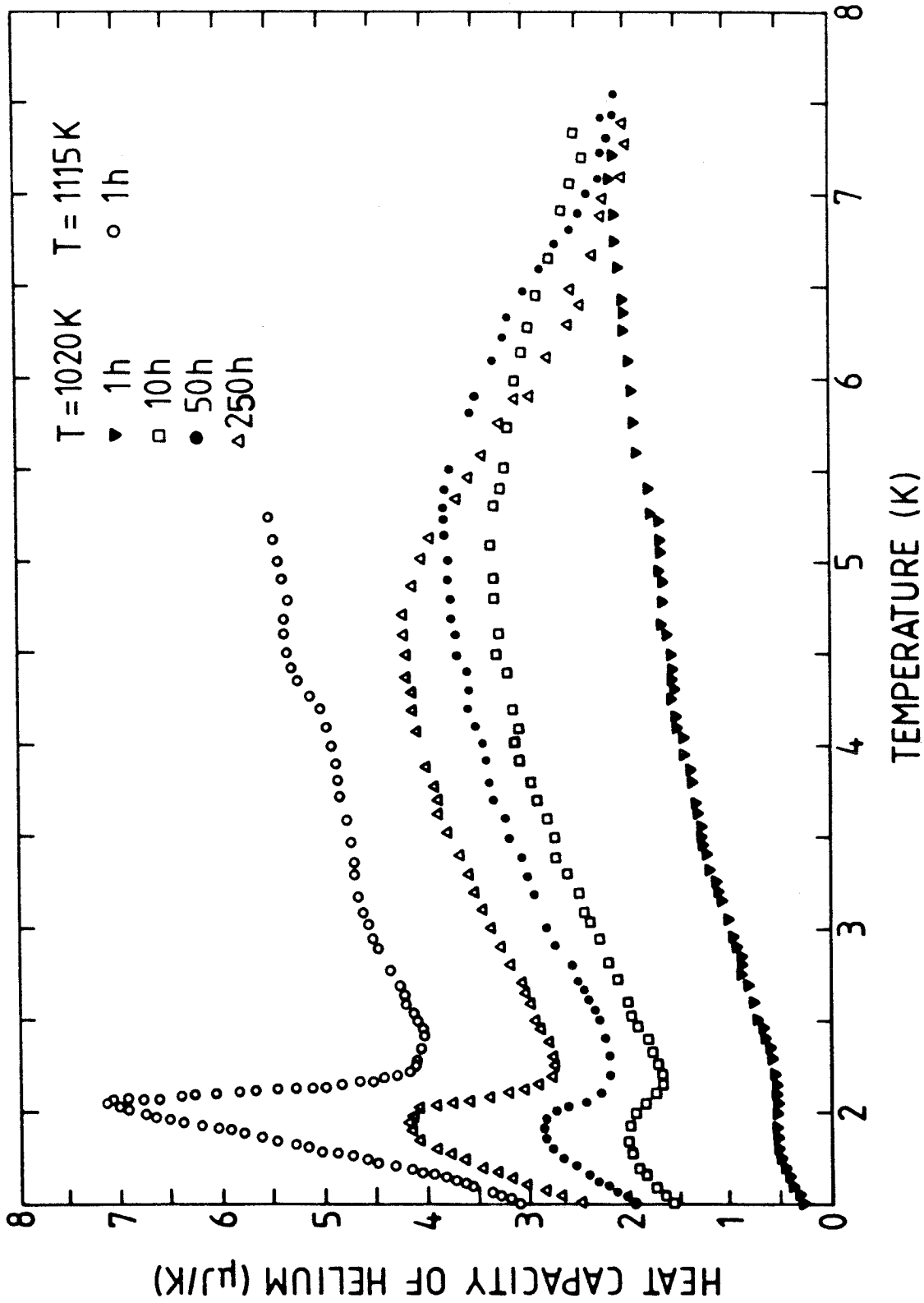


Fig.(5.3): Heat capacity of helium confined in bubbles after annealing the specimen at $T_a = 1020\text{ K}$ for $t_a = 1, 10, 50,$ and 250 h and at $T_a = 1115\text{ K}$ for $t_a = 1\text{ h}$. The total mass of helium in this specimen was $3.20\text{ }\mu\text{g}$.

again to cause the observed enhancement of the heat capacity in this temperature range.

The measurement of the heat capacity after $t_a = 10$ h at $T_a = 1020$ K revealed a two-peak structure. The heat capacity peak due to superfluid helium could be clearly observed and had a maximum at $T_p = (1.80 \pm 0.04)$ K, in good agreement with the data for the first specimen, while second peak occurred at around 5 K. We attribute this second maximum of the heat capacity again to melting of helium in bubbles.

Inspecting closely the heat capacity data of fig.(5.2) a similar tendency of the heat capacity can be recognized, though it is not so clearly depicted.

The last two measurements at $T_a = 1020$ K were qualitatively similar, see fig.(5.3). They show the development of the superfluid heat capacity peak and displacement of its maximum to higher temperatures, a behaviour familiar from our earlier observations (see table I). They also show the displacement of the second maximum of the heat capacity to lower temperatures, indicating that the average density of helium in bubbles decreased slowly with t_a . This observation is also supported by our TEM results. A slower change of the thermodynamic state of helium in the bubbles would be more favored in this case of isothermal annealing (compared to isochronal annealing), since it is caused by thermally activated transport properties of helium in the metal at T_a , which have a linear dependence on t_a but depend exponentially on T_a .

In relationship to the temperatures T_p we would like to make the following remark: To the extent to which T_p for the measurement after $t_a = 1$ h can be reliably deduced from fig.(5.3), it turns out to be not less than 1.80 K. We recall further that the lowest T_p

obtained from our first series of measurements was at (1.83 ± 0.04) K. Thus it appears that the heat capacity peak due to superfluid helium in bubbles develops at around 1.80 K, a temperature comparable or even a little higher than the upper λ -point of bulk helium, see fig.3.1. Furthermore, since confined liquid helium of a given state (density), is known /60/ to displace its superfluid transition to lower temperatures compared to that of the bulk phase of equal density, it follows that our observed T_p 's are too high to be attributed to bubbles located in the immediate neighborhood of the upper λ -point of the phase diagram of confined helium. They indicate that the heat capacity of superfluid helium in bubbles in Cu develops later than the appearance of liquid helium in the bubbles. The reason why bubbles located close to the melting line appear to be ineffective in producing a heat capacity peak will be examined in more detail in a later section.

Due to practical limitations of increasing further the annealing time at $T_a = 1020$ K, we have continued the annealing program of this specimen by choosing a higher annealing temperature, namely $T_a = 1115$ K. The heat capacity of the specimen has been measured after annealing times of $t_a = 1, 11,$ and 111 h. The heat capacity of helium for the first two of these measurements is shown in fig.(5.4). The measurement after $t_a = 1$ h is shown also in fig.(5.3) for comparison purposes and to indicate the absence of the "melting peak" at this new annealing temperature.

After the annealing step of $t_a = 111$ h macroscopic changes were observed on the surfaces of our specimen. As far as we could prove (see section 5.2.2) its microstructure appeared considerably changed, and a considerable fraction of helium may have escaped. We feel that its heat capacity would be difficult to compare with our

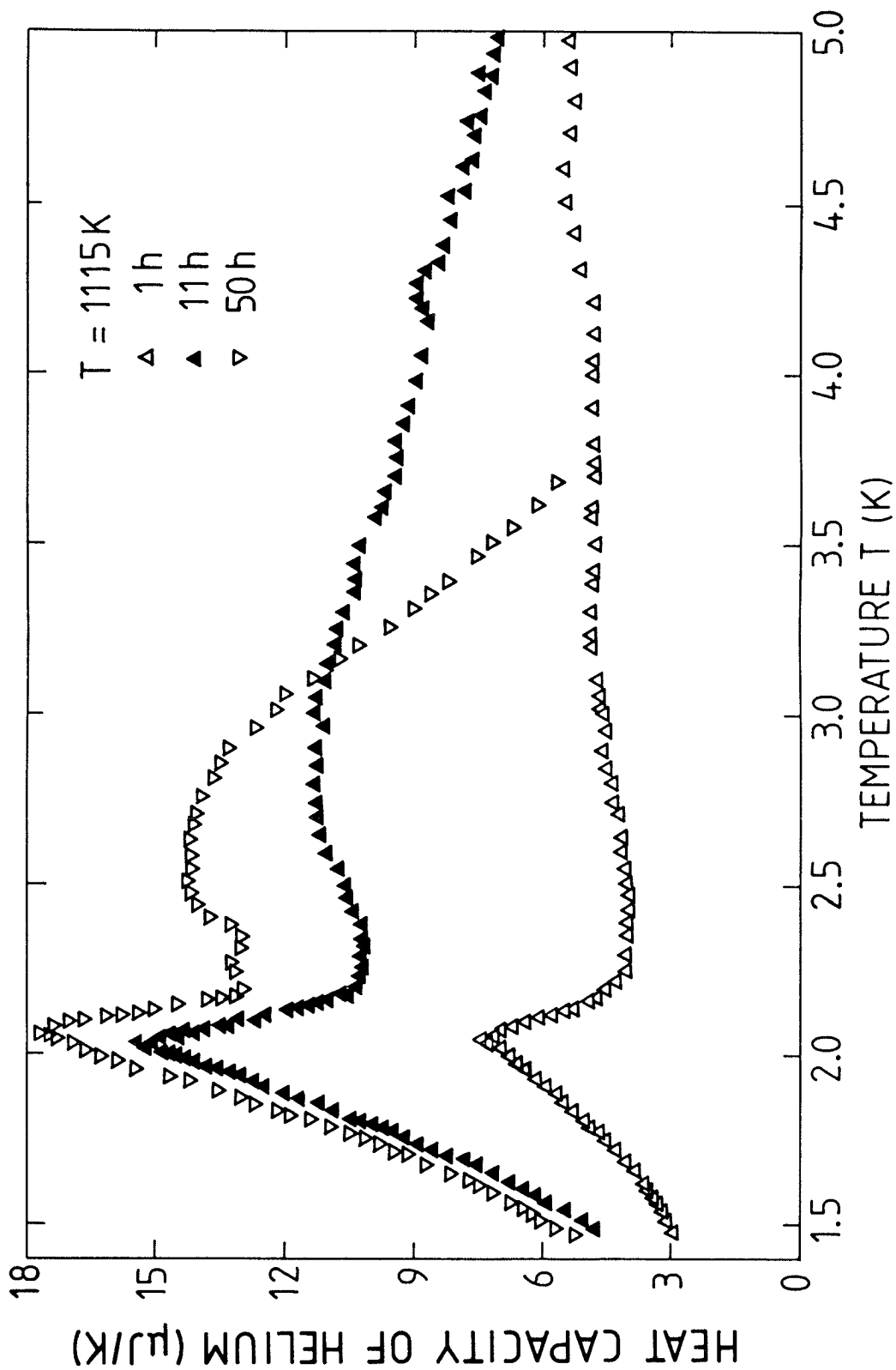


Fig.(5.4): Heat capacity of helium after annealing the same specimen as in fig.(5.3) at $T_a = 1115\text{ K}$ for $t_a = 1, 11, \text{ and } 50\text{ h}$.

previous measurements and therefore it will not be presented here. To proceed further, we measured the heat capacity of a TEM-specimen ($m_{Cu} = 6.31$ mg) which had been annealed at $T_a = 1115$ K for $t_a = 50$ h. The heat capacity of helium was then normalized to that of the calorimetry specimen to correspond to the same helium mass and is included in fig.(5.4). Although the absolute mass of helium in this specimen was only ca. 170 nmole, its heat capacity at T_p was about four times larger than the background heat capacity of our calorimeter. Due, however, to the fast increase of the latter heat capacity with temperature, see fig.(4.5), the helium contributed only 20 % at 4 K. For this reason, a considerable systematic error cannot be excluded for this measurement above 3 K. We can, however, be sure that the form of the heat capacity of helium shown in fig.(5.3) is reliable, since the total measured heat capacity displayed the same qualitative features in the whole temperature range

T_a (K)	t_a (h)	T_p (K)	$(T_{\lambda SVP} - T_p)$ (K)	$C_{He}(T_p)$ (μ J/K)
1020	1	----	-----	----
"	10	1.80 ± 0.04	0.37 ± 0.04	2.05
"	50	1.85 ± 0.04	0.32 ± 0.04	2.85
"	250	1.95 ± 0.03	0.22 ± 0.03	4.30
1115	1	2.05 ± 0.01	0.12 ± 0.01	7.40
"	11	2.02 ± 0.01	0.15 ± 0.01	15.20
"	50	2.06 ± 0.01	0.11 ± 0.01	17.70

Table II: Annealing program and superfluidity-related calorimetric data for specimen containing 2600 appm helium. The notation here is the same as in table I.

of measurements.

Table II summarizes calorimetric data obtained from the 2600 appm specimen. It can be seen that the temperature of the superfluid peak increased only up to $T_p = (2.05 \pm 0.01)$ K and then varied randomly. Thus, apart from the fact that the maximum T_p in this case is higher than that deduced from the data of table I, the behaviour of T_p 's in both cases was qualitatively the same. The heat capacity, see table II, has been observed to increase (cf. table I) and at $T_a = 1115$ K it became finally 15 (2.5) times larger than the background heat capacity at 2 (3) K respectively.

At $T_a = 1115$ K and after $t_a = 11$ h and $t_a = 50$ h the heat capacity showed an additional rounded peak which reached its maximum at 2.8 K and appears more pronounced in the second of these measurements. Similar variation of the heat capacity above 2 K can also be seen in fig.(5.2) for the measurement after $T_a = 1220$ K. Presumably the origin of this anomaly was the same in both specimens, though it has been observed after annealing the specimens at different temperatures. There is, however, sufficient reasoning to believe that this effect is of different origin than the heat capacity peaks of fig.(5.3), although they have been observed in the same temperature range. To have again melting as its origin, it would be necessary to have a relatively large fraction of bubbles with radius less than $40 \text{ \AA}$, which therefore would be detectable in the TEM. As it will be shown later they have not been detected.

In combination with the observed microstructure of the specimens (see section 5.2.2) we tend to associate this feature of the heat capacity with the existence of thin helium films adsorbed on the inner surface of very big ("grain boundary") bubbles (having radius of ca. $0.5 \text{ \mu m}$, see sec 5.2.2) in our specimens. Such films should have thickness less than a few monolayers in order to be able to

exhibite such a heat capacity variation /61/. We do not have precise information on the thickness of these films and therefore it is difficult to decide whether the observed heat capacity peaks have to be attributed to a solid-to-liquid transformation ("monolayer melting"/62/) or if they are due to a configurational (symmetry-induced) transition. The latter has been observed /63/ to occur for submonolayer helium films on Grafoil, a substrate similarly smooth as in our case but, of course, with a different symmetry. We wish, however, to mention that a similar variation of the heat capacity above 2 K has been observed /64/ for a 0.6 monolayer thick helium film on a Cu substrate.

And, in order to avoid any confusion, we should emphasize here that the bubbles responsible for the occurrence of these heat capacity peaks are of completely different nature and very different size than the bubbles producing the heat capacity peak at 2 K. They might not contribute at all to the latter heat capacity anomaly. It is further easy to see that they have to be "non-equilibrium" bubbles, i.e., eq.(2.5) should not be valid for them. Otherwise, the thickness of helium films in them would be impossible to become so small as to exhibit the observed variation of the heat capacity. The low limit of the thickness, $d_{lim.}$, of helium films in equilibrium bubbles (containing ideal gas, and therefore having radius greater than $10^3 \text{ \AA}$, see fig.(2.2)) can be easily shown to be:

$$d_{lim.} = (2 \gamma m) / (3 k_B T_a \rho) \quad (5.2).$$

Inserting in this expression values for the surface energy γ ; the mass of the helium atom m ; Boltzmann's constant k_B ; saturation density of liquid helium ρ ; and a representative temperature T_a of 10^3 K one finds $d_{lim.} = 35 \text{ \AA}$.

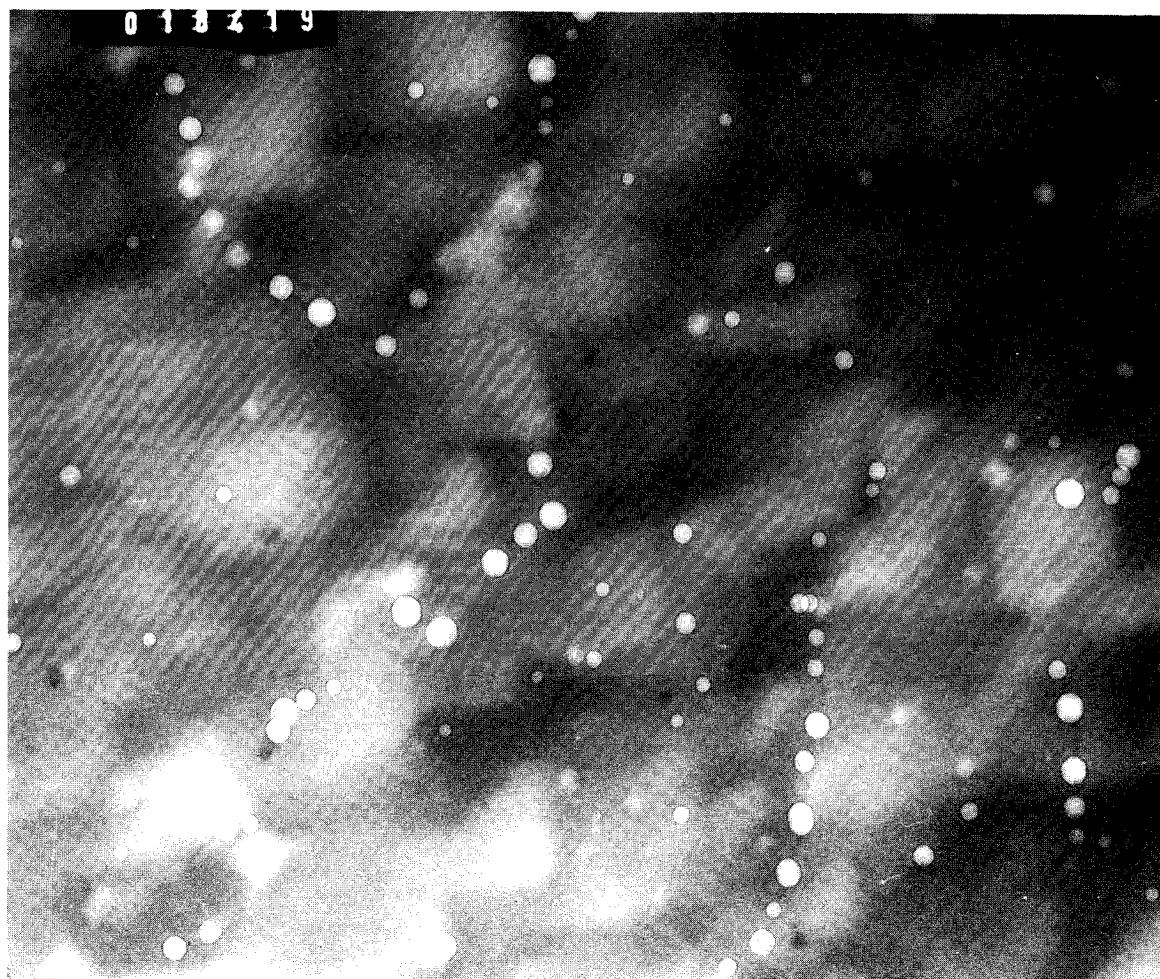


Fig.(5.5): Typical TEM micrographs of underfocused helium bubbles in post-implantation annealed Cu specimens..

(a): Bubbles of average radius of $35 \text{ \AA}$ obtained in a Cu specimen implanted with 2600 appm helium after annealing at $T_a = 1020 \text{ K}$ for $t_a = 1 \text{ h}$.

(b) The bubbles shown have an average radius of $108 \text{ \AA}$. The helium concentration in the specimens was 1200 appm. Final annealing at $T_a = 1220 \text{ K}$ for $t_a = 2 \text{ h}$ was given to the specimen.

cused helium bubbles appear as well defined light areas in the darker-contrasted volume of the specimen. Under such conditions, the inner diameter of the dark ring surrounding the plane projection of a bubble is equal to the true diameter of the bubble within $\pm 10 \%$ /65/.

5.2. Electron microscope investigations.

5.2.1. TEM results.

Transmission Electron Microscope (TEM) investigations were performed on specimens which had been implanted with the same helium concentration and were annealed under identical conditions as the corresponding heat capacity specimens. Electropolishing the TEM-specimens (after annealing) as described in section 4.3, sufficiently thin and contamination-free TEM-foils could be routinely obtained.

TEM micrographs of underfocused typical helium bubbles are shown in fig.(5.5). They correspond to different bubble-sizes and specimens implanted with different helium concentrations, given in the caption of the figure. As it can be see from fig.(5.5), underfo-

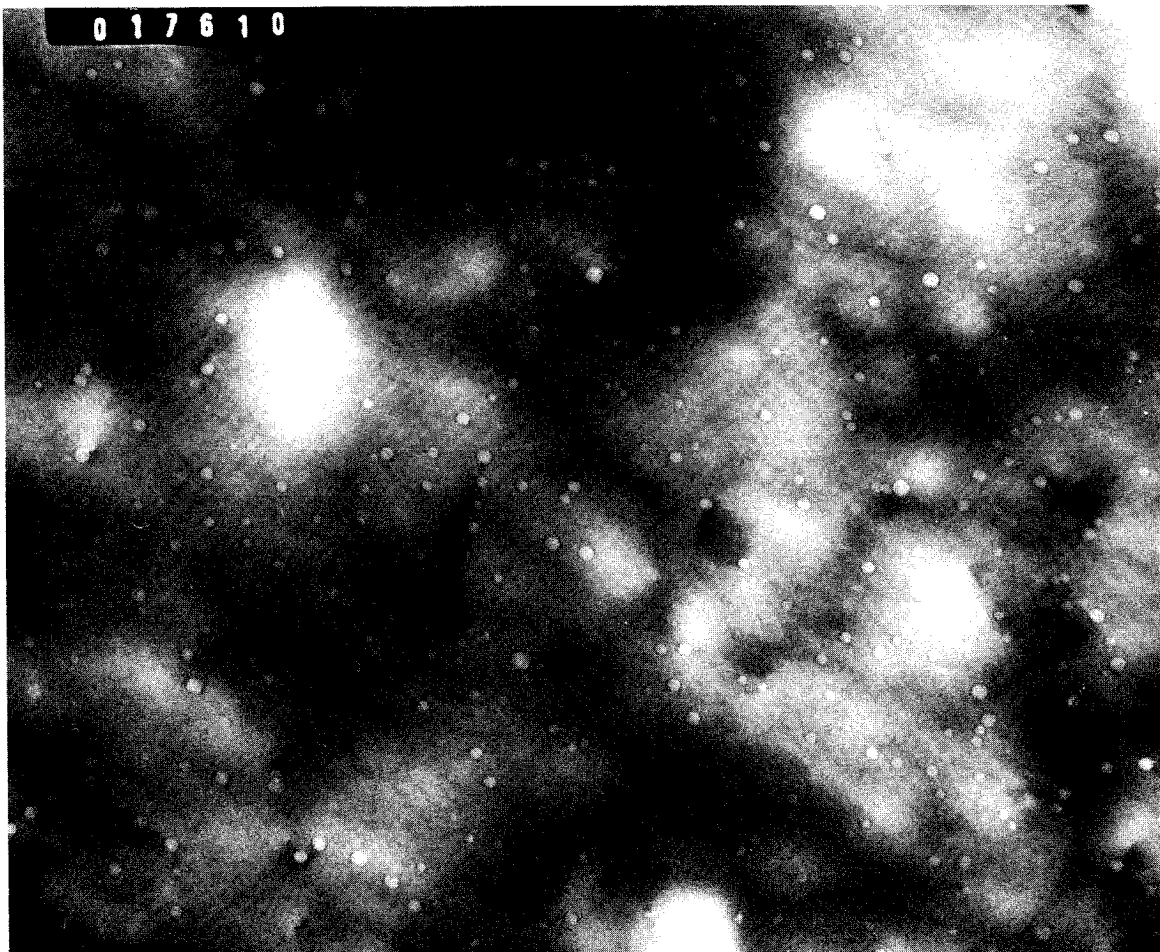


Fig.(5.5a): (For caption see next page).

The micrographs of fig.(5.5) provide a visual presentation of the confining geometry of bubbles. They demonstrate in a very persua-ting way that this new confining geometry possesses fundamentally important features for investigations of confined helium. These aspects as well as their physical implications will be pointed out and discussed in a later section. In this section we would like to dis-cuss first the morphology of bubbles in relationship to the micro-structure of our specimens and then present our quantitative TEM results. Our intention will be to demonstrate that we have a confi-ning geometry that can be known in detail and with higher accuracy than for other confining geometries.

To begin with, we should mention that due to our electropolishing procedure (see sec. 4.3) the transparent areas of the foils examined in our TEM investigations were located approximately 50 μm away from both original surfaces of our specimens. Therefore, the bubbles involved in our investigations were "bulk" bubbles whose nucleation and growth should not have been influenced by the presence of surfaces. In addition the bubbles used in quantitative evaluations were intragrain bubbles.

The bubbles appeared homogeneously distributed in the transpa-rent volume of our specimens. A significant fraction of them was located along dislocation lines of the metal matrix, an observation usually accepted /66/ as indication that dislocations are preferred nucleation sites for helium bubbles in metals. Although dislocations are out-of-contrast in the micrographs of fig.(5.5), it is rather easy to recognize some alignment of bubbles probably associated with the presence of dislocations. It can also be seen from fig.(5.5) that the bubbles were facettted, the number of facets being six. Facettted helium bubbles are typically observed in other fcc and bcc metals and alloys. Facetting of gas bubbles in metals has been

considered /67/ as providing evidence for bubbles grown at thermal equilibrium. In the evaluation of our micrographs the projection of bubbles on magnified prints of microfilms were approximated by circles of equal area. Facetting will be also omitted in the discussion of the properties of confined helium, where the bubbles will be treated as spheres.

We have not observed substantial size differences between bubbles located on dislocations or in the Cu matrix and therefore distinction has not been made between them in the evaluation of the data.

Size distributions of bubbles, typical of our investigations are shown in fig.(5.6). The fraction of bubbles per $\text{\AA}$ diameter normalized to the total number, N_0 , of bubbles counted each time (exceeding always 800) is plotted versus the diameter of the bubbles for diffe-

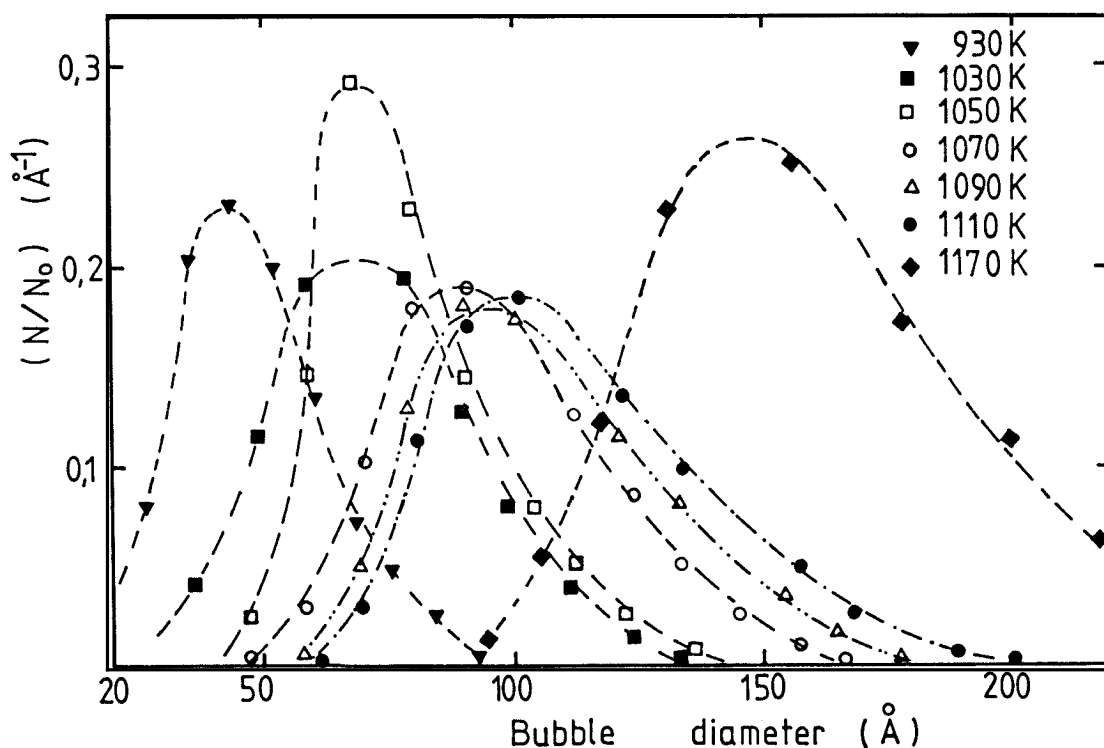


Fig.(5.6): Typical size distributions of helium bubbles in Cu for specimens containing 1200 appm helium. Each specimen was annealed for $t_a = 2$ h and up to the temperature T_a given in the figure.

rent annealing temperatures given in fig.(5.6). One can easily see the displacement of the maxima of the size distributions to larger diameters with increasing T_a , indicating the increase of the average size of the bubbles. In our investigations the size distributions were always monomodal and regular. Their half-widths increased also slowly with T_a . A few of them are included as "error bars" in fig.(5.7).

The average radius of bubbles, $\bar{r}_b$, obtained by means of the procedure described in sect.4.3, and its variation with the annealing temperature is shown in fig.(5.7) for the isothermal annealing experiments performed with the 1200 appm-specimen. TEM investigations on two pieces cut from the calorimetry specimen (after it was annealed at $T_a = 1200$ K) demonstrated that the average bubble-radii obtained from these specimens were within 3 % the same as that of the original TEM specimen. Noticing that an assumed size-difference would be more pronounced and consequently more easily observable at the final annealing stage, we can rather safely conclude that the bubbles grew in the same way in both kinds of specimens. This observation provides us with confidence that the bubble-size data of fig.(5.7) can be reliably employed to interpret our calorimetric observations in terms of the finite size behaviour of superfluid helium in bubbles.

The data of fig.(5.7) show that the increase of $\bar{r}_b$ in our specimens was accelerated with increasing T_a . A qualitatively similar increase of $\bar{r}_b$ has been recently observed in an isochronal annealing study of a thin Cu foil containing 7700 appm helium [68]. This latter investigation showed considerably bigger bubbles differing by more than a factor of two from the data of fig.(5.7) at comparable annealing temperatures. This difference is too large to be attributed only to the difference of the helium-concentrations in the specimens.

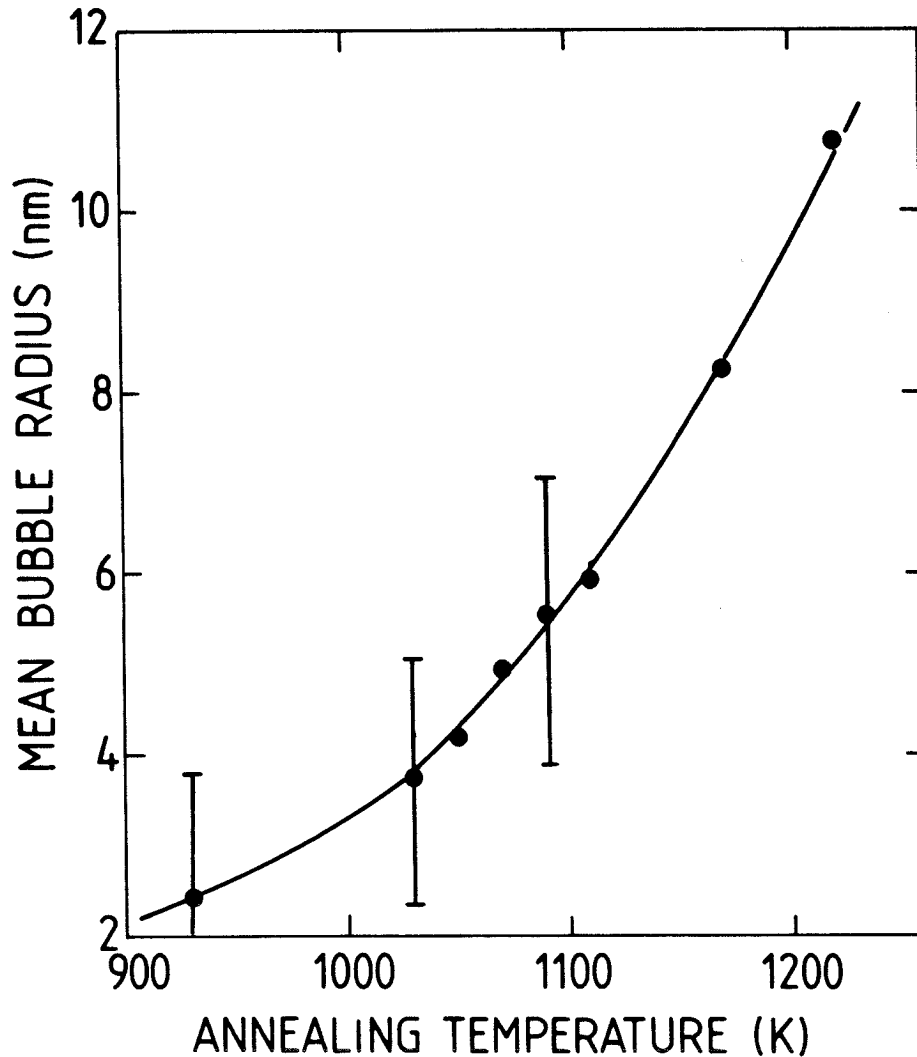


Fig.(5.7): Increase of the average radius of helium bubbles in Cu with T_a for isochronal annealing experiments ($t_a = 2$ h). The concentration of helium in the specimens was 1200 appm and they were annealed to progressively higher temperatures. The bars show typical half-widths of the corresponding size distributions.

(The average radii of bubbles obtained with specimens containing 2600 appm helium (to be presented later) are well comparable with the data of fig.(5.7) and therefore exclude a strong dependence of $\bar{r}_b$ on the concentration of helium). It might however be explained if differences of the experimental procedure followed in the one and the other case are taken into account: The data of fig.(5.7) show

namely the size of bubbles grown in bulk specimens (which were then thinned and examined in the TEM), while the data of ref./68/ involve bubbles grown in a thin TEM foil (subjected to "in situ" annealing in the TEM). This means essentially that in the latter case the presence of surfaces resulted in a faster growth of bubbles. Faster growth of near-to-surface bubbles has also been observed in other cases /69/.

The volume density of the bubbles, ρ_b , corresponding to the data of fig.(5.7), is shown in fig.(5.8) as function of T_a . Obviously, growth of bubbles took place with simultaneous decrease of the total number of bubbles in the specimens. This variation of ρ_b ,

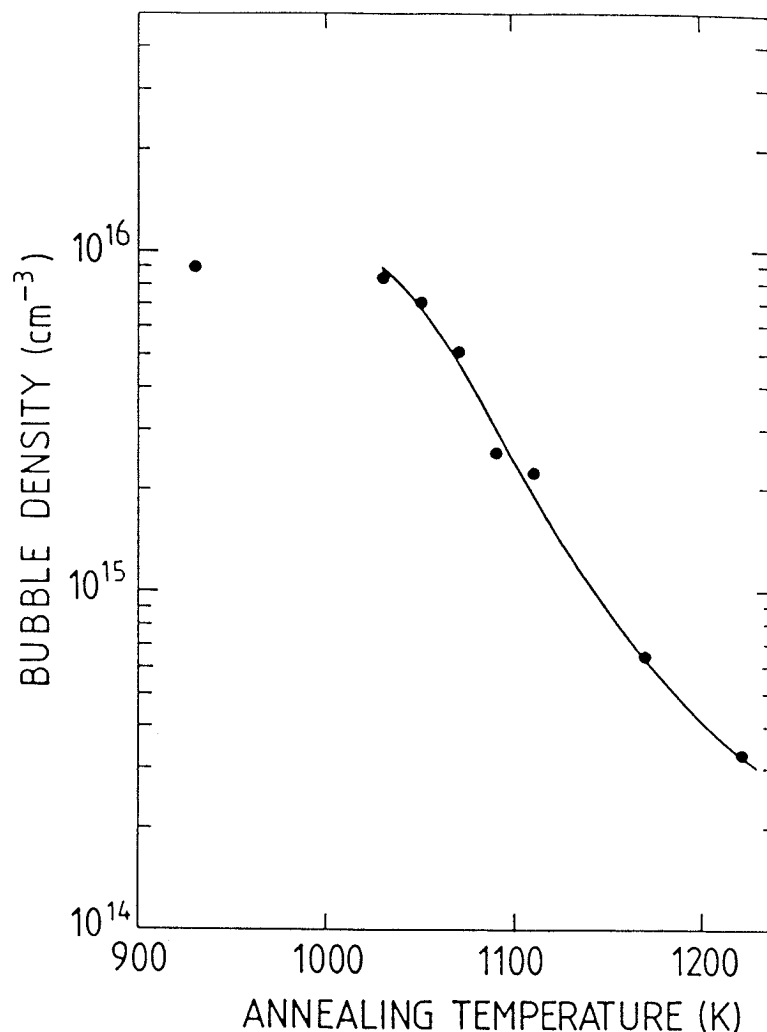


Fig.(5.8): Variation of the volume density of bubbles with annealing temperature for specimens containing 1200 appm helium /70/.

fig.(5.8), shows that the bubbles interacted with each other at T_a either by exchanging helium atoms or by coagulating.

By combining the results of fig.(5.7) and fig.(5.8) it is found that the total volume occupied by bubbles in the specimen increased with annealing temperature. Assuming that the total mass of helium in the specimen was constant (i.e. that no release has taken place), the average density of helium in the bubbles should have decreased monotonously as the bubbles became larger in size, as it is actually expected.

The data of fig.(5.7) and fig.(5.8) cannot, however, be used to draw conclusions concerning the mechanism of growth of helium bubbles in Cu. Because each time the annealing temperature is varied, both nucleation and growth of bubbles at T_a are simultaneously activated, and therefore their influence is mixed in the data.

We intended to obtain information on the mechanism of growth of helium bubbles in Cu in addition to the knowledge of their size and in parallel to our low temperature calorimetric investigations.

TEM specimens containing 2600 appm helium, identical with the calorimetry specimen were annealed isothermally at two different temperatures, namely $T_a = 1020$ K and $T_a = 1115$ K, and TEM data were taken and evaluated by means of our standard procedure of sec. 4.3.

Table III gives the annealing conditions, the average radii of bubbles and the widths (at half height) of their size distributions which have been obtained from these experiments. The size distributions themselves are given in fig.(5.9), see sec.5.4. We will discuss in detail the variation of $\bar{r}_b$ and the corresponding variation of the volume density of bubbles with t_a in a later section (sec.5.6.2)

T_a (K)	T_a/T_m	t_a (h)	$\bar{r}_b$ (Å)	Γ (Å)
1020	0.754	1	34.8	17
"	"	10	40.9	20
"	"	50	45.8	22
"	"	250	50.8	25
1115	0.824	1	66.1	31
"	"	11	76.6	34
"	"	50	82.3	37

Table III: Annealing conditions, average bubble radius, $\bar{r}_b$, and half-widths of the size distributions, Γ , obtained with specimens containing 2600 appm helium.

in relationship to the growth mechanism of bubbles.

As it can be seen from table III, the average size of the bubbles increased slowly with annealing time at both annealing temperatures. At $T_a = 1020$ K and $t_a = 1$ h it was $\bar{r}_b = 34.8$ Å, essentially the same to $\bar{r}_b = 37.1$ Å, obtained with the 1200 appm specimen after it had been annealed at $T_a = 1030$ K for $t_a = 2$ h. These average bubble radii correspond to specimens which showed for the first time the presence of a very small fraction of superfluid helium in bubbles in the heat capacity measurements, see fig.(5.2) and fig.(5.3). Thus they correlate very well with each other and with the thermodynamic state of helium in them. Moreover they are in excellent agreement with the prediction of an EOS (see sec.2.3) adequate for the description of dense helium in bubbles.

The steep increase of $\bar{r}_b$ observed by increasing the annealing temperature, table III, can be understood. A little too pronounced

appears, however, the increase of $\bar{r}_b$ observed at $T_a = 1115$ K between $t_a = 1$ h and $t_a = 11$ h. We notice that this increase was accompanied by a similarly pronounced increase of the heat capacity (see fig.(5.4)).

Apart from these details, by comparing the data of fig.(5.7) with that of table III, it can be seen that on an approximate scale which ignores the differences of the annealing programs the average bubble radii are very well comparable, although the concentration of helium differed by almost a factor of 3 in the specimens. This implies that there might be only a weak dependence of $\bar{r}_b$ on the helium concentration for the investigated concentrations.

5.2.2. A SEM observation.

As mentioned in section 5.1.2, our heat capacity specimen showed macroscopic openings along grain boundaries which at several places had developed to microcracks, after a final annealing at $T_a = 1115$ K for $t_a = 111$ h was given to it. Similarly, development of microcracks on 12 μm thick pure Cu specimens containing helium has been reported /68/ to take place above 900 K. Although the origin of this deterioration and the influence of helium on it is not yet clarified, it is reasonable to expect it to be correlated with very pronounced changes of the size of helium bubbles located at grain boundaries and their immediate neighborhood. To obtain more information on that point we examined three of our specimens containing 2600 appm helium in a Scanning Electron Microscope (SEM). They had been annealed at $T_a = 1115$ K for $t_a = 11, 50, \text{ and } 111$ h. To avoid surface characteristics we removed by electropolishing a 30 μm thick layer from the surfaces of the specimens and examined electropolished areas in the SEM. In all three cases a series of big

concave features was observed to decorate the full length of several grain boundaries, while other grain boundaries and the interior of the grains were free of them. These features are interpreted as grain boundary cavities containing helium. These "grain boundary bubbles" had a radius (deduced from SEM pictures) approaching $0.5\text{ }\mu\text{m}$ and therefore being more than one order of magnitude larger than that of typical bulk bubbles. This huge size-difference indicates that "grain boundary bubbles" are very unlikely to be equilibrium bubbles. Therefore it requires an effective mechanism leading to biased condensation of vacancies at grain boundaries in order to be reasonably explained. This biased flow of vacancies might be related to the tendency of the material for recrystallization and the accompanying flow or readjustment of grain boundaries. Otherwise, it is difficult to recognize the driving force of the process leading to such a pronounced size-difference in the absence of externally applied stress.

Independent of the origin of the anomalous growth of grain boundary bubbles, they offer the only possibility to explain the heat capacity peaks observed above 2 K in our last heat capacity measurements.

5.3. Determination of the amount of helium in our specimens.

In order to determine the amount of helium in our specimens with better accuracy than given by the beam current integrator, see sec.4.1, we have outgased several pieces of them after the heat capacity measurements were taken. The specimens were heated up to their melting temperature in an UHV outgasing apparatus equipped with a mass spectrometer. The apparatus /71/ had a detection limit of about 10^9 helium atoms. The released amount of helium was determined by measuring the partial pressure of helium during

heating the specimens.

The results of these experiments can be summarised as follows:

a) For specimens of both nominal helium concentrations the amount of released helium was substantially less than that nominally implanted, in both cases the same fraction ca.0.6.

The observed difference is however attributed to the fact that the really implanted amount of helium in the specimens was substantially less than that indicated by the beam-current integrator of the cyclotron. The difference might have been caused because the geometry of implantation was not optimally chosen.

b) The average helium concentration from TEM specimens annealed up to different final annealing temperatures and from the corresponding heat capacity specimens which had undergone the complete annealing program were the same. This observation provides additional support to the belief that release during annealing was negligible.

c) Slight differences in the concentration of helium were found among TEM specimens implanted with the same nominal helium concentration. They are attributed to minor inhomogeneities introduced by fluctuations of the beam current during implantation.

According to these results the real amount of helium in our specimens was:

1.19 μg for the "1200 appm" specimen

and 3.20 μg for the "2600 appm" specimen.

These masses will be used in the interpretation of our heat capacity results.

5.4. Interpretation of calorimetric observations.

Our calorimetric data are concerned with the low temperature behaviour of solid and liquid helium in spherical bubbles and focus mainly onto its superfluid transition along the λ -line of the phase diagram. They show pronounced modification of the form, the magnitude, and the temperature of the heat capacity peak of superfluid helium in bubbles. Although this modification originates mainly from the fact that liquid helium is confined effectively in all three dimensions, the influence and the variation of its pressure as well as the influence of substrate effects at low temperatures have to be taken in addition into account in a satisfactory interpretation of our observations. The pressure and the influence of the confinement vary simultaneously with the size of the bubbles and therefore have to be incorporated in a self-consistent description.

A basic fact of our experiments is that the size of the bubbles and therefore the density of dense helium gas in it change at the annealing temperature, while the influence of these parameters on the properties of condensed phases of helium is then detected below 10 K. Considerable attention has therefore to be paid to the evolution of the thermodynamic state of helium as taking place at T_a and how it is linked to the low temperature observations.

5.4.1. The thermodynamic state of helium in bubbles.

Annealing of our specimens should cause all helium to be collected in bubbles. Release of helium from bulk low-dose specimens becomes significant only in the immediate neighborhood of their melting point [72]. Therefore, we can assume that the total mass of helium in our specimens was constant throughout the experi-

ments presented in sec.5.1, but notice that our conclusions will not depend crucially on the fulfillment of this assumption.

For the conditions of our experiments (bulk low-dose specimens post-implantation annealing under zero external stress) the size and volume density of the bubbles and their variation is determined by the annealing conditions. At T_a the bubbles can grow, and, as our TEM results show, they did so in our specimens. Furthermore since the annealing temperatures of the specimens were sufficiently high it is reasonable to accept that the bubbles were at thermal equilibrium at T_a . The equilibrium condition, i.e. eq.(2.5), is rewritten here as:

$$r_b = 2 \gamma / P(n, T_a) \quad (5.3)$$

to emphasize that it gives a computed bubble radius provided that the density of helium, n , is known and can be inserted into eq.(2.9) to calculate the pressure, $P(n, T_a)$, of helium gas at T_a . Density to radius relationships for helium bubbles in Cu were presented in fig.(2.2) and show that the density of helium in bubbles decreases as their size increases. (In the calculation of the radius of bubbles in fig.(2.2) and in all calculations involving eq.(5.3) we will assume $\gamma = \gamma_{\text{bulk}}$).

Taking now into account that after any particular annealing step the bubbles in our specimens follow isochores (= const. density lines) as the specimen is cooled to low temperatures the link between the low temperature observations and the processes at T_a becomes obvious.

This condition is particularly useful because it provides the possibility to support our observations with thermodynamic calculations. Calculating, for example, the radius of bubbles by inserting into eq.(2.9) $T_a = 10^3$ K and a helium density of 0.2 gr/cm³ (max.

density of superfluid helium corrected for substrate effects, see later) we find $r_b = 43 \text{ \AA}$. This is to be compared to an average TEM-radius of $35 \text{ \AA}$ corresponding to the heat capacity measurements which showed for the first time superfluid helium in bubbles. The agreement of the two radii is better than it seems because bubbles contributing to the heat capacity peak at this stage belong to the high side of the size distributions, see fig.(5.9), and therefore have radius larger than the average.

The importance of this agreement extends, however, somewhat deeper and can be seen as follows:

- a) It shows clearly that bubbles of radius less than $40 \text{ \AA}$ should contain solid helium at low temperatures in agreement with our first calorimetric observations. That the heat capacity of solid helium was too small to be detected in $\bar{r}_b < 25 \text{ \AA}$ suggests strongly that it had a high Debye temperature and therefore it should have also high density, since these two parameters are related as: $\Theta_D \propto \rho^{2.6}$ [73]. The belief on the existence of high density helium in small bubbles in metals is thus supported for the first time by thermodynamic data which in addition were obtained from bulk specimens.
- b) Together with the smooth increase of the heat capacity of helium observed in subsequent experiments it demonstrates that our heat capacity data depict the behaviour of helium in bulk (and equilibrium) bubbles. Thus it establishes the comparability with our TEM results.

Fig.(5.9) shows measured size distributions of bubbles corresponding to samples of which the heat capacity data are shown in fig.(5.2)-(5.4). Calculated pressures along the interphase lines of the low temperature phase diagram of helium are given in the upper abscissa of fig.(5.9). They correspond to the bubble diameters of the lower abscissa and have been deduced from density-pressure data of bulk helium [74] along its melting and λ -line. The densities

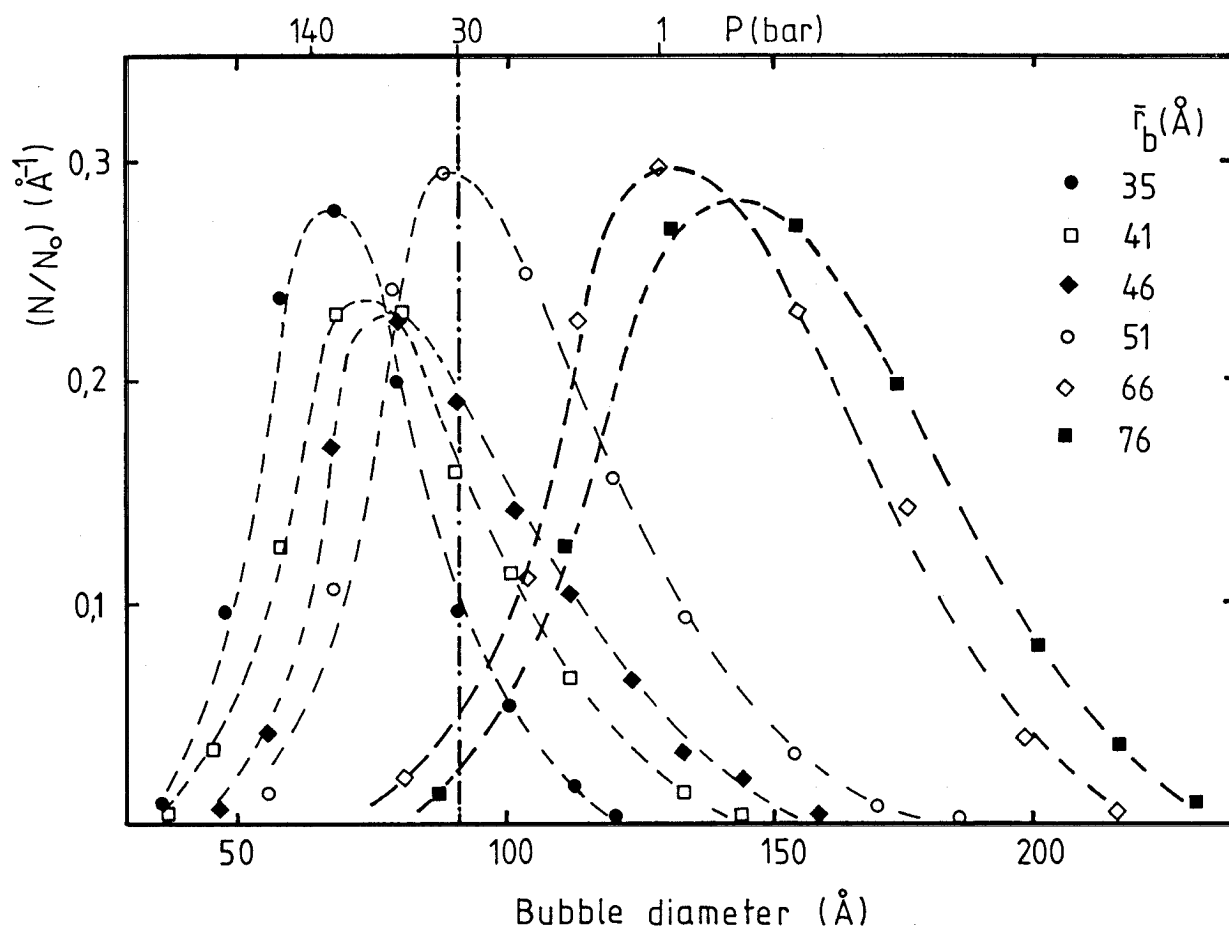


Fig.(5.9): Measured size distributions of bubbles. Upper abscissa gives calculated pressures of helium at low temperatures along the melting and λ -line of its phase diagram.

have been calculated by combining eq.(5.2) and eq.(2.9) (at $T_a = 1030$ K). Liquid helium densities were then found by assuming the existence of one dense monolayer of solid helium in contact to the surface of the bubbles at low temperatures.

The vertical dash-dotted line of fig.(5.9) at $86 \text{ \AA}$ corresponds to the pressure at the upper λ -point of the phase diagram of bulk helium, see fig.(3.1). According to fig.(5.9), the average pressure in the bubbles at low temperatures decreased and therefore progressively more bubbles passed to the liquid phase as the size of the bubbles increased. This plausible picture is in good qualitative agreement with the heat capacity data of fig.(5.3) which showed

melting as well as progressive development of the heat capacity peak of superfluid helium in bubbles. Furthermore fig.(5.9) shows that for $\bar{r}_b \geq 65 \text{ \AA}$ the fraction of bubbles filled with solid helium at low temperatures should be negligible and thus provides support to our argumentation of section 5.1.2 on the origin of the heat capacity peaks observed above 2 K for the last experiments of each series.

However, due to the Van der Waals substrate force a considerable fraction of helium in bubbles will be solid at low temperatures independent of the size of the bubbles and the density of the homogeneous gas phase in it at high temperatures. For confined helium under pressure neither is it established nor can it be decided from our data how large this fraction will be. In fact, experimental data on that point reveal two distinct cases. It has been observed /75/, for example, that solid helium nucleates easily at the confining walls of grafoil and has a pressure dependent thickness reaching several monolayers above 20 bar.

On the other hand, helium has been observed to remain liquid at pressures exceeding appreciably the bulk solidification pressure in vycor glass and fine powders /76/. Since there is no obvious criterion (at present) for one or the other behaviour, we will consider the influence of two solid monolayers on our data, whose existence and properties are well established from other investigations /77/ of confined helium at the liquid-gas equilibrium limit. Our choice is supported by the observation that solid helium does not wet the surfaces of Cu /78/.

The density of the first (second) monolayer will be taken to be

$\rho_{m1(2)} = 0.259 \text{ (0.183) gr/cm}^3$, respectively, and the same thickness of $d_s = 3.6 \text{ \AA}$ will be assumed for both /79/. The density of

liquid helium, ρ_l , in bubbles can then straightforwardly be calculated as

$$\rho_l = \{ \rho(T_a) - \rho_{m1}(1-(1-d_s/r_b)^3) - \rho_{m2}\{(1-d_s/r_b)^3 - (1-2d_s/r_b)^3\} \} (1-2d_s/r_b)^{-3} \quad (5.3)$$

by means of simple geometry and with $\rho(T_a)$ the density of the homogeneous gas phase calculated as described previously. This correction has been taken into account in deducing the pressures given in fig.(5.9). Substrate effects cause liquid helium to appear in bubbles at higher density than in the case of bulk helium. Enhanced densities for confined helium have been reported in other cases, e.g. /76/. Our calculated densities are in satisfactory agreement with those deduced for helium confined in vycor glass /80/.

5.4.2. A comparison of calorimetric observations from both specimens.

Fig.(5.10) shows heat capacity data of helium plotted against the average radius of the bubbles. Circles (diamonds) correspond to the specimen containing 1.19 (3.20) μg helium respectively. Filled symbols provide the magnitude of the heat capacity of helium at T_p , $C(T_p)$, while open ones the corresponding heat capacity at 2.5 K, $C(2.5 \text{ K})$. The $C(T_p)$ data include information on superfluidity and its geometry induced modification. On the other hand, although the temperature of 2.5 K is arbitrarily chosen, the $C(2.5 \text{ K})$ data show reliably the increase of the heat capacity of normal liquid (and solid) helium in bubbles as the latter has weak temperature dependence at temperatures above the superfluid peak, see fig.(5.2).

It can be seen from fig.(5.10) that both the $C(T_p)$ as well as the $C(2.5 \text{ K})$ data fall on the same lines for both specimens within their error. The measurements corresponding to $\bar{r}_b = 76 \text{ \AA}$ and $\bar{r}_b = 82 \text{ \AA}$

for the specimen of 3.20 μg helium constitute an exception needing examination in more detail. However, it can be rather safely stated on the basis of fig.(5.10) that for average bubble radii up to ca.70 $\text{\AA}$ the thermodynamic and superfluid state of helium in bubbles and their evolution with $\bar{r}_b$ were similar in both specimens. This similarity is important as it points to the fact that our heat capacity data have not been influenced by unwanted contributions of inherent or

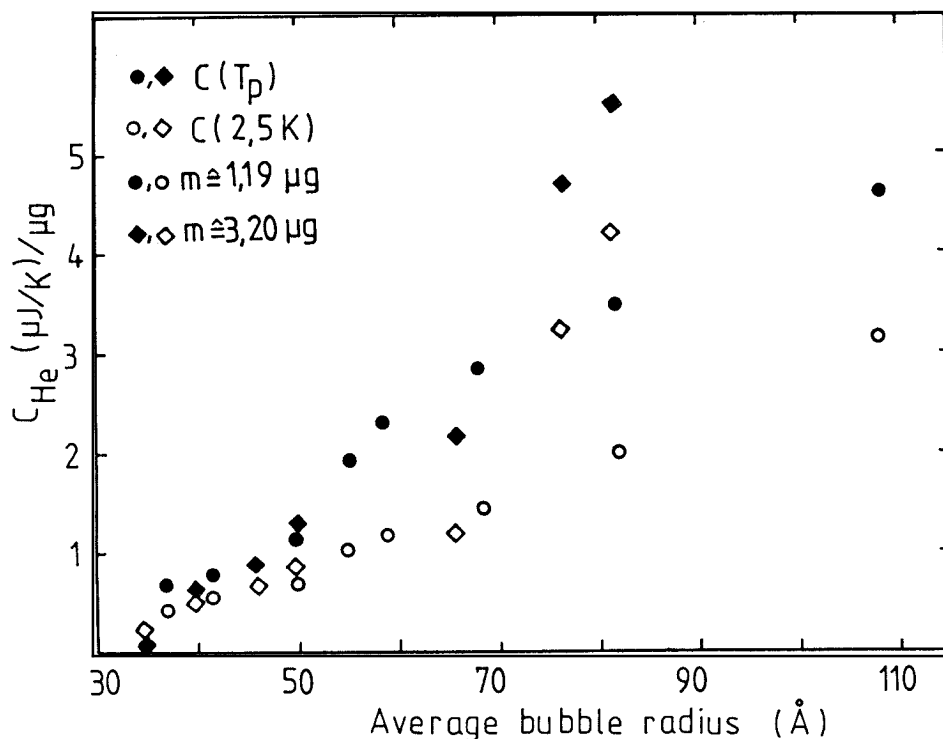


Fig.(5.10): Comparison of heat capacity data obtained from both our specimens. The magnitude of the heat capacity at T_p (filled symbols) and that at 2.5 K (open symbols) per μg helium mass are plotted vs. average bubble radius.

experimental origin. In combination with the agreement obtained by thermodynamic calculations (see previous section) it supports our belief that our heat capacity data depict the behaviour of helium in "bulk" bubbles in our specimens.

In fig.(5.2) we have plotted together with our data the heat

capacity of an equal mass of bulk liquid helium at SVP, which is known to have a λ -singularity at 2.172 K. It can be seen that as a result of the confinement the heat capacity peak of superfluid helium in bubbles remains finite and is depressed far below the bulk value.

In addition to the heat capacity data, the temperatures of the heat capacity peaks, T_p , of superfluid helium show similar behaviour with $\bar{r}_b$ for both our specimens. The heat capacity peak of superfluid helium has been observed first at around 1.80 K for both specimens.

5.5. Finite size aspects of superfluidity of helium in bubbles.

5.5.1. Remarks on the confining geometry.

The present work introduces the confining geometry of bubbles and used it in a detailed investigation of superfluidity of confined helium. Visual presentation of the bubble-geometry has been given in fig.(5.5). Here, attention will be paid to point out general features and differences of the confining geometry of bubbles in comparison to formerly investigated geometries. This is well justified by the fact that the confining geometry of bubbles is new, and has been developed on the basis of new concepts.

As it can be seen from fig.(5.5), the helium was confined in our investigations in spherical bubbles, whose radius was varied between $25 \text{ \AA}$ and $110 \text{ \AA}$. In this way we obtained a zero-dimensional (zero-D) and highly uniform confinement of helium. Both, zero-D and uniformity are desirable and to a great extent unique properties of our geometry.

The importance of uniformity of the confinement has been discus-

sed in section 3.1. In relationship to dimensionality it should be remarked that previous attempts to investigate the superfluid transition of helium in a zero-D confining geometry (:helium in fine powders /81/) were abandoned as it has been realized that sufficient information on the confining space could not be obtained in a satisfactory way. Thus, it is difficult to make quantitative comparisons of our observations with existing literature data. Intuitively it is however expected that the zero-D nature of our confining geometry will result in stronger modification of superfluid parameters of helium than in the corresponding 1-D and 2-D cases.

The salient and unique feature of the confining geometry of bubbles is, however, the zero connectivity of the bubbles. Each bubble in our specimen can be regarded as an extremely small Bose system consisting of about 10^4 helium atoms (!!). We have investigated the low temperature behaviour of an ensemble of such microscopic Bose systems that are completely isolated and therefore act independently of each other.

This illustrative picture can be considered as physical definition of the system of bubbles involved in our investigations. At the same time it emphasizes somewhat more the strict (and in some sense ideal) character of the confinement of helium in bubbles. This later statement becomes obvious by referring to former confining geometries, see section 3.1, which involved continuous helium specimens having at least one spatial extension extending to macroscopic distances.

It is obvious that any intrinsic length relevant to the properties of helium in the temperature range of our investigations is explicitly bound by the diameter of the bubbles, i.e., to less than $200 \text{ \AA}$. This constraint leads, of course, to modification of the superfluid

transition of helium in bubbles which underlines our heat capacity data. Noteworthy is further that by switching the superfluidity off one is left with an effectively restricted phonon fluid that can exhibit finite size behaviour /82/. It might do so already around 2 K where the dominant phonon wavelength of liquid helium is of the same order of magnitude as the size of the bubbles.

Nonetheless, the size of the bubbles was obtained in our investigations by a direct and accurate technique. Our procedure contrasts again fundamentally to absorption techniques and modeling assumptions formerly employed to obtain information on the confining dimension. A distinction is therefore necessary: The average size of the bubbles reported in this work is a directly evaluated statistical average, therefore free from any modeling of the system.

5.5.2. On the appearance of the heat capacity peak of superfluid helium in bubbles.

We can calculate the geometry-induced displacement, $\Delta T_{\lambda}(d)$, of the superfluid transition to lower temperatures by using eq.(3.7a). As discussed in a previous section, bubbles corresponding to the upper λ -point of the phase diagram of bulk helium have a radius of $43 \text{ \AA}$. Correcting this value for the existence of one (two) solid monolayers close to the surface of the bubble and then substituting into eq.(3.7a) we find $\Delta T_{\lambda}(d) = 0.10$ (0.12) K respectively. Consequently, the superfluid transition of helium in bubbles would be expected to appear first around 1.65 K, since the geometry and pressure induced displacements are expected to be simply additive. This simple estimation does not, however, take into account the displacement of the melting line /83/ of confined helium to higher pressures, see fig.3.1. In analogy with recent observations /84/ we

could have expected it to displace the transition to even lower temperatures, probably as low as 1.5 K.

In contrast to these expectations we observe that the heat capacity peak of superfluid helium in bubbles appears first around 1.80 K and develops at the first stages somewhat abruptly. (Notice, for example, that the average bubble radii (table III) for the first and second heat capacity measurements differ by less than two helium-monolayers).

In agreement with our observations, previous investigations of superfluidity of confined helium in bubbles /85/ as well as in vycor glass under pressure /86/ did not show heat capacity maxima below 1.80 K. They have however not been discussed.

To understand our observation we begin with the fact that a minimum mass of liquid helium (distributed in bubbles of different sizes) is needed before the heat capacity peak becomes observable. The biggest of them contribute more to the heat capacity because they contain more liquid mass under lower density and because they experience less the influence of the confinement. Thus, they dominate the heat capacity peak and can shift its temperature to higher values. However, the difference of 0.15 K between expected and observed T_p 's appears to us too big to be explained only by this biasing effect. For this reason we have examined other possible explanations.

We can rather well exclude that this retarded appearance of the superfluid heat capacity peak occurs as a result of the strong confinement of superfluid helium. Our argument can be expressed as follows: The "critical confining size" at which the heat capacity peak of superfluid helium disappears is known to be of the order of $10 \text{ \AA}$ for 2-D confined helium. A similar value has been deduced

from onset of superflow data /41/ on 1-D confined helium, which in addition was found to be independent of pressure. Thus, it appears unlikely that the corresponding "critical size" for zero-D confined helium would exceed much $10 \text{ \AA}$ and thus is considerably smaller than the radius of bubbles under consideration.

Substrate effects would be similarly irrelevant, provided that the thickness of the solid layer nucleated close to the surface of the bubbles is not pressure dependent. Otherwise, one would have /87/ 5 to 6 solid monolayers in bubbles considered here and therefore the fraction of the liquid-mass per bubble would be ca.10%.

This would, of course, make the observation of the heat capacity peak of superfluid helium in such bubbles extremely unfavorable. First because of the liquid-mass reduction, but furthermore because of indirect strengthening of the confinement which would result in further depression of the heat capacity peak. Within this picture one would then expect the development of the heat capacity peak of confined helium to be favored for lower-pressure bubbles and therefore its maximum be shifted to higher temperatures, as it is actually observed.

An important check for this interpretation can be seen as follows: The radius of equilibrium bubbles and the pressure (density) of liquid helium in it are related as described in section 5.4.1. By choosing metals of different surface energies it will therefore be possible to vary appreciably the radius of bubbles containing liquid helium under a given pressure. Thus, one will have the opportunity to vary the strength of the confinement (while keeping the influence of substrate effects constant) and examine more closely whether substrate effects indeed determine the appearance of the heat capacity peak of confined helium.

5.5.3. On the displacement of the superfluid transition to lower temperatures.

The temperatures of the heat capacity peaks, T_p , of superfluid helium in bubbles are plotted in fig.(5.11) versus average bubble radius. Different symbols in fig.(5.11) correspond to T_p 's obtained with different specimens. It can be seen that T_p increased in both cases with $\bar{r}_b$ and reached 2.01 ± 0.01 (2.05 ± 0.01) K for average bubble radii of 59 (66) $\text{\AA}$, respectively. These temperatures agree well to 2.03 K (deduced from fig.(2) of reference 55) at which the heat capacity peak of superfluid helium in bubbles in Al has been observed. They disagree with the corresponding temperature reported in ref./88/ for helium bubbles in Si.

As mentioned in section 5.1, we attribute the observed displacement of T_p to higher temperatures partly to the decrease of the average pressure of liquid helium in bubbles and partly to weakening of its confinement. For convenience we divide the discussion of our observations into: a) Interpretation of the observation $T_p = \text{const.}$ for $\bar{r}_b$ larger than ca. 60 $\text{\AA}$, and b) Discussion of the variation of T_p with $\bar{r}_b$.

to a): In this size range T_p changed randomly. A detailed explanation for this random variation cannot be offered. The average of these T_p 's is found to be 2.00 ± 0.03 K.

A qualitative interpretation of the observation that T_p did not further increase for $\bar{r}_b \geq 60 \text{\AA}$ can be given by taking into account that the pressure of liquid helium in bubbles (which is related to their size) plays in some sense the role of the driving force for the displacement of the heat capacity peak to higher temperatures. This statement can be easily understood by the fact that helium in growing bubbles reaches at some r_b (see later) the liquid-gas

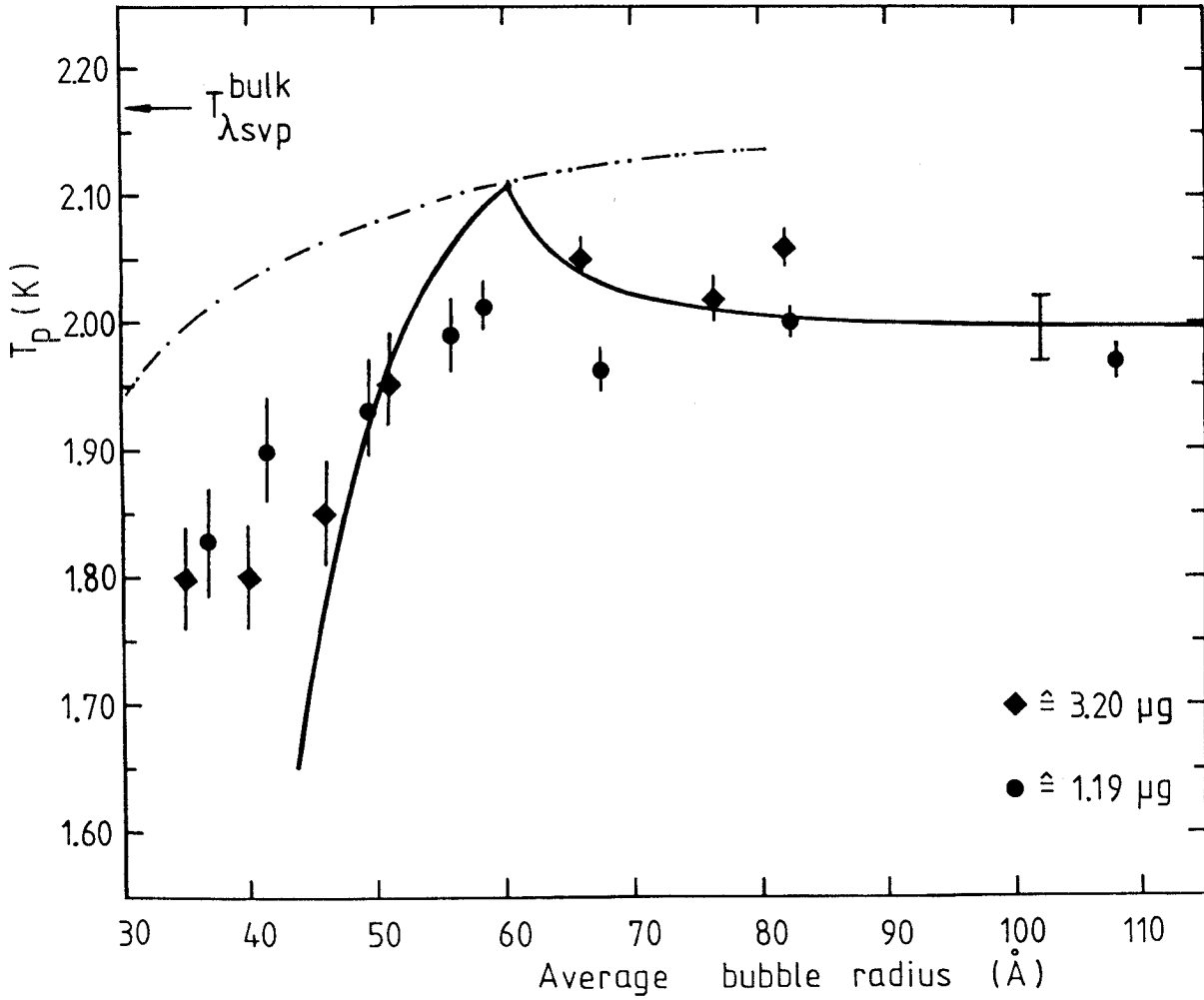


Fig.(5.11): Temperatures of the maximum of the heat capacity, T_p , plotted vs. average bubble radius. Different symbols account for data obtained with different specimens. Notice that all observed T_p 's are significantly lower than the λ -point of bulk helium at SVP. The continuous line shows calculated variation of the superfluid transition temperature and is discussed in the text.

equilibrium state. Bubbles exceeding this size start then becoming only partly filled with liquid helium at low temperatures. At this state, liquid helium experiences only the influence of the confinement whose strength is determined by the spatial extension of the liquid-filled part of the bubbles. This dimension, however, becomes progressively smaller than the increasing geometric size of the

bubbles. Therefore, displacement of T_p to higher temperatures ceases.

Within this interpretation the highest T_p 's observed in our investigations correspond to the liquid-gas equilibrium state, established in bubbles contributing dominantly to the heat capacity peak of superfluid helium. In subsequent experiments, involving bigger bubbles, the relevant size for the superfluid properties ("effective confining dimension") became different than the average size of the bubbles. The position of T_p on the temperature axis should therefore be determined by two counteracting contributions:

- a) The contribution of smaller bubbles of the size distribution (predominant bubbles) containing still liquid helium under pressure and therefore tending to displace T_p to higher temperatures, and
- b) An opposite contribution from larger progressively emptying bubbles.

To provide support to this interpretation we have calculated the radius of bubbles corresponding to the liquid-gas equilibrium limit by means of the procedure described in section 5.4.1. It is found to be ca. $60 \text{ \AA}$, and is thus in good agreement with our observations.

The above interpretation leads to the following implications:

- a) The differences of $(T_{\lambda \text{ SVP}} - T_p)$ corresponding to average bubble radii of $59 \text{ \AA}$ and $66 \text{ \AA}$ represent the geometry-induced displacement of the superfluid transition to lower temperatures and therefore should agree with the prediction of eq.(3.7a). They do not however do so. The observed displacement is larger by a factor of ca. 3 in both cases. This disagreement is not understood. We notice that in order to eliminate it we would have to use as confining dimension $\bar{r}_b/2$ in eq.(3.7a). This effective confining dimension is surprisingly small. First because it is only half of the average bubble radius,

but in addition because the dominant bubbles are likely to have radius larger than the average, see sec.5.5.2.

b) The difference between the highest observed T_p 's for the two specimens might be attributed to the random variation of T_p 's. It can also be due to differences of the annealing program to which the specimens were subjected. In that case it is apparent that the liquid-gas equilibrium state was established in the second specimen in larger bubbles.

c) Measurements corresponding to $\bar{r}_b > 60 \text{ \AA}$ involved a mixed confining geometry in the sense that, as described above, bubbles full of liquid helium as well as helium films condensed on bubble surfaces existed in the specimen. This mixing (or progressively occurring crossover from zero-D to 2-D confined helium) is however believed not to have influenced the behaviour of T_p in a particular way. In more detail, spherical shells of condensed helium in bubbles might be regarded as quasi-zero-D confined helium behaving not differently than bubbles full of liquid helium. This is because the thickness of these films should not be much smaller than their lateral extension. The latter can be indirectly concluded by the fact that the heat capacity peaks for the last experiments, see, for example, fig.(5.2), did not show additional broadening. The same conclusion can be drawn from calculations of the thickness of such films. As it will be seen later, under the assumption that the bubbles were at thermal equilibrium at the annealing temperature, the thickness of such films should be of the order of $30 \text{ \AA}$.

to b): Taking as a reference the λ -point of bulk superfluid helium at SVP, the observed displacement of the superfluid transition, $\Delta T_\lambda^{\text{ob.}}$ ($= T_{\lambda \text{ SVP}} - T_p$), might be written as the sum of two contributions, namely:

$$\Delta T_\lambda^{\text{ob.}} = \Delta T_\lambda(P) + \Delta T_\lambda(d) \quad (5.4)$$

where $\Delta T_{\lambda}(d)$ is the geometry-induced displacement, and $\Delta T_{\lambda}(P)$ the corresponding contribution due to the pressure.

According to sec.3.2, $\Delta T_{\lambda}(d)$ should vary as $d^{-3/2}$, where d is:

- a) The radius of bubbles determining T_p , properly corrected for substrate effects. d increases with $\bar{r}_b$, for $\bar{r}_b < 60 \text{ \AA}$ and therefore $\Delta T_{\lambda}(d)$ should decrease.
- b) For average bubble radii above $60 \text{ \AA}$, d is the thickness of liquid helium films. As discussed above, it can become considerably less than the geometric size of the bubbles. It finally becomes almost independent of $\bar{r}_b$ (at large $\bar{r}_b$), resulting in constant $\Delta T_{\lambda}(d)$.

According to fig.(5.9), the size distribution of bubbles results in a broad spectrum of liquid helium pressures in bubbles contributing to the superfluid heat capacity peak. The dash-dotted line of fig.(5.11) shows how the temperature of the transition would vary if $\Delta T_{\lambda}(P)$ were zero. It has been calculated from eq.(3.7a) by accepting two monolayers of solid helium. It makes clear that $\Delta T_{\lambda}(P)$ cannot be omitted. On the other hand, it cannot be deduced directly. However, since the average pressure of liquid helium decreases as $\bar{r}_b$ grows, $\Delta T_{\lambda}(P)$ should also decrease, becoming zero for $\bar{r}_b$ above $60 \text{ \AA}$.

We have attempted to understand quantitatively the behaviour of $T^{ob.}$ by means of a calculation involving no free parameter. It is based on the density-radius relationship (established by means of combination of eq.(5.2) and eq.(2.9)) which was computed for the annealing temperatures involved in our experiments.

Proceeding as described in sec.5.4 we calculated the density of liquid helium in bubbles of various radii less than $65 \text{ \AA}$. Next, we

deduced the pressure-induced displacement of the superfluid transition, $\Delta T_{\lambda}(P)$, by using the phase diagram of bulk helium and calculated the corresponding geometry-induced displacement, $\Delta T_{\lambda}(d)$, by using eq.(3.7a).

For $\bar{r}_b > 60 \text{ \AA}$, on the other hand, it has been assumed that helium condenses to uniform films in bubbles at low temperatures. Their thickness was calculated by using simple geometry and by assuming a solid monolayer of density 0.259 g/cm^3 and a density of 0.147 g/cm^3 (saturation density of bulk liquid) for the liquid part. Calculated film thicknesses range between $35.5 \text{ (30.6) \AA}$ for $\bar{r}_b$ of $70 \text{ (105) \AA}$, respectively. Knowing the thickness we applied eq.(3.7a) to calculate $\Delta T_{\lambda}(d)$, after a monolayer of solid helium was subtracted.

The result of this calculation is shown in fig.(5.11) together with the observed T_p data. The variation of the transition temperature to the superfluid state with $\bar{r}_b$ is shown as continuous line. The dash-double dotted line shows how it would vary if the bubbles remained full of liquid helium at the liquid-gas equilibrium limit. The "error bar" in fig.(5.11) shows upper and lowest positions of the calculated curve, obtained if T_a is taken to be $1 \text{ (1.2) } 10^3 \text{ K}$, respectively.

It can be seen that there is a very satisfactory agreement to the observed T_p data. Seemingly the calculation predicts faster increase of the transition temperature at small $\bar{r}_b$ than observed. This is not a real difference. It is due to the fact that the calculation takes into account the behaviour of the average bubble, while the experimental data concern bubbles containing liquid helium.

For average bubble radii above $80 \text{ \AA}$ the calculated transition temperature varies only slightly with $\bar{r}_b$, as a result of the weak dependence of the thickness of the films on $\bar{r}_b$. This weak depen-

dence implies that the size distribution of the confining dimensions becomes progressively strongly peaked. The calculation, for example, shows that for $\bar{r}_b$ between $10^2 \text{ \AA}$ and $10^3 \text{ \AA}$ the thickness of helium films decreases by only ca. $3 \text{ \AA}$, approaching the limiting thickness, $d_{lim.}$, given by eq.(5.2).

An important implication of the evolution of the system (as it is revealed by our calculation) can be seen as follows: Although the thickness of the films for $\bar{r}_b$ above $100 \text{ \AA}$ is practically constant, their lateral extension increases as $\bar{r}_b$. Thus the system will progressively approach true 2-D behaviour. Investigation of this system might therefore reveal whether and how crossover effects to the 2-D behaviour manifest themselves in a calorimetric study. We notice that such an observation will be greatly favored by the very high homogeneity of the confinement mentioned above.

5.5.4. On the magnitude of the heat capacity of helium in bubbles.

The data of figs.(5.2)-(5.4) show that the (constant-volume) heat capacity of helium confined in bubbles increased with the size of the bubbles in the whole temperature range of measurements. They involve solid and liquid helium. Solid helium (solid-filled bubbles in the first experiments or as a solid monolayer in later ones) adds a small contribution to the heat capacity. Apart from its heat of melting, depicted most clearly by the data of fig.(5.3), solid helium is otherwise negligible. Therefore, the heat capacity data is dominated by the contribution of the liquid phase, to which we concentrate next.

We have not observed any truncation sign of the heat capacity peaks of superfluid helium, although we have a very homogeneous confining geometry. Thus our observations do not favor the inter-

pretation of the truncated heat capacity peaks of liquid helium films of comparable thickness condensed on grafoil /89/ which were related to the homogeneity of the confinement.

The main factors considered to account for the increase of the heat capacity peak of superfluid helium in bubbles are:

- a) Progressive increase of the mass of liquid helium with the size of the bubbles. According to our TEM data, see for example fig.(5.9), the number of bubbles filled with solid helium should be very small in our specimens for measurements above $\bar{r}_b^0 = 60 \text{ \AA}$. The increase of the mass of liquid helium in these experiments should therefore be limited to the change of the mass of the second monolayer.
- b) As $\bar{r}_b^0$ increases up to ca. $60 \text{ \AA}$, the confining dimension of liquid helium in bubbles increases, resulting in growth (and sharpening) of the heat capacity peak. The maximum of the heat capacity for this purely superfluidity-related increase is predicted by the theory (see. sec.3.2) to vary as in eq.(3.12).
- c) In addition, decrease of the pressure of liquid helium in bubbles can also be expected to cause an increase of the heat capacity peak. Experimentally, the relative importance of this contribution for confined helium is not well established.

For measurements corresponding to $\bar{r}_b^0 > 60 \text{ \AA}$ the magnitude of the heat capacity at the peak temperature, $C(T_p)$, increased by a factor of ca.2 for both our specimens. For the same measurements T_p remained constant at $2.00 \pm 0.03 \text{ K}$.

This increase of $C(T_p)$ with $\bar{r}_b^0$ is very unlikely to be due to weakening of the confinement of superfluid helium in bubbles, despite the fact that it varies as eq.(3.12) predicts. Strong evidence for this assertion is provided by the fact, that, as the data of fig.(5.2) most clearly show, successive heat capacity curves appear displaced upwards almost parallel from each other. Thus, the $C(T_p)$ data

involve a variable "background" which is irrelevant to superfluidity of helium in bubbles. Subtracting this "background" from the heat capacity data at T_p we find that the magnitude of the heat capacity anomaly due to superfluid helium increased with $\bar{r}_b$ up to ca. $60 \text{ \AA}$ and then remained roughly constant. This can also be seen from fig.(5.10) by observing that the distance between the filled and open symbols at the same $\bar{r}_b$ did not appreciably change above $60 \text{ \AA}$. This behaviour supports our assertion. It might be interpreted as showing that the effective confining dimension of superfluid helium did remain roughly constant for $\bar{r}_b > 60 \text{ \AA}$, in agreement with the observation $T_p = \text{const.}$, and our calculation presented in the previous subsection.

To identify the origin of the "background" increase, we briefly discuss the increase of the heat capacity at temperatures above the superfluid peak. In this temperature range the mass of liquid helium and its density (and their variation with $\bar{r}_b$) are of most importance, and should account for the observed increase of the heat capacity. Specifically for the measurements with $\bar{r}_b > 60 \text{ \AA}$ the decrease of the density of liquid helium in small bubbles of the size distribution is considered to be the dominant contribution to the observed increase of the heat capacity. The same conclusion can be drawn by observing that the heat capacity curves, see fig.(5.2) show a clear tendency to approach each other below the peak, and comparing this behaviour to heat capacity data of bulk helium.

As it can be seen from fig.(5.2) and fig.(5.4) the last heat capacity measurements of each series (except the measurement after $T_a = 1115 \text{ K}$ and $t_a = 50 \text{ h}$) tend to meet at around 5 K . This important feature might be understood by taking into account that as the temperature rises, helium in bubbles becomes a homogeneous classical fluid. Its constant-volume specific heat would then tend to

reach a temperature independent value, which, for bulk helium under low pressure, is reached at around 10 K and equals 12.5 (J/mole K). If we deduce the corresponding value of the specific heat from our data we find it to be, for both investigated specimens, ca.9 (J/mole K). The difference can be attributed either to the fact that at 5 K the limiting value of the specific heat has not been yet reached and/or to the fact that the first monolayer should not contribute effectively since it is expected to melt at higher temperature /63/ than 5 K.

5.6. Additional aspects of our observations.

In previous sections we have concentrated to the low temperature behaviour of helium in bubbles and in particular to modifications of its superfluid properties. In this section we discuss additional aspects of our observations. We compare first thermodynamic parameters of helium in bubbles with theoretical prediction and other observations. Then our observations on the growth of helium bubbles in Cu will be discussed.

5.6.1. The density and pressure of helium in bubbles.

Our calorimetric observations can be viewed as providing quantitative information on the thermodynamic state of helium in bubbles in a metal. In that respect they are the first extensive data based on thermodynamic observations. Furthermore, our investigations involve "bulk" bubbles and in addition extend to considerably larger bubble-radii than other experimental investigations of the density of helium in bubbles in metals (see sec.2.3). It is therefore of considerable importance to examine our observations under this point of view and compare them to the predicted thermodynamic state of dense helium in bubbles.

Our observations show unambiguously that helium condensed to solid at low temperatures in bubbles of average radius less than $35 \text{ \AA}$. Solid helium in bubbles smaller than $25 \text{ \AA}$ should have high density. Thus, these first observations strengthen the belief that the density of helium in small bubbles exceeds greatly the density of liquid helium.

In bubbles larger than $35 \text{ \AA}$ helium has been observed to undergo the transition to the superfluid state along the λ -line of its phase

diagram, fig.3.1.

Fig.(5.12) summarizes our data on the density of helium and shows its variation with the average bubble radius. The density has been deduced by using the temperatures of the heat capacity peaks and the low temperature phase diagram of bulk helium. Symbols of different shape in fig.(5.12) correspond to data obtained with specimens containing different helium concentrations. Filled circles

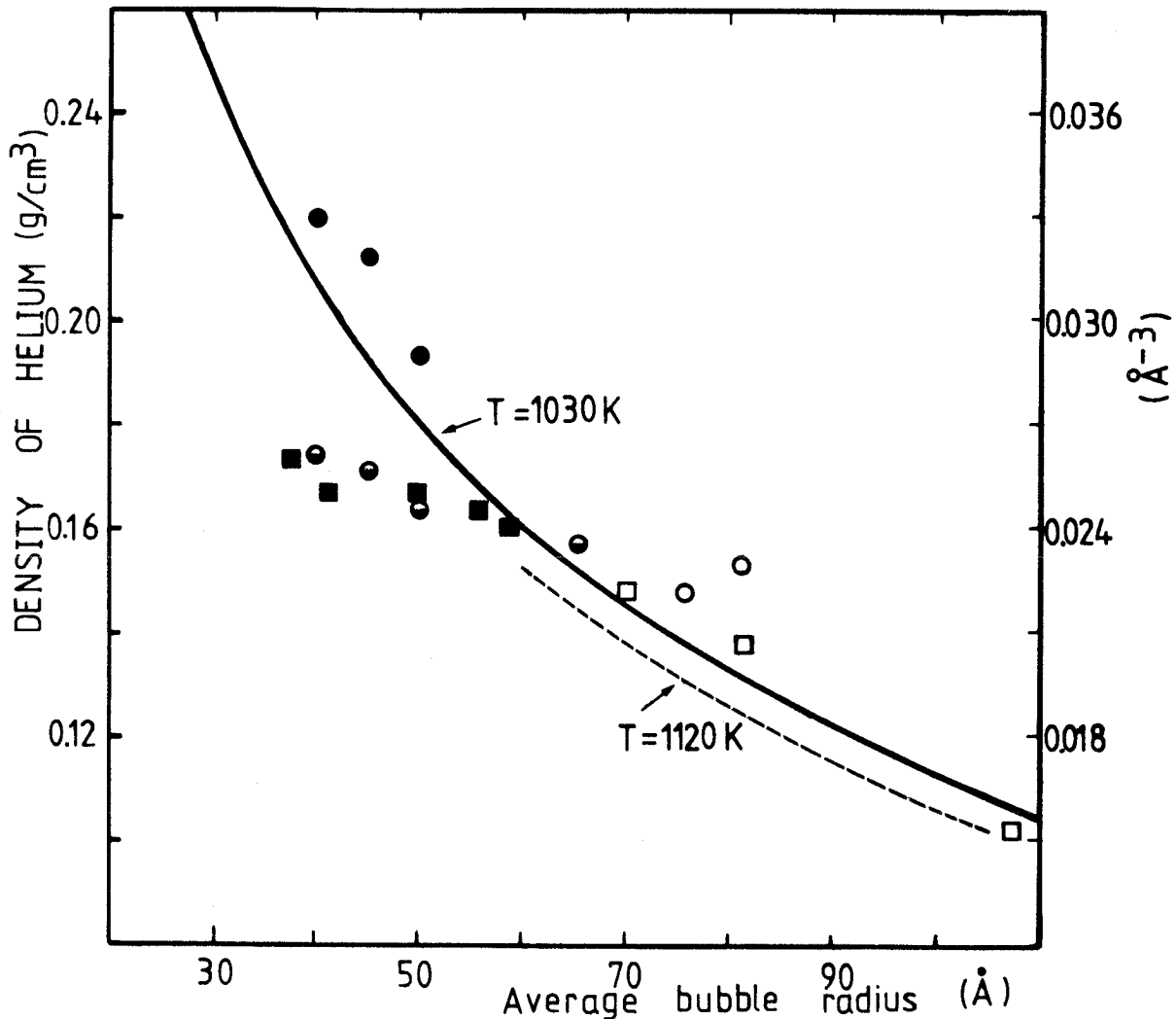


Fig.(5.12): Density of helium in bubbles as deduced from the heat capacity data vs. average bubble radius. The curves shown are predicted by an EOS for dense helium and are discussed in the text.

show the average of the density of solid and superfluid helium corresponding to the heat capacity data of fig.(5.3). All other points correspond to the superfluid transition of helium whose temperature was corrected (with the help of eq.(3.7a)) for its geometry induced displacement (see sec.5.5) to lower temperatures.

To obtain the helium-gas density for measurements involving bubbles only partly filled with liquid helium at low temperatures (open symbols in fig.(5.12)) we proceeded inversely as in sec.5.5.4. We assumed validity of eq.(3.7a) and applied it to deduce the thickness of liquid helium films condensed on bubble surfaces at low temperatures. The density of the homogeneous gas phase at high temperatures was then calculated by means of simple geometry. In this calculation we used a density of 0.147 (0.259) g/cm³ for the liquid part (the solid monolayer), respectively.

Together with our data we include in fig.(5.12) the variation of the density of helium with $\bar{r}_b$ as predicted by an EOS (eq.(2.9)) (continuous line). This curve was computed by assuming equilibrium bubbles at $T = 1030$ K and therefore applies to observed data below $\bar{r}_b = 60 \text{ \AA}$. The dashed line is the corresponding isotherm at $T = 1120$ K.

It can be seen that the agreement between predicted and deduced densities appears to be very satisfactory in the whole radii range. Such a nice agreement might in fact be surprising in view of uncertainties related to the strong modification of the properties of solid and liquid helium in bubbles. It is, however, at least partly justified by the fact that the low temperature properties of condensed phases of helium are strong functions of its density. For example, the density of liquid helium changes by only ca.20 % along the λ -line of its phase diagram.

In good agreement to the observed data of fig.(5.12) are also

calculated values for the average density of helium obtained from combination of the TEM data and the mass of helium in the specimens.

The deviation of the observed densities for $\bar{r}_b \lesssim 50 \text{ \AA}$ (closed squares and half-filled circles) to lower values than predicted can be easily understood. It is mainly due to the fact that the corresponding heat capacity peaks were produced by bubbles of radius larger than the average radius of the corresponding size distributions (cf. fig.(5.9). Thus, these particular points provide a measure of the density of (liquid) helium biased to lower values in respect to the average density. If they are corrected by deducing an average radius for liquid-filled bubbles, see fig.(5.9), they come into close agreement to the plotted isotherm. Alternatively, one would have to average the density of solid and liquid helium in bubbles, as applied for the filled circles of fig.(5.12). The tendency shown by these later points to lie slightly above the predicted values is within the expected uncertainty, introduced mainly by the modification of the low temperature phase diagram of helium which is only approximately taken into account in deducing the densities.

The results of other experimental investigations do not overlap with the data of fig.(5.12). Most close to our data lies the measured density of $0.040 \text{ \AA}^{-3}$, obtained by the EELS investigation /17/ for helium bubbles of $\bar{r}_b = 25 \text{ \AA}$ in an Al foil. It corresponds roughly to the upper left corner of fig.(5.12) and thus seems to be in good agreement to our observations. An upper limit for the density of helium in bubbles in Cu has been reported /68/ to be ca.0.50 of the atomic density of Cu at $\bar{r}_b$ around $40 \text{ \AA}$. From our data we deduce it to be ca.0.30 for bubbles of comparable size. The difference might be due to the experimental procedure used to obtain the density and the bubble radius (cf. discussion in sec.

5.2.1).

Calculated low-temperature pressures of helium in bubbles were given in the upper abscissa of fig.(5.9). The pressure of the dense gas at T_a can be obtained either from eq.(2.5) or by eq.(2.9). It is found to range between 10 (3) Kbar in bubbles of $\bar{r}_b \approx 35$ (100) Å. It might however be more representative to provide the pressure in the bubbles at $T = 300$ K. Calculating it by eq.(2.9) where we insert measured densities of fig.(5.12) it is found to range between 4.5 to 1.3 Kbar for the same bubble radii as above.

5.6.2. On the growth mechanism of helium bubbles in Cu.

The time dependence of the average radius of bubbles for the data of table III (isothermal annealing) is shown in fig.(5.13) in a

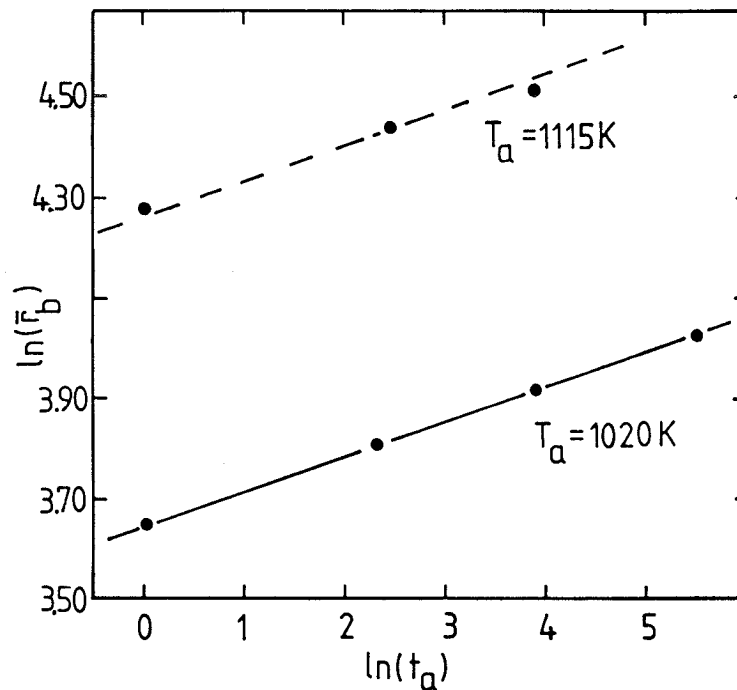


Fig.(5.13): Time dependence of the average radius, $\bar{r}_b$, of helium bubbles in Cu for isothermal annealing experiments at $T_a = 1020$ K and $T_a = 1115$ K. The concentration of helium in the specimens was 1700 appm.

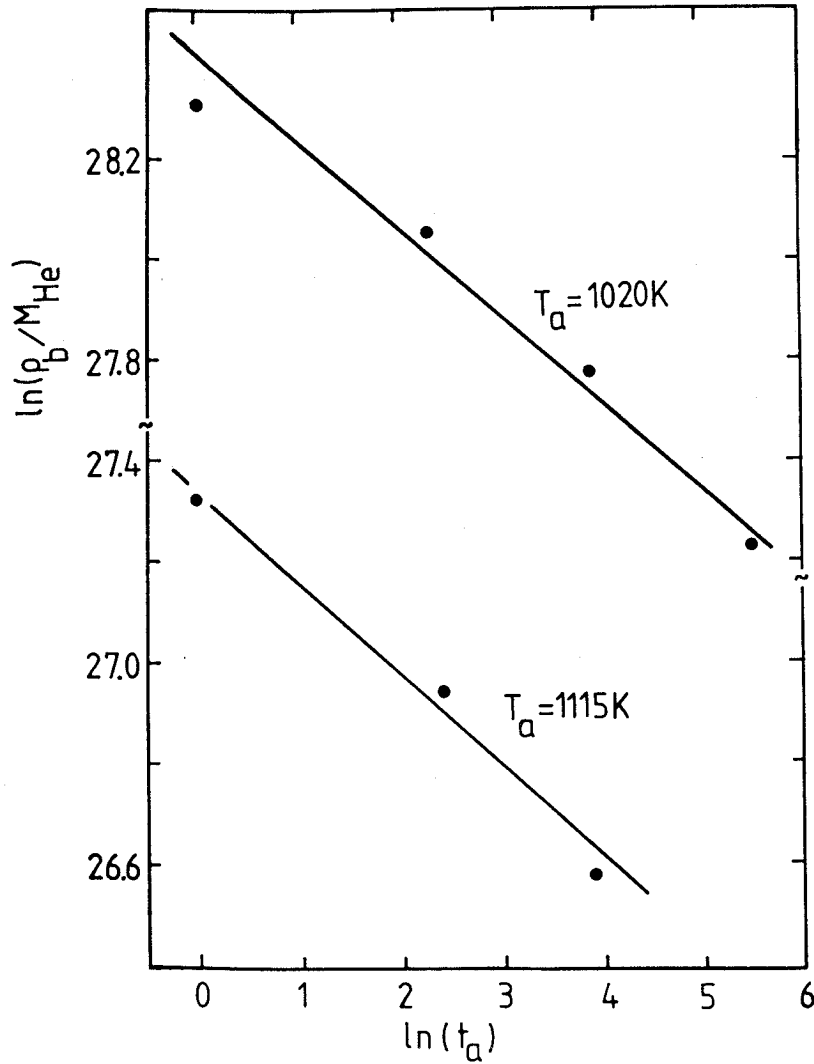


Fig.(5.14): Time dependence of the volume density of helium bubbles for isothermal annealing experiments at $T_a = 1020$ K and $T_a = 1115$ K. The concentration of helium in the specimens was 1700 appm.

log-log plot. It can be seen that the data obtained at both investigated annealing temperatures fall on parallel straight lines whose slope is 0.07. This slope is considerably less than that corresponding to the largest possible growth exponent ($z = 5$) allowed by the growth mechanisms described in sec. 2.3.

The volume density of the bubbles divided by the concentration of helium, M_{He} , in the specimens, for the same specimens as that used to obtain the data of Fig.(5.13) is plotted in fig.(5.14) vs.

annealing time. The concentration of helium was obtained by outgassing each specimen separately as described in sec.5.3. Such a plot eliminates scattering of the measured ρ_b values (caused by minor differences of M_{He} in the specimens) without introducing further complications.

The slope of the straight lines of fig.(5.14) is 0.15, again much smaller than the smallest slope allowed by eq.(2.6b). Thus, the slopes deduced from the data of figs.(5.13)-(5.14) indicate much slower time dependence of $\bar{r}_b$ and ρ_b than expected by eq.(2.6)-(2.7). It should however be remarked that these data involve bubbles containing dense helium, which has been observed to solidify or condense to liquid at low temperatures (see sec.5.1.2). Therefore its thermodynamic state at T_a was far from being an ideal gas, as assumed in the derivation of eq.(2.6)-(2.7).

The observed slopes are in qualitative agreement to theoretical prediction concerning the growth of "non-ideal" helium bubbles in metals mentioned already in sec.2.2. It is predicted /5,14/ that the logarithmic slope of $\bar{r}_b$ should have values ranging between 1/6 (or even less) to 1/3 for growth by migration and coalescence, depending on the details of the mechanism. Furthermore, similarly small slope is predicted for growth by Ostwald ripening. The slope of ρ_b should then be similarly modified, since ρ_b is directly related to $\bar{r}_b$.

The fact that the observed slope for ρ_b is roughly twice as large as that for $\bar{r}_b$ can be satisfied by both growth mechanisms, migration and coalescence through volume diffusion and Ostwald ripening. Thus, on the basis of the observed slopes it is impossible to distinguish which mechanism is operating. On the other hand, the measured size distributions of bubbles, see, for example, fig.(5.9), do not follow the relationship $r_m = 2 \bar{r}_b$ at small $\bar{r}_b$ and therefore seem (at least) to allow mixing of both mechanisms.

In former investigations /90/ helium bubbles in Cu have been directly observed to migrate and coalesce. This information cannot however be considered as reliable indication in favor of growth by migration and coalescence. Owing to differences in the experimental procedure (annealing of thin foils or pulse-annealing in situ in a TEM) but on the other hand to the considerably larger bubbles involved, these observations are not directly comparable to ours.

A quantitative investigation of the growth of small helium bubbles in stainless steel /14/ showed deviating growth exponents from their expected values. In that case, however, the deviations were probably not so pronounced as in our case.

In summary, our data seem to emphasize the necessity of applying other criteria for the deduction of the mechanism of growth of helium bubbles in Cu. Such criteria have been already discussed in the literature /5/.

6. SYNOPSIS AND PROSPECTS.

We have introduced helium in pure Cu specimens (100 μm thick) by implanting them homogeneously with α -particles at room temperature. Due to the extremely low solubility of helium in metals, it precipitated in bubbles whose size was varied by post-implantation annealing of the specimens at temperatures, T_a , ranging between 830 K and 1200 K.

Phase transitions of helium in bubbles of average radius between 35 $\text{\AA}$ and 110 $\text{\AA}$, and in particular its transition to the superfluid state were investigated by means of heat capacity measurements between 1.4 K and 5 K. In parallel, the average radius, the size distribution, and the volume density of the bubbles were measured by transmission electron microscope investigations.

Specimens implanted at two different helium concentrations were investigated. The total mass of helium in the specimens was a few μg . Therefore, in order to be able to measure its heat capacity we have constructed a sensitive small-specimen calorimeter, capable of measuring the heat capacity of a few nmole of superfluid helium.

Our calorimetric observations indicate that helium condenses to solid in bubbles of average radius less than 35 $\text{\AA}$. In larger bubbles, it liquifies and undergoes the transition to the superfluid state along the λ -line of its phase diagram. At an average bubble radius of ca. 60 $\text{\AA}$ helium reaches the liquid-gas equilibrium state. We have observed strong modification of the form, the magnitude, and the temperature of the superfluid transition of helium in bubbles relative to the behaviour of bulk helium. The heat capacity peak of superfluid helium in bubbles appears rounded, and is depressed far below the bulk value. It appears first at 1.80 K (for

$\bar{r}_b = 35 \text{ \AA}$) and is then displaced to higher temperatures up to 2.00 K ($\bar{r}_b = 60 \text{ \AA}$) where it remains approximately constant. These modifications are attributed to the influence of the finite size of the bubbles on the superfluid transition of helium (i.e. finite size effects). They are in qualitative agreement with the results of investigations of confined helium in other confining geometries.

The geometry of bubbles is a new confining geometry, introduced in this work for the first time. As pointed out in sec.5.5.1 it possesses several desirable and unique features for investigations of confined helium. In brief, it offers the possibility to study properties of an ensemble of extremely small Bose "particles" of spherical shape which are completely isolated from each other. Thus, this geometry creates the first true and highly homogeneous zero-dimensional confinement of helium.

In addition, as we show, the radius and size distribution of bubbles can be known with considerably better accuracy than in formerly investigated confining geometries.

To interpret our observations we have assumed that the bubbles were at thermal equilibrium at the annealing temperature. At low temperatures we took into account for the existence of two solid monolayers of helium nucleated close to the surface of the bubbles. We were able to support our calorimetric observations with thermodynamic calculations based on an EOS for "superdense" helium in bubbles and our TEM data. Within this interpretation we also calculated the temperature of the superfluid transition of helium as function of the average radius of bubbles. For the geometry-induced displacement of the superfluid transition we applied the mean field description of Ginzburg-Pitaevskii-Mamaladze (GPM).

The calculated transition temperatures are in satisfactory agreement with our observations.

Of course, this work cannot (and should not) be considered as completed. In contrast, it opens new questions and, as we believe, it can offer several new possibilities for investigations of properties of confined systems.

First, it would be important to investigate the superfluid properties of helium in bubbles in a metal of different surface energy than that of Cu, in order to identify why the heat capacity peak of superfluid helium appears first at a considerably higher temperature than expected. Further one might attempt to understand the random variation of the temperature of the heat capacity peak and examine in more detail the origin of the discrepancy between the prediction of the GPM model and the observed behaviour as the bubbles reach the liquid-gas equilibrium state.

A straightforward extension of our investigations would be to measure the heat capacity of liquid helium in bubbles at still lower temperatures, i.e., $T < 1.5$ K. One expects, namely, that the only possible thermal excitations (phonons) will "freeze" progressively as the temperature is lowered. According to theoretical prediction /82/ the heat capacity would tend to become temperature independent for this zero-D system.

There seems to be considerable freedom for varying parameters important for the properties of such a system. Choosing a different metal, different implantation conditions, and/or a different gas in the bubbles, one might have the possibility to investigate properties of various homogeneously confined systems in all three dimensions.

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