# PHYSICAL REVIEW B

## CONDENSED MATTER AND MATERIALS PHYSICS

**THIRD SERIES, VOLUME 59, NUMBER 17** **1 MAY 1999-I**


## BRIEF REPORTS

*Brief Reports are accounts of completed research which, while meeting the usual* **Physical Review B** *standards of scientific quality, do not warrant regular articles. A Brief Report may be no longer than four printed pages and must be accompanied by an abstract. The same publication schedule as for regular articles is followed, and page proofs are sent to authors.*

---

# Temperature dependence of the diffuse-scattering fine structure in equiatomic CuAu


O. Malis and K. F. Ludwig, Jr.
*Department of Physics, Boston University, Boston, Massachusetts 02215*

W. Schweika
*Forschungszentrum Jülich, Jülich, Germany*

G. E. Ice and C. J. Sparks
*Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830*



(Received 23 October 1998)



The temperature dependence of the diffuse-scattering fine structure from disordered equiatomic CuAu is studied using *in situ* x-ray scattering. In contrast to $Cu_3Au$ the diffuse peak splitting in CuAu is found to be relatively insensitive to temperature. Consequently, no evidence for a divergence of the antiphase length-scale at the transition temperature is found. At all temperatures studied the peak splitting is smaller than the value corresponding to the CuAuII modulated phase. An extended Ginzburg-Landau approach is used to analyze the temperature dependence of the diffuse peak profiles in the ordering and modulation directions. The estimated mean-field instability point is considerably lower than is the case for $Cu_3Au$. [S0163-1829(99)02118-9]


The existence of fine structure associated with diffuse-scattering peaks in disordered metallic alloys has been known from diffraction studies for over thirty years.[1] Recently, however, Reichert, Moss, and Liang[2] carried out the first *in situ* study of the temperature dependence of the diffuse-scattering fine structure in a disordered alloy $Cu_3Au$. Their evidence for an unexpected divergence of the antiphase domain separation in the disordered $Cu_3Au$ alloy at the first-order transition has prompted renewed interest in the phenomenon. Reichert, Moss, and Liang concluded[2] that Fermi surface-induced effects[3] could not solely account for such behavior and suggested that entropic effects must be important. This experiment triggered at least two theoretical attempts to explain the temperature dependence of the diffuse splitting. Ozolins *et al.*[4] were able to predict a temperature dependence of the splitting using a cluster expansion approach and attributed it to simple entropic effects. Another theoretical approach due to Tsatskis[5] attributes the behavior of the splitting to the temperature- and wave vector dependence of the self-energy. However, the detailed accuracy of the theoretical models remains unclear. Tsatskis' high-temperature expansion is not expected to be valid near the transition point, and his $\alpha$ expansion itself requires the input of short-range order (SRO) parameters to calculate the diffuse scattering. Wolverton *et al.*[6] predict a peak symmetry that differs in detail from that actually observed in $Cu_3Au$. Their calculations yield peaks along the reciprocal lattice diagonals rather than along the axes. Moreover, for CuAu, they predict a splitting of the (100) diffuse peak along the [100] direction, which is in contradiction with published x-ray[7] and electron[1] measurements. Clearly further experimental and theoretical investigations are required to resolve these outstanding issues.

This paper presents an *in situ* investigation of the temperature dependence of the diffuse scattering from equiatomic CuAu. Unlike $Cu_3Au$, CuAu exhibits a stable one-dimensional long-period superlattice phase designated CuAuII between 385 and 410 °C. The CuAuII phase consists of an array of periodic antiphase boundaries with an average modulation wavelength ten times the size of the underlying unit cell. Since CuAuII is not the ground state, entropic effects are expected to play a major role in stabilizing the

modulated phase and presumably in determining the nature of equilibrium fluctuations in the disordered phase.

A splitting of the diffuse peaks in disordered equiatomic CuAu was reported in early electron diffraction studies[1] and investigated in detail by Hashimoto[7] with x rays. Hashimoto, however, performed his experiment on quenched samples at room temperature and therefore was not able to study the structure of the disordered phase in equilibrium or to examine its temperature dependence. Moreover, given the large atomic mobilities in the alloy at high temperature, it is possible, indeed likely, that his samples underwent significant ordering during the quench. This possibility is supported by a recent time-resolved x-ray study of ordering kinetics in CuAu which is reported elsewhere.[8] The relatively rapid initial ordering kinetics that we observe in the alloy suggests that accurate measurements of the diffuse scattering must be performed at high temperature.

The diffuse-x-ray-scattering measurements reported here were performed at the National Synchrotron Light Source, Brookhaven National Laboratory. The samples studied were (421) and (100) cuts of a CuAu single crystal ingot grown by Monocrystals, Inc. The composition of the (421) cut was measured using fluorescence analysis and found to be 50.5 $\pm 0.2$ at. % Cu. During the experiment the samples were kept at temperatures between 410 and 600 °C in vacuum or in a high-purity He atmosphere. Most of the x-ray data was taken on beamline X14 as part of an anomalous diffuse scattering project[9] and measured at three x-ray energies 8959, 10 500, and 11 914 eV. Data at all three energies displays the same trends. A mosaic, sagittal-focusing graphite (002) crystal spectrometer was used to separate the elastic signal from the resonant Raman by distributing it on a linear position-sensitive proportional counter.[10] The contribution due to Compton scattering is small and has not been removed from the data. The HWHM resolution of this experimental setup is better than 0.04 reciprocal lattice units (r.l.u.). More information about this setup can be found in Ref. 10, and references therein. Additional x-ray data on the (100) diffuse peaks was taken on beamline X20C using a multilayer monochromator and CCD array detector. The resolution of this setup is 0.01 r.l.u.

All measurements of the diffuse-scattering fine structure in $Cu_xAu_{1-x}$ alloys have shown a qualitatively similar symmetry of the scattering due to SRO (see Fig. 1 of Ref. 2). Around the (100) superlattice position the scattering due to SRO reaches its maximum in a ring in the $(1kl)$ plane and has satellites on the $[1k0]$ and $[10l]$ lines. These satellites are due to medium-range in-plane antiphase correlations between fluctuations ordering in the (100) direction and have a structure reminiscent of the CuAuII modulated phase. The $(h00)$ cross section of the diffuse peak reflects the degree of order in the [100] direction and will be referred to as the ordering direction. The $(1k0)$ and $(10l)$ cross sections probe the degree of in-plane correlations and will therefore be referred to as modulation directions. The scattering around other reciprocal lattice points can be derived using symmetry arguments.

Our experiment agrees with earlier investigations on the symmetry of the diffuse satellites. In addition to the SRO scattering, CuAu also exhibits strong size effects which shift the peaks considerably from their symmetric positions around the superlattice positions. Figure 1 presents $l$ scans of the diffuse scattering due to SRO around the (210) peak at three different temperatures. With increasing temperature the satellite peaks broaden to form a single peak with a relatively flat top. The size-effect contribution to scattering on this line is minimal and has been removed making use of its antisymmetry with respect to $l=0$.[11] The data has been normalized by comparison with scattering from a powder nickel standard. The intensity of the diffuse peaks is at least an order of magnitude smaller than reported by Hashimoto, therefore confirming our concern that his sample underwent significant ordering during the quench.

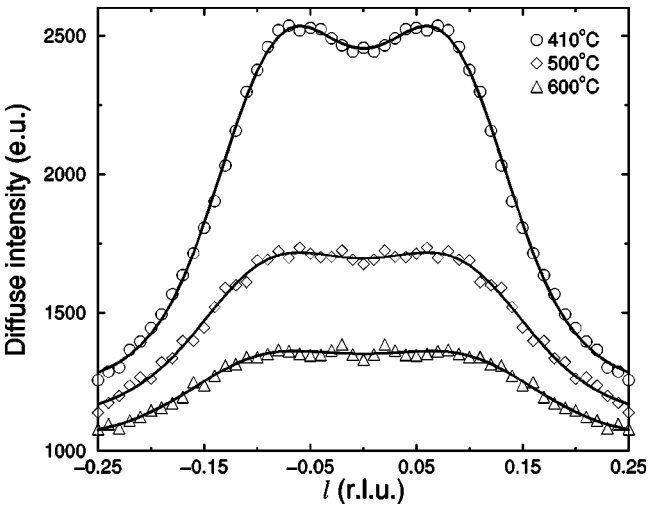


FIG. 1. Diffuse scattering due to SRO along the $(21l)$ line at three temperatures above the order-disorder transition temperature of CuAu.

In a simple mean-field approach the equilibrium fluctuations in the disordered phase produce diffuse-scattering peaks that have a Lorentzian $\mathbf{q}$ dependence. The half-width at half maximum (HWHM) of this Lorentzian is equal to the inverse of the correlation length $\xi$ and depends on temperature as $(T-T_0)^{\nu}$. $T_0$ is the instability (spinodal) temperature and $\nu=1/2$ is the mean-field correlation length exponent. The diffuse satellites we observe are characterized by two correlation lengths, one in the ordering direction and another in the modulation direction. At 410 °C the correlation length in the modulation direction is approximately 9 Å and is twice the correlation length in the ordering direction.

To estimate the diffuse peak splitting in the modulation direction, we fit the satellite peaks with individual Lorentzians plus a constant background. The fit also allows for the contribution of the two off-axis satellite peaks. Figure 2 shows the temperature dependence of the peak separation $\delta l$. The splitting decreases with decreasing temperature, but the magnitude of the overall change is small, less than half the change observed in $Cu_3Au$[2] over a comparable temperature range, and may be an artifact of the fitting procedure. There is no visible evidence of a diverging antiphase length scale at the transition temperature. It is noteworthy that at all temperatures studied the values of $\delta l$ are smaller than 0.2 r.l.u., the value expected from the modulation wavelength of the ordered CuAuII phase. At 410 °C, for example, the measured $\delta l$ corresponds to a modulation wavelength of approximately 13 unit cells as compared to 10 unit cells in CuAuII.

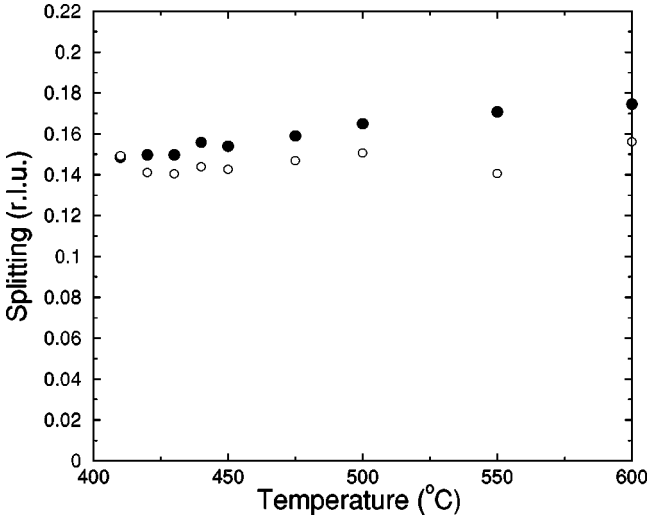


FIG. 2. Temperature dependence of the CuAu fine structure diffuse-scattering splitting from a fit of the scattering in the modulated direction with two Lorentzians (filled circles) and a fit with Eq. (3) (open circles).

We have studied in detail the temperature dependence of the two correlation lengths characterizing the diffuse peaks. In the modulation direction, the widths of the (210) satellite peaks obtained from the fit mentioned above show little change with temperature and would suggest a very low pseudospinodal point at approximately 150 °C. In the ordering direction, however, the satellite peak widths display a much stronger temperature dependence. Figure 3 presents the temperature dependence of the square of the (100) diffuse peak widths in the ordering direction. A straight line fitted through the low-temperature experimental points would extrapolate to a pseudospinodal temperature located at approximately 320 °C.

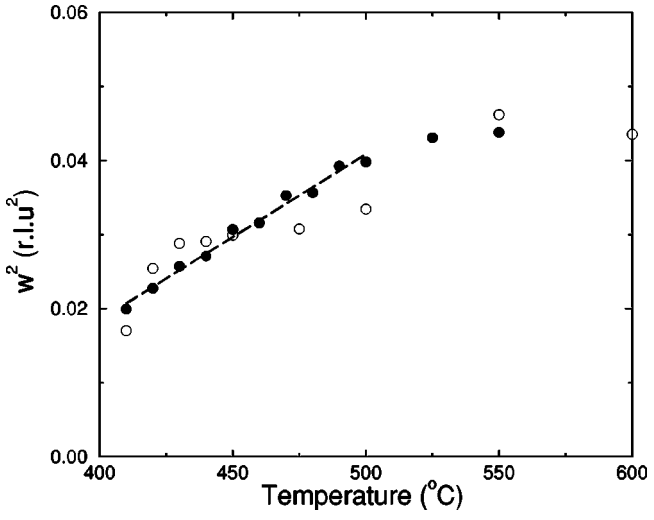


FIG. 3. Temperature dependence of the square widths of the (100) diffuse peaks measured in the ordering direction (filled circles) and calculated from the *m* and *n* parameters obtained from the fit of the satellites in the modulated direction with Eq. (3) (open circles). If a straight line is fit through the low-temperature experimental points it extrapolates to a pseudospinodal temperature at approximately 320 °C.

The contradiction between the behaviors of the correlation lengths in the ordering and modulation directions would suggest that the fitting of the satellite peaks with two individual Lorentzians is too simplistic to account for the effects associated with the antiphase correlations. Another approach proposed to describe such correlations uses a Ginzburg-Landau free energy functional with a negative gradient term[12,13]

$$F(\eta)=F_0+\frac{1}{V}\int dr[a_T\eta^2-e|\nabla_{\mathrm{mod}}\eta|^2+f(\nabla^2_{\mathrm{mod}}\eta)^2 + e|\nabla_{\mathrm{ord}}\eta|^2] \quad (1)$$

where $\eta$ is the order parameter and $a_T=a_0(T-T_0)$. $F_0$, $a_0$, $e$, and $f$ are positive parameters approximately independent of temperature, $V$ is the volume, and $a$ is the lattice parameter. In principle, the coefficients of the two gradient square terms can be different but it will be shown below that the experimental data is well described with only one parameter.

The structure factor then can be written as

$$I(\mathbf{q})=\left(\frac{a}{2\pi}\right)^3\frac{k_bT/2}{a_T-e(q^2_{\mathrm{mod}}-q^2_{\mathrm{ord}})+fq^4_{\mathrm{mod}}}, \quad (2)$$

where $q_{\mathrm{mod}}$ is the component of the wave vector in the modulation direction and $q_{\mathrm{ord}}$ is the component in the ordering direction. In the ordering direction this model predicts that at $q_{\mathrm{mod}}=0$ the diffuse peak has a Lorentzian shape with a width that goes to zero at $T_0$, which is the instability point of the disordered phase with respect to the ordered phase. At the satellite peak $q_{\mathrm{mod}}=\sqrt{e/2f}$ the width of the Lorentzian in the ordering direction goes to zero at $T_1=T_0+e^2/4fa_0$ ($\approx$320 °C in our case) which is the instability point of the disordered phase with respect to the modulated phase. In the modulation direction the satellites have a non-Lorentzian line shape but their peak width also goes to zero at $T_1$.

At each temperature we fit the diffuse satellites in the modulation direction with the numerical convolution of the following function:

$$I(\mathbf{q})=\frac{C}{m-nq^2_{\mathrm{mod}}+q^4_{\mathrm{mod}}}+\mathrm{const} \quad (3)$$

with an experimental resolution function. Here $C=k_bT(a/2\pi)^3/2f$, $m=a_0(T-T_0)/f$, and $n=e/f$. The $C$, $m$, and $n$ parameters are allowed to change with temperature. The peak splitting calculated from $n$ (Fig. 2) is consistent with our previous findings that the diffuse splitting does not change significantly with temperature. This functional form produces slightly smaller values for the peak splitting.

Figure 4 shows the temperature dependence of $m$. The straight line through the lower temperature points extrapolates to $T_0\approx$270 °C. The $T_1$ calculated from the fit parameters is approximately 20° above $T_0$ in reasonable agreement with the estimation from the ordering direction. Moreover, the values of the inverse square of the correlation length in the ordering direction predicted from $m$ and $n$ are in good quantitative agreement with the actual measured values as seen in Fig. 4. Considering the 10% uncertainty of the measured peak widths due to the intrinsic broad nature of the diffuse peaks and the large background due to displacement

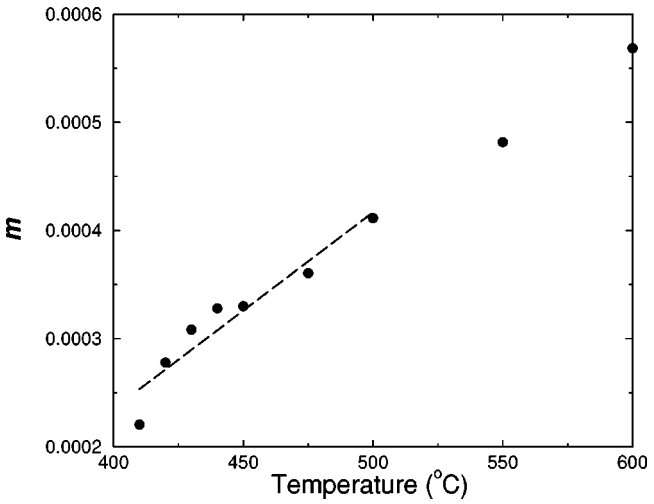


FIG. 4. Temperature dependence of the $m$ parameter obtained from a fit of the satellites in the modulated direction with Eq. (3). The straight line extrapolates to a pseudospinodal temperature approximately equal to 270 °C.

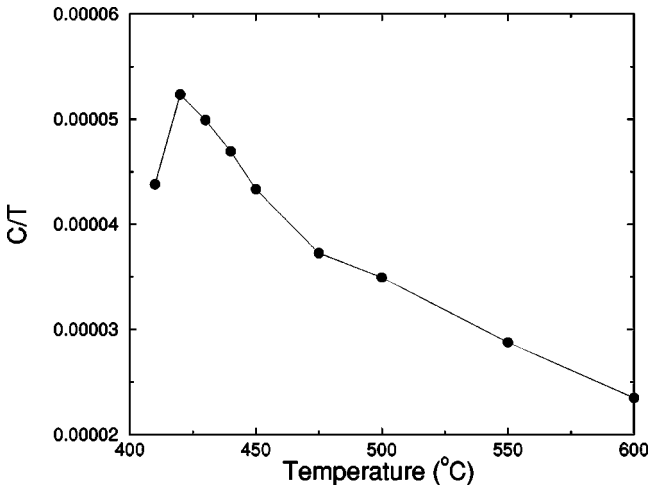


FIG. 5. Temperature dependence of $C/T$ obtained from a fit of the satellites in the modulated direction with Eq. (3).

scattering, this agreement may be somewhat fortuitous. However, the data suggests that the gradient square coefficients in the ordering and modulated directions differ by no more than 20%.

Figure 5 shows the temperature dependence of $C/T$. We observe a consistent deviation of $C/T$ from a constant which makes the maximum peak intensity appear to diverge at a higher temperature than expected from the behavior of the correlation length. This increase in scattering with decreasing temperature cannot be explained by the simple Ginzburg-Landau approach and may be due to a noncritical increase of the number of atoms participating in these fluctuations beyond that expected from simple mean-field spinodal theory.

In conclusion, we have presented a detailed *in situ* study of the diffuse scattering fine structure in equiatomic CuAu. The satellite splitting is smaller than in the equilibrium CuAuII phase and exhibits little or no temperature dependence. In particular, there is no evidence of a divergence at the transition temperature. The temperature dependence of the correlation lengths in the modulation and ordering direction was explained coherently within the context of an extended Ginzburg-Landau mean-field approach. The estimated pseudospinodal was found to be at least 90° below the ordering transition temperature $T_{tr}$. This value, approximately 0.13 $T_{tr}$, is considerably larger than the offset found in $Cu_3Au$ (0.05 $T_{tr}$).[14] This conclusion is not qualitatively changed if we instead use scaling exponents suggested by Monte Carlo simulations of CuAu.[15]

The authors would like to thank K. Elder, B. Chakraborty, and W. Klein for numerous useful discussions. We would also like to acknowledge the experimental help of J. Bai. This work was supported by NSF Grant No. DMR-9633596. The NSLS is supported by the U.S. DOE Division of Materials Sciences and Division of Chemical Sciences.

[1] K. Sato, D. Watanabe, and S. Ogawa, J. Phys. Soc. Jpn. **17**, 1647 (1962).
[2] H. Reichert, S. C. Moss, and K. S. Liang, Phys. Rev. Lett. **77**, 4382 (1996).
[3] S. C. Moss, Phys. Rev. Lett. **22**, 1108 (1969).
[4] V. Ozolins, C. Wolverton, and A. Zunger, Phys. Rev. Lett. **79**, 955 (1997).
[5] I. Tsatskis, J. Phys.: Condens. Matter **10**, L145 (1998).
[6] C. Wolverton, V. Ozolins, and A. Zunger, Phys. Rev. B **57**, 4332 (1998).
[7] S. Hashimoto, Acta Crystallogr., Sect. A: Found. Crystallogr. **39**, 524 (1983).
[8] K. R. Elder, O. Malis, K. Ludwig, B. Chakraborty, and N. Goldenfeld, Europhys. Lett. **43**, 619 (1998).
[9] O. Malis, K. F. Ludwig, W. Schweika, G. E. Ice, and C. J. Sparks (unpublished).
[10] X. Jiang, G. E. Ice, C. J. Sparks, L. Robertson, and P. Zschack, Phys. Rev. B **54**, 3211 (1996).
[11] B. Borie and C. J. Sparks, Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr. **27**, 198 (1971).
[12] W. McMillan, in *Melting, Localization and Chaos*, edited by P. Vashista and R. Kalia (North-Holland, New York, 1981), p. 111.
[13] B. Chakraborty and Z. Xi, Phys. Rev. Lett. **68**, 2039 (1992).
[14] K. F. Ludwig, G. B. Stephenson, J. L. Jordan-Sweet, J. Mainville, Y. S. Yang, and M. Sutton, Phys. Rev. Lett. **61**, 1859 (1988).
[15] W. Schweika, in *Structural and Phase Stability of Alloys*, edited by J. L. Moran-Lopez, F. Mejia-Lira, and J. M. Sanchez (Plenum, New York, 1992), p. 53.