Anomalous Temperature Dependence of the X-Ray Diffuse Scattering Intensity of Cu_3Au

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The fine structure of the equilibrium diffuse x-ray scattering of a $Cu_3Au(110)$ crystal reveals an unexpected temperature dependence of the fourfold peak splitting associated with Fermi surface imaging. The separation of the split diffuse maxima increases with temperature corresponding to a proliferation of correlated microdomains in a real space picture. As current alloy theories based on the calculation of the configurational energy do not cover such a temperature dependent microstructure, the results of this study outline the importance of the entropy contribution to the alloy free energy. [S0031-9007(96)01652-3]

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Diffuse scattering from disordered solid solutions is one of the major tools for the study of fundamental properties of these materials. The most important aspect of such measurements is the access to the local chemical order and effective pair interaction parameters [1] as determined from the short range order (SRO) part of the diffuse scattering. Local pair displacement parameters arising from different atomic sizes of the constituents can also be retrieved from the size effect (SE) part of the diffuse scattering [2].

As has first been suggested by Krivoglaz [3] and Moss [4], and subsequently demonstrated for the Cu-Pd and Cu-Al alloy systems [5], the fine structure of the SRO diffuse intensity reveals details about the electronic structure as well. Fermi surface extremities are imaged in the splitting of diffuse spots at special points in reciprocal space related to the relevant Kohn construction. First principles calculations of the electronic structure of binary alloys as a function of the average composition [6] have since confirmed this interpretation of diffuse scattering features. Recent progress in alloy theory, including long-range interactions in large systems [7], now permits a quantitative comparison between experiment and theory.

The binary alloy system Cu-Au has been of special interest since it serves as a model for discontinuous order-disorder transitions. Cu_3Au and $CuAu_3$ order in the $L1_2$ structure at temperatures below the order-disorder transition temperature T_0 of 663 and 473 K, respectively. Despite numerous investigations of their diffuse scattering with x rays [8] as well as with electron diffraction methods [9], the fine structure has never been clearly resolved at temperatures above T_0. This is due mainly to experimental difficulties and the inherently weak cross section of the diffuse scattering. These problems have been overcome only recently with the advent of powerful x-ray sources and new methods for the data treatment [10].

Quantitative measurements of the SRO diffuse scattering are usually performed at low temperatures in order to reduce the thermal diffuse (one-phonon) scattering (TDS). For this, the samples are annealed in the disordered state at elevated temperatures and subsequently quenched into a metastable state at low temperature. In such cases it has been important to demonstrate that the diffuse scattering has not undergone appreciable changes upon quenching. The SRO diffuse scattering from a quenched sample should therefore resemble the equilibrium structure at high temperatures, with the obvious proviso that one must be careful about using an equilibrium thermodynamic description.

For Cu_3Au, one expects [4] a fourfold splitting of the SRO diffuse scattering that peaks about the $L1_2$ superstructure positions of this system. Figure 1(a) depicts schematically two symmetry-equivalent planes in reciprocal space which consist of two interpenetrating fcc lattices having the superstructure positions at the face centered sites. The splitting, associated with a characteristic wavelength of SRO fluctuations, occurs around the superstructure positions in planes parallel to the fcc faces of each sublattice and is quantified by $m = \sqrt{2}\, q_b$ (along {100} directions, the peaks are separated by $2q_b$). Since we have measured the diffuse scattering at elevated temperatures, $T > T_0$, in the disordered phase where a large part of the scattering is due to TDS, we have not attempted to decompose the total diffuse intensity into its various components. This requires special care in choosing the appropriate plane for the measurements of the diffuse scattering since antisymmetric contributions in the SE scattering distort the total diffuse scattering considerably. Therefore we have concentrated on the (100) and (010) reflections, around which the splitting occurs in the $(1, k, l)$ and $(h, 1, l)$ plane. Here the individual terms for the SE scattering are either small for a small momentum transfer q or symmetrical with respect to the (100) superstructure position.

The experiment has been carried out at the beam line X2A of the National Synchrotron Light Source (NSLS) at the Brookhaven National Laboratory. All the measurements have been performed at temperature in a UHV chamber. The temperature has been measured by a thermocouple which was placed inside a hole on one side of the single crystal. The mechanically polished and etched

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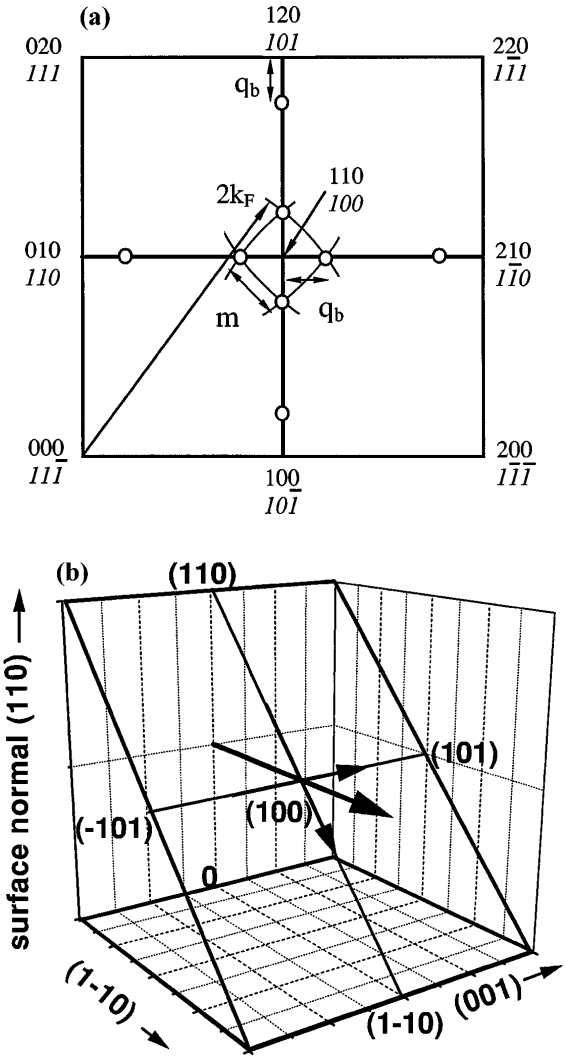

FIG. 1. Reciprocal space of Cu_3Au in different planes. (a) $(h, k, 0)$ and $(1, k, l)$ plane showing the origin of the Fermi surface-induced peaks that modulate the diffuse intensity maxima. $m = \sqrt{2}\, q_b$ and denotes the separation distance of the split peaks. (b) $(1, k, l)$ plane of a $Cu_3Au(110)$ single crystal. The arrows indicate the lines along which the measurements have been performed.

crystal exposed a (110) surface. Figure 1(b) shows the geometry involved in this experiment.

The bulk stoichiometry of the crystal has been determined using two methods yielding $x_{\mathrm{Au}} = 0.251$ from an electron microprobe analysis and $x_{\mathrm{Au}} = 0.243$ from a Rutherford backscattering analysis. In order to test the quality of the crystal, we checked both equilibrium and nonequilibrium features of the order-disorder phase transformation. Figure 2 establishes the presence of a first order phase transition in this crystal. The integrated intensities of the (100) and (201) superstructure reflections drop by more than 5 orders of magnitude within a temperature range of 0.3 K, whereby the intensities in the disordered phase are estimated by the statistical fluctuations in the background. The temperatures have been recorded relative to the phase transition temperature which has been

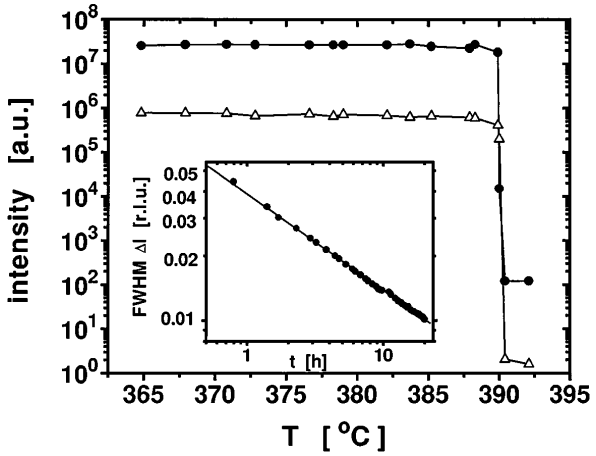

FIG. 2. Integrated intensity of the (100) and (201) superstructure reflections (marked by circles and triangles, respectively). The two curves are offset by a constant factor. The inset shows the time evolution of the ordered domain size as measured by the FWHM Δl of the (100) superstructure reflection along the l direction in reciprocal lattice units (r.l.u.). The crystal has been quenched from the disordered state to $T_f = T_0 - 25$ K.

set to 663 K. We have also measured the bulk ordering kinetics at the (100) superstructure reflection for a quench to $T_0 = 25$ K, yielding a power law exponent of $a = 0.45 \pm 0.04$ for the late stage growth $L(t) = a_0/\Delta l(t) \sim t^a$ of the ordered domains (see inset of Fig. 2). This compares well with results obtained by Shannon, Harkless, and Nagler [11].

The measurements in the disordered phase have been performed with a moderate resolution setup of 0.003 reciprocal lattice units (r.l.u.) in both horizontal and vertical directions. Figure 1(b) displays schematically the three different line scans done at the (100) and (010) positions. Angular dependent corrections have been employed for the correction for polarization effects and changes in the scattering volume. The raw data have been normalized to the same intensity at the (100) position. We performed several identical scans at each temperature and found no time dependence in the results. Equilibrium conditions are therefore established almost immediately after changing the temperature. Measurements around the (100) and (010) positions provided identical results.

Figure 3 shows the results of three scans through the (100) position at $T = T_0 + 3.7$ K. As expected, a fourfold splitting occurs in the $(1kl)$ plane. The symmetry of the split peaks around the (100) position confirms the absence of significant antisymmetric size effect contributions in this plane. The scan along $(0.5 + h, 0.5 - h, 0)$ intersecting the $(1kl)$ plane at an angle of 45° shows no splitting. Using arguments about the dimensions of the Fermi surfaces of Cu and Au [4], the separation distance $m = 0.075 \pm 0.007$ r.l.u. taken from Fig. 3 is quite consistent with $m = 0.055$ r.l.u. obtained by Ohshima, Harada, and Moss for a $Cu_{24.4}Au_{75.6}$ alloy [12]. The total diffuse scattering is given by $I = I_{\mathrm{SRO}} + I_{\mathrm{SE}} + I_{\mathrm{TDS}} + I_{\mathrm{HS}} + I_{\mathrm{CS}}$ with I_{HS} and I_{CS} denoting defect induced (Huang) and

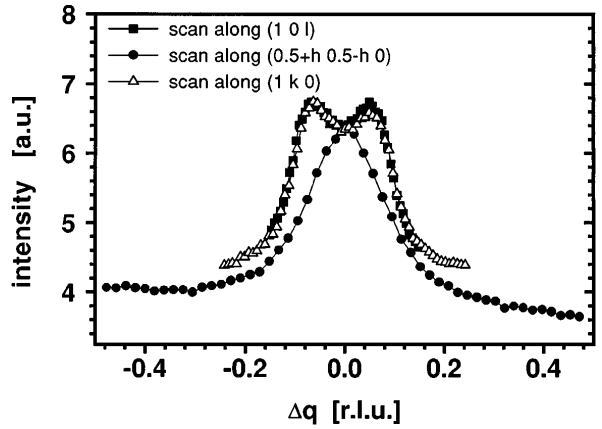

FIG. 3. Total diffuse scattering along different lines through the (100) superstructure position at $T = T_0 + 3.7$ K. The separation distance for the split peaks is $2q_b = 0.106 \pm 0.01$ r.l.u.

incoherent (Compton) scattering. Since I_{SRO} is the Fourier transform of the pair correlation function $\alpha(\mathbf{r})$, it is apparent that, for the reproduction of the distinct scattering features in Fig. 3, correlations up to high order coordination shells are essential.

In Fig. 4 the total diffuse scattering along the $(10l)$ direction is shown for two different temperatures. The separation $2q_b$ of the split peaks is clearly expanded on heating. There is, nevertheless, some arbitrariness in the determination of the value for the characteristic wavelengths of the SRO fluctuations. In the present study we used the fit curve composed of two Gaussians, rather than the two individual Gaussians, in order to determine the positions of the split peaks. Since TDS, HS, and CS exhibit a very smooth q dependence in the vicinity of the (100) superstructure position, the change of $2\Delta q_b = 0.046$ r.l.u. in the separation distance along the line $(10l)$ must be attributed to the SRO part of the diffuse intensity.

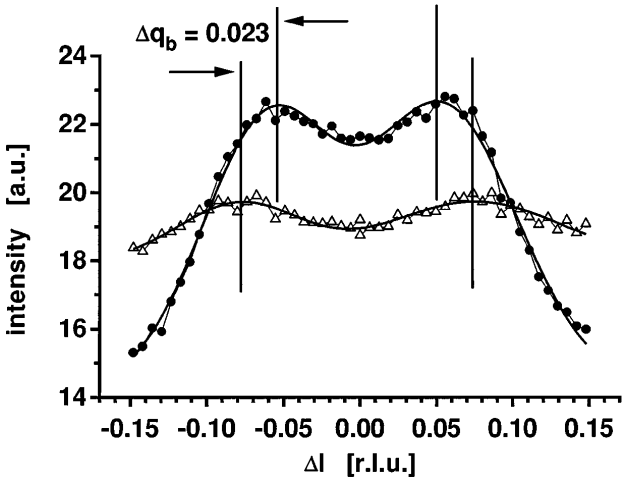

FIG. 4. Total diffuse intensity along the line $(10l)$ at $T = T_0 + 2.6$ K (circles) and $T = T_0 + 52.3$ K (triangles). The lines are fits with two Gaussians.

The positions of the split maxima can be found using the vector $2\mathbf{k}_F$ spanning flat portions of the Fermi surface. It is evident that the influence of the Fermi surface is not sufficient to explain this anomalous temperature behavior of the diffuse scattering. Because of electron-phonon scattering, the Fermi surface will be smeared out upon increasing the temperature, but $2\mathbf{k}_F$ should retain its value within the small range of temperatures of our investigation. The change in the peak splitting is reversible with cooling.

Figure 5 summarizes the temperature dependence of the peak splitting along the $(10l)$ direction, where it is shown to increase monotonically. The accessible range of temperatures is limited by the continuously decreasing peak-to-background ratio as the TDS is increasing and the SRO is decreasing with temperature. The data for the separation distance $\Delta l = 2q_b$ along $(10l)$ have been fitted according to a power-law $\Delta l \sim (T - T_0)^s$. Using the phase transition temperature T_0 as the onset temperature, we found an exponent of $s = 0.38 \pm 0.15$ [13]. Split diffuse peaks along {100} directions correspond, according to Hashimoto [14] and Krivoglaz [15], to an inhomogeneous disordered state composed of a correlated arrangement of microdomains with a preferred separation a_0/q_b between domains of the same phase that is dictated by $2\mathbf{k}_F$ [i.e., $\mathbf{G}_{110} + \mathbf{q}_b = 2\mathbf{k}_F$ in Fig. 1(a)]. The temperature dependence of the average distance $d = a_0/q_b$ between domains of the same phase in the heterogeneous state above T_0 is shown in the inset of Fig. 5.

There have been some attempts to calculate the SRO diffuse scattering and the correlation function for alloys at finite temperatures. Gyorffy *et al.* [16] calculated the correlation function of Cu_3Pd for several temperatures in the disordered phase which showed no temperature dependent splitting. Having obtained the energetics of an alloy system either by LDA calculations [7] or from experimental data for the pair correlation function at one temperature [17], Monte Carlo simulation techniques can

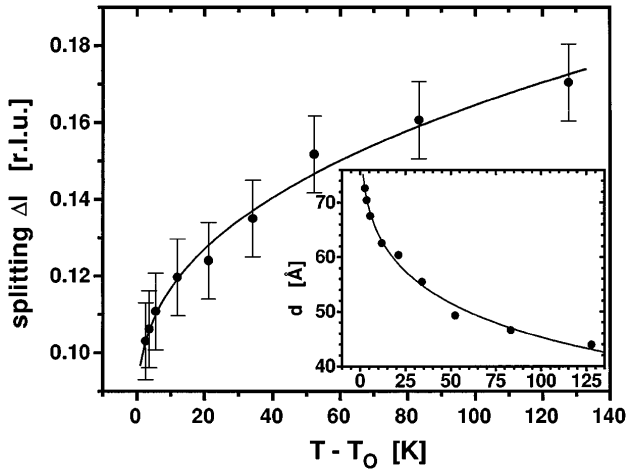

FIG. 5. Temperature dependence of the separation distance $\Delta l = 2q_b$ along the line $(10l)$ (the full line is a fit to a power law). The inset displays the corresponding real space antiphase domain separation distance d vs $T - T_0$.

be employed in order to study the configurational entropy contribution to the free energy. Results from these simulations indicate that the splitting of the diffuse peaks is decreasing with increasing temperature for the alloy $Cu_{0.702}Pd_{0.298}$ [7], while it is increasing for $Cu_{0.856}Al_{0.144}$ [17]. The peaks themselves are becoming broader and weaker at higher temperatures until the split peaks can no longer be distinguished as separate peaks. The simulation results for the Cu-Pd alloy are in contrast to our findings in Cu_3Au even though both systems exhibit the $L1_2$ ground state with {100} as special points. Currently, there are no three-dimensional first-principles theories which are capable of explaining such a temperature dependent fine structure of the diffuse scattering.

There is more experimental evidence, however, for this anomalous (unexpected) behavior of the diffuse scattering. Kulik, Gratias, and deFontaine [18] have shown that irradiated $Cu_{1-x}Pd_x$ alloys, with x ranging from 0.20 to 0.24, exhibit a similar temperature dependence in the fine structure of the total diffuse scattering. In their study the samples have been maintained artificially in the disordered state by high energy electron irradiation at temperatures well below the phase transition temperature where long-range order would be the stable equilibrium state. Since increasing the temperature drives the system closer to its equilibrium state, the role of the temperature is often reversed for irradiated systems. Their observed shrinking in the separation distance with increasing temperature is therefore in accordance with our findings. In order to explain their results the authors used a one-dimensional Ising chain model employing the cluster variation method for the statistics of the system. The model incorporates the configurational entropy correctly and attributes the temperature dependence of the peak splitting to entropic effects.

To conclude, we have carried out the first measurements of the fine structure of diffuse scattering in the high temperature disordered phase of a binary alloy. We have shown that, upon decreasing the temperature in the disordered phase of Cu_3Au, the modulation wave vector $\mathbf{q}_b$ approaches a point of high symmetry (special point) which is characteristic for the long-range ordered low temperature phase. Obvious discrepancies between the results obtained, experimentally in this work and by Kulik *et al.* [18], and by simulation techniques for Cu-Pd alloys suggest the importance of the entropy contribution to the free energy of alloys. Since the correlation function as measured by the SRO diffuse scattering is used as a crucial test for alloy theories, special care has to be taken to incorporate the SRO fluctuations at elevated temperatures into theory in a proper way, and this is currently being studied by Tsatskis [19]. The anomalous behavior of the fine structure of the diffuse scattering certainly indicates that its features cannot be attributed solely to the energetics of the system, i.e., Fermi surface-induced effects. Finally, our results emphasize that the quenching process from elevated temperatures in the disordered phase has to be controlled carefully in order to ensure that measured diffuse scattering intensity corresponds to an equilibrium state at the annealing temperature.

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[1] L. Reinhard and S. C. Moss, Ultramicroscopy **52**, 223 (1993).
[2] B. E. Warren, B. L. Averbach, and B. W. Roberts, J. Appl. Phys. **22**, 1493 (1951); B. Borie and C. J. Sparks, Acta Crystallogr., Sect. A **27**, 198 (1971).
[3] M. A. Krivoglaz, *Diffuse Scattering of X-Rays and Neutrons by Fluctuations*, (Springer, Berlin, 1996); M. A. Krivoglaz and Hao T'U, *Defects and Properties of the Crystal Lattice* (Izd. Naukova dumka, Kiev, 1968) (in Russian).
[4] S. C. Moss, Phys. Rev. Lett. **22**, 1108 (1969).
[5] K. Ohshima and D. Watanabe, Acta Crystallogr., Sect. A **29**, 520 (1973); R. O. Scattergood, S. C. Moss, and M. B. Bever, Acta Metall. **18**, 1087 (1970).
[6] B. L. Gyorffy and G. M. Stocks, Phys. Rev. Lett. **50**, 374 (1983).
[7] Z. W. Lu *et al.*, Phys. Rev. B **50**, 6642 (1994); F. J. Pinski *et al.*, Phys. Rev. Lett. **66**, 766 (1991).
[8] J. M. Cowley, J. Appl. Phys. **21**, 24 (1950); S. C. Moss, J. Appl. Phys. **35**, 3547 (1964); P. Bardhan and J. B. Cohen, Acta Crystallogr., Sect. A **32**, 597 (1976); B. D. Butler and J. B. Cohen, J. Appl. Phys. **65**, 2214 (1989).
[9] S. Hashimoto and S. Ogawa, J. Phys. Soc. Jpn. **29**, 710 (1970); D. Watanabe and P. M. J. Fisher, J. Phys. Soc. Jpn. **20**, 2170 (1965).
[10] L. Reinhard *et al.*, Phys. Rev. B **45**, 2662 (1992); G. E. Ice *et al.*, Phys. Rev. Lett. **68**, 863 (1992).
[11] R. F. Shannon, C. R. Harkless, and S. E. Nagler, Phys. Rev. B **38**, 9327 (1988).
[12] K. Ohshima, J. Harada, and S. C. Moss, J. Appl. Crystallogr. **19**, 276 (1986).
[13] Since the value of the exponent s is not well defined when the onset temperature is used as a free fit parameter, we have extracted the error bars with T_0 as the onset temperature.
[14] S. Hashimoto, Acta Crystallogr., Sect. A **30**, 792 (1974); Acta Crystallogr., Sect. A **37**, 511 (1981); Acta Crystallogr., Sect. A **39**, 524 (1983).
[15] M. A. Krivoglaz, Sov. Phys. JETP **57**, 205 (1983).
[16] B. L. Gyorffy *et al.*, in *Alloy Phase Stability*, edited by G. M. Stocks and A. Gonis, NATO-ASI Series E (Kluwer Academic Publishers, Dordrecht, 1989), Vol. 163.
[17] H. Roelofs *et al.*, Scr. Mater. **34**, 1393 (1996).
[18] J. Kulik, D. Gratias, and D. deFontaine, Phys. Rev. B **40**, 8607 (1989).
[19] I. Tsatskis (private communication).