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Temperature dependence of the diffuse-scattering fine structure in Cu-Pd alloys

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The temperature dependence of the diffuse-scattering fine structure in disordered $Cu_{0.79}Pd_{0.21}$ and $Cu_{0.75}Pd_{0.25}$ alloys is studied using *in situ* x-ray scattering. The fine structure is complex, with correlation lengths in the plane of the satellites surrounding a given superlattice point being significantly larger than in the perpendicular direction. In agreement with theoretical predictions, the temperature dependence of the peak splitting in this alloy is significantly less than is the case for Cu_3Au. Moreover, the temperature dependence is more pronounced at 21% Pd concentration than at 25% Pd.

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The diffuse-scattering fine structure due to antiphase correlations in disordered metallic alloys has been known for many years.[1] However there has recently been a resurgence of interest in the phenomenon. In particular, Reichert, Moss, and Liang[2] (RML) were the first to systematically examine the temperature dependence of the satellite peak splitting (inversely related to the antiphase modulation wavelength in real space) in a metallic alloy. An important experimental strength of their measurements is that they were performed *in situ*, at high temperature. This offers significant advantages over performing experiments *ex situ* on quenched samples that may have evolved structurally during the quenching process. The particular alloy they investigated, Cu_3Au, does not exhibit an equilibrium long-period superlattice (LPS) ordered phase, but does exhibit satellite peaks indicative of antiphase correlations above the first-order ordering transition. RML reported a significant decrease of the satellite peak splitting with decreasing temperature, which they suggested could not be explained by Fermi-surface-induced effects[3] alone but rather required the inclusion of entropic effects. Since the original measurement, Malis *et al.*[4] have also reported an *in situ* study of the diffuse-scattering fine structure in equiatomic CuAu, a composition that does exhibit an equilibrium LPS phase. They found interesting temperature dependence of the susceptibility and correlation length and little or no decrease in satellite splitting with decreasing temperature.

Although much of the attention in the field has thus far focused on the Cu-Au alloys, the Cu-Pd alloys offer a very intriguing comparison. As a function of composition and temperature, the Cu-rich Cu-Pd alloys exhibit a simple ordered phase, one-dimensional LPS phases, and two-dimensional LPS phases. The existence of antiphase correlations in the alloy has long been attributed to Fermi-surface effects.[5] The composition dependence of the diffuse-scattering fine structure in the disordered Cu-Pd alloys has been reported by several authors (as reviewed by Tsatskis[6]). In accord with the Fermi-surface hypothesis, the satellite splitting increases monotonically with Pd composition above 15%. Based on their first-principles energy calculations and related simulations, Wolverton *et al.*[7] suggested that the temperature dependence of the peak splitting is smaller than is the case in Cu_3Au. Using a very different theoretical approach incorporating self energies, Tsatskis[6] also calculated the temperature dependence of the peak splitting in Cu-Pd and predicted that it is much smaller than in Cu_3Au. However to date we know of no experimental investigations of this issue.

This paper presents an *in situ* investigation of the temperature dependence of the diffuse-scattering fine structure from two disordered Cu-Pd alloys: $Cu_{0.79}Pd_{0.21}$ and $Cu_{0.75}Pd_{0.25}$. These two alloys exhibit the two important LPS ordered structures found in the Cu-Pd system. The 21% Pd alloy has a first-order transition at approximately 492 °C to an incommensurate one-dimensional LPS phase with a modulation wavelength of approximately 12 fcc unit cells. The antiphase walls in the LPS phase are conservative. In contrast, the 25% Pd alloy has a first-order transition at approximately 475 °C to a two-dimensional LPS phase, with conservative antiphase walls in one direction and nonconservative walls in the other direction. This is followed by another first-order transition at approximately 445 °C to a conservative one-dimensional LPS phase. The two-phase regions at the first-order transitions are all relatively narrow in temperature.

The diffuse x-ray scattering measurements reported here were performed on the X20C and X14 beam lines of the National Synchrotron Light Source at Brookhaven National Laboratory. At the X20C beam line, data taken on the 21% Pd sample used a W-Si multilayer monochromator while data taken on the 25% Pd sample used a Si(111) monochromator. In both cases the photon energy was 6.9 keV. A charge-coupled-device-based x-ray detector from Princeton Instruments was used for rapid data collection. The half width at half maximum (HWHM) resolution of this experimental setup is better than 0.01 r.l.u. On the X14 beam line, only the 21% Pd sample was studied. Data collection there utilized a Si(220) monochromator, a photon energy of 8.9 keV, and a standard four-circle geometry with a focusing analyzer crystal.[8] The HWHM resolution of this experimental system is better than 0.04 r.l.u. A full diffuse-scattering data set out to $q_{max}=4$ r.l.u was collected at 530 °C, but

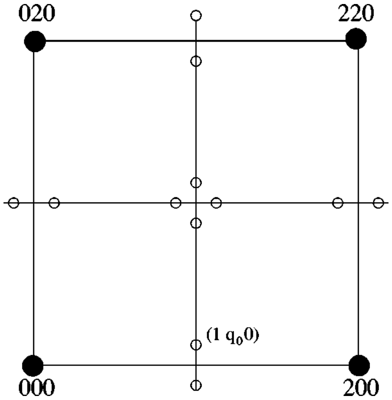

FIG. 1. A schematic of the diffuse scattering from disordered Cu-Pd alloys. Open dots represent the fourfold split peaks and q_0 denotes the separation distance of the satellite peaks from the superlattice point.

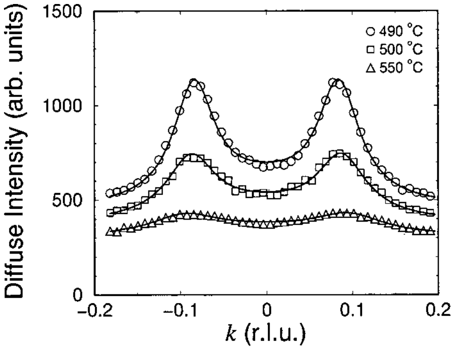

FIG. 2. Diffuse scattering along the (1 k 0) line at three temperatures above the order-disorder transition temperature of $\mathrm{Cu}_{0.79}\mathrm{Pd}_{0.21}$. The solid lines are fits as discussed in the text. The curves at 490 °C and 500 °C are offset upward by 200 and 100 u, respectively, for increased clarity.

here we focus only on the scattering near the (100) superlattice point. For this purpose, shorter data sets were collected at several temperatures within 0.2 r.l.u of the (100) superlattice point. Since the data collected on the two beam lines are consistent, we focus below only on the results from the X20C station.

The samples were single crystals grown at the Office National d'Etudes et de Recherches Aerospatiales. The 21% Pd crystal was cut to a (100) orientation and the 25% Pd crystal was cut to a (110) orientation. The composition of the crystals was verified by microprobe. During the experiment the samples were kept at temperatures between 470 °C and 560 °C in vacuum or in a high-purity He atmosphere. The order-disorder transition temperature was determined from the evolution of the superlattice intensity during slow temperature ramps.

In Cu-rich Cu-Pd alloys it is believed that parallel sheets of Fermi surface spanned by reciprocal space vectors $2q_F$ lying near the [110] directions give rise to effective interactions $V(\mathbf{q})$ between ions that cause ordering fluctuations to develop with a spatially periodic antiphase relationship. This then results in short-range order satellite peaks lying along two of the three reciprocal space axes passing through each superlattice point (see Fig. 1). In the mean-field formalism of Krivoglaz, Clapp, and Moss, the short-range order diffuse scattering is related to the effective interactions between ions $V(\mathbf{q})$ as[9]

$$I^{KCM}(\mathbf{q})=\frac{1}{1+2c(1-c)\beta V(\mathbf{q})}. \tag{1}$$

Tsatskis and co-workers[10] have modified this by including a self-energy term $\Sigma(\mathbf{q})$:

$$I(\mathbf{q})=\frac{1}{c(1-c)[-\Sigma(\mathbf{q})+2\beta V(\mathbf{q})]}. \tag{2}$$

Since $V(\mathbf{q})$ and $\Sigma(\mathbf{q})$ have complicated wave-number dependences, the fine structure of the diffuse scattering is also expected to be complicated. In order to present our results in a coherent way, however, it is desirable to parametrize the observed scattering in a manner that is physically reasonable. In the limit that the system approaches an instability point T_{in} such that the denominators of Eqs. 1 and 2 approach zero for some wave vector q_0 then these line shapes approach the usual mean-field Lorentzian form with a susceptibility $I(q_0)/T$ and a width $w(T)\sim\xi^{-1}(T)$, where $\xi(T)$ is a correlation length. In the case of the Cu-Pd alloys studied here, any ordering instability point (or pseudospinodal) must lie below the first-order phase transition to the ordered state. This fact, coupled with the relatively modest value of the peak splitting, prevents the satellite peaks from being sufficiently separated from each other that they can be fit individually with a single Lorentzian. We have therefore chosen to fit our data by modeling the reciprocal space fine structure as the sum of Lorentzians, each centered at a satellite position.

In addition to the short-range order scattering, the x-ray scattering includes contributions from thermal diffuse and size-effect scattering. The absolute contributions of these terms can be roughly estimated from the existing literature.[11] Although we do not have an exact normalization of the data presented here, we do know their normalization to within approximately 30% based on comparisons with full diffuse-scattering data sets not discussed here. Thus we conclude that the first-order size-effect scattering should make a contribution of approximately 5% of the peak short-range order scattering. Estimation of the thermal diffuse scattering is less certain, but simple estimates would suggest that it also should be significantly less than the short-range order scattering near the relevant superlattice points. Thus we conclude that we can model these other contributions to the scattering as a linear background in the fitting process. Although this simple model of a sum of Lorentzians on a linear background cannot accurately reproduce all of the fine-structure details, it produces robust fit results and effectively parametrizes the satellite peak position q_0, height $I(q_0)$, and widths.

For the $\mathrm{Cu}_{0.79}\mathrm{Pd}_{0.21}$ sample, the diffuse scattering at three different temperatures is shown in Fig. 2 for k scans along (1 k 0) [i.e., through the (100) superlattice point]. As can be seen by eye, the satellite peaks grow and narrow with de-

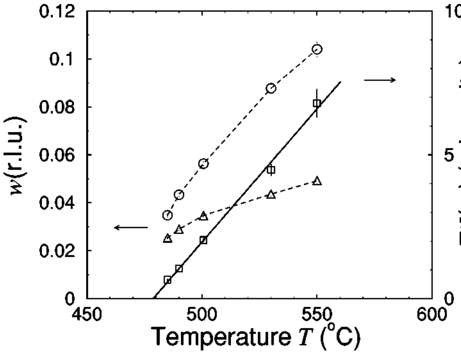

FIG. 3. Temperature dependence of the widths w_{perp} (circles) and w_{in} (triangles) of the (100) diffuse peaks and the inverse peak intensity $T/I(q_0)$ (squares) in $\mathrm{Cu_{0.79}Pd_{0.21}}$. The solid line is a linear fit to the inverse peak intensity. Except where shown, statistical error bars are smaller than the symbol sizes.

creasing temperature. Moreover, the peak positions in the k scan clearly move inward with decreasing temperature. As discussed above, the evolution of the fine structure was parametrized by fits to a sum of Lorentzians centered at each of the four positions around the (100) superlattice point. The resulting fit curves are shown as solid lines in the figure. The satellite peak widths are approximately independent of direction in the plane of the four satellites surrounding a superlattice point. We denote this width w_{in}. However the width in the direction perpendicular to this plane, denoted w_{perp}, is significantly larger. The temperature evolutions of the fit peak intensities and widths are presented in Fig. 3. Error bars are shown for those cases in which the statistical uncertainties on the fit parameters are larger than the plotting symbols. We include two data points from temperatures below the first-order transition. We believe that these represent metastable equilibrium values since our kinetics studies of the alloys indicate that nucleation of the ordered phase is very slow at these temperatures.[12]

The temperature dependence of the diffuse scattering in the 25% Pd sample near the (100) superlattice point was similarly fit. The resulting peak intensity and width parameters are displayed in Fig. 4.

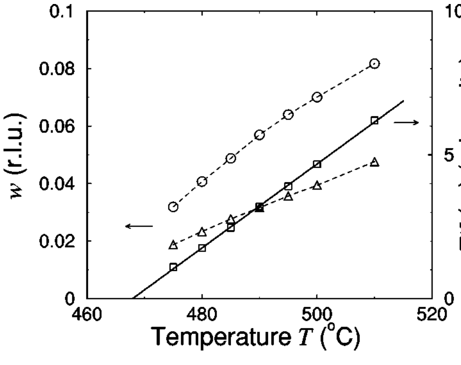

FIG. 4. Temperature dependence of the widths w_{perp} (circles) and w_{in} (triangles) of the (100) diffuse peaks and the inverse peak intensity $T/I(q_0)$ (squares) in $\mathrm{Cu_{0.75}Pd_{0.25}}$. The solid line is a linear fit to the inverse peak intensity. Statistical error bars are smaller than the symbol sizes.

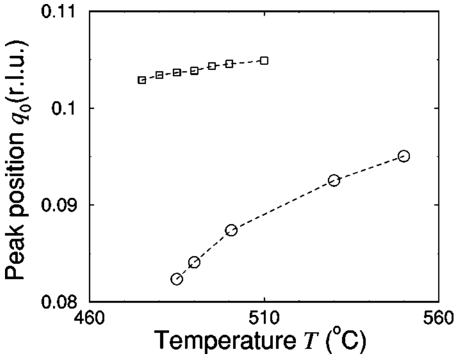

FIG. 5. Temperature dependence of the peak separation q_0 in $\mathrm{Cu_{0.79}Pd_{0.21}}$ (circles) and $\mathrm{Cu_{0.75}Pd_{0.25}}$ (squares). Statistical error bars are smaller than the symbol sizes.

The inverse intensities are approximately linear with temperature, suggesting the existence of a pseudospinodal ordering point below the first-order phase transitions in these two alloys. They extrapolate to pseudospinodal (instability) points of approximately 478±1 °C for the 21% Pd sample and 468±1 °C for the 25% Pd sample. These represent depressions of approximately 14 °C and 7 °C below the first-order transition points for the two samples, respectively. The quoted uncertainties are purely statistical. Systematic errors due to temperature uncertainties are likely to be slightly larger—we estimate the overall uncertainty in pseudospinodal temperatures here to be ±3 °C. The peak widths are also systematically decreasing as the pseudospinodals are approached. However we feel that the uncertainties in the curve parametrization process make pseudospinodal determination from the widths less accurate than those we obtained from $T/I(\mathbf{q})$. Ceder *et al.*[13] have performed mean-field calculations of the Cu-Pd phase diagram without including the possibility of two-dimensional LPS phases. Their phase diagram predicts that, in this concentration regime, the depression in temperature ΔT between the first-order transition and the pseudospinodal decreases rapidly with increasing Pd content. This is in accord with our experimental results, though the actual ΔT is somewhat smaller than predicted by their theoretical phase diagram (at 21% Pd, the calculations of Ceder *et al.* have a $\Delta T \sim 80$ °C while we measure $\Delta T \sim 14$ °C).

Figure 5 shows the fit changes in satellite peak positions q_0 as a function of temperature. In agreement with the theoretical work of Ozolins *et al.*[14] and Tsatskis,[6] the temperature dependence of peak splitting is much smaller than reported in $\mathrm{Cu_3Au}$.[2] There is approximately a 15% change in the satellite peak position over the 65 °C temperature range measured in the 21% Pd alloy, but only a 2% change over the 35 °C range measured in the 25% Pd alloy. Thus we see a significant decrease in the temperature dependence with increasing Pd content. For the 21% Pd alloy, there is a clear downward curvature in the q_0 vs T plot. This trend is reproduced in the calculations of Tsatskis[6] performed for a higher Pd concentration (29.8% Pd).

In conclusion, we have found that the temperature dependence of the peak splitting in Cu-Pd alloys is significantly less than in $\mathrm{Cu_3Au}$, in agreement with theoretical predictions. In addition, we have found that the temperature dependence is much weaker at higher Pd concentration studied (25%) than at the lower concentration (21%). We do not know of a theoretical rationale for this behavior.

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