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

Reichert, Moss, and Liang (RML) have recently reported [1] the observation of an *increase* in the splitting of the short-range-order (SRO) diffuse scattering peaks in disordered Cu_3Au alloys as the temperature was raised above the order-disorder transition. The major point of their work was that this temperature-dependent increase was "anomalous" and "unexpected" and that "currently, there are no three-dimensional first-principles theories which are capable of explaining such a temperature-dependent fine-structure of the diffuse scattering." RML further noted that the standard method of Monte Carlo (MC) simulations of local density approximation (LDA)-derived first-principles alloy Hamiltonians, applied by Lu, Laks, Wei, and Zunger (LLWZ) to a different system—disordered Cu_3Pd alloys [2], "indicate that the splitting of the diffuse peak is *decreasing* with increasing temperature for $Cu_{0.7}Pd_{0.3}$ . . . in contrast with our finding in Cu_3Au." Inspection of the paper of LLWZ [2] shows that the temperature dependence of the SRO splitting was simply not calculated or even mentioned there. Thus, RML's characterization of the results of Ref. [2] is incorrect. And, since Cu_3Pd (for which there are no T-dependent experiments on equilibrated samples) is different from Cu_3Au, we undertook T-dependent SRO calculations here. We find that the T-dependent splitting in Cu_3Au is trivial consequence of the *configurational* entropy, which is properly included in standard three-dimensional first-principles alloy theories [2].

Figure 1 shows the calculated SRO intensity in disordered Cu_3Pd and Cu_3Au, as obtained from MC simulations. The alloy Hamiltonian was derived by mapping the fully relaxed LDA total energies of ≈35 ordered structures onto a cluster expansion [2] containing ≈60 pair and six multibody terms. The calculated low-T splitting wave vectors in Cu_3Pd $q_b = 0.13(\frac{2\pi}{a})$ and in Cu_3Au $q_b = 0.05(\frac{2\pi}{a})$ are in reasonable agreement with the measured values of $q_b = 0.18$ and $q_b = 0.05$ of RML [1], respectively. Our calculations show a very small *increase* of the splitting with increasing temperature in Cu_3Pd, and a much larger relative increase in Cu_3Au, in agreement with the experiments of RML [1] for the latter. We conclude that the existence of SRO splitting, its magnitude and qualitative temperature dependence are entirely explainable from standard first-principles alloy theory using MC entropy [2], in contrast to the assertion of RML [1].

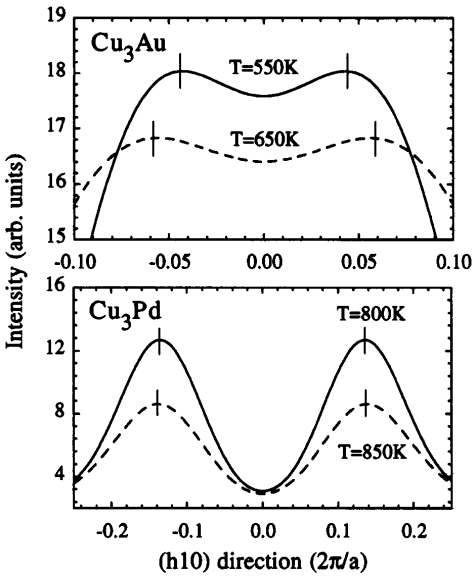

FIG. 1. The calculated SRO peaks in Cu_3Au and Cu_3Pd.

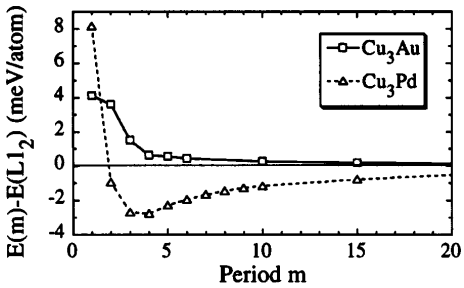

FIG. 2. Structural energies $\Delta E(m) = E(m) - E(L1_2)$ of m-period $L1_2$ superstructures in Cu_3Au and Cu_3Pd.

Our calculation also provides physical insight into the difference between the behavior of Cu_3Au and Cu_3Pd. The existence of SRO splitting in Cu_3Au (but not in Cu_3Pd) results simply from the configurational entropy: Figure 2 depicts the cluster-expanded $T = 0$ K structural energies $\Delta E(m) = E(m) - E(\infty)$ of $L1_2$ "long period superstructures" (LPS), formed from $L1_2$ by inserting an antiphase boundary every m cells and have superlattice peaks at $(1\ \frac{1}{2m}\ 0)$. Minima in the energies $\Delta E(m)$ indicate stable LPS's, also reflected by minima in the effective interactions $V(\mathbf{k})$ between the W and X points. In Cu_3Pd, a structure with an intermediate m value is predicted (Fig. 2) to be more stable [$\Delta E(m) < 0$] than $L1_2$ ($m = \infty$) even at $T = 0$ K, so the splitting in SRO is an energetic effect and is reflected in the shape of $V(\mathbf{k})$. In Cu_3Au, however, we find that $\Delta E(m) > 0$ at $T = 0$ K for all m, and therefore these LPS's are not ground state structures, so the SRO splitting cannot possibly be a $T = 0$ *energetic*, but must rather be a $T > 0$ *entropic* effect.

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