Comment on "Nucleated and Continuous Ordering in Cu_3Au"

In a recent Letter by Ludwig *et al.*[1] the early-stage ordering kinetics in Cu_3Au were studied. For samples quenched from a disordered state to temperatures just below the order-disorder transition, it was shown that within the resolution of the experiment, the short-range-order diffuse intensity near the (100) superlattice point *initially* relaxed in a manner consistent with the predictions of (linear) spinodal ordering theory;[2] the corresponding spinodal temperature (T_{sp}) was found to be $\Delta T = T_{tr} - T_{sp} = 34$ K below the order-disorder transition temperature (T_{tr}) of 663 K, in good agreement with the value of Chen, Cohen, and Ghosh[3] of $\Delta T = 24.2$ K.

As mentioned by Ludwig *et al.*, the measured values of ΔT are significantly smaller than the theoretical prediction of 172 K according to de Fontaine and Kikuchi.[4] In this calculation, the tetrahedron[5] (T) approximation of the cluster-variation method[6] (CVM) was used to calculate the solid-state portion of the Cu-Au phase diagram, with parameters fitted to the Cu_3Au, CuAu, and $CuAu_3$ transition temperatures, and the spinodal ordering instability was calculated as the locus of temperatures at which the disordered state becomes unstable with respect to ordering waves of (100) type. It will now be shown that the CVM approach is basically correct in that, if higher cluster approximations are used in the CVM, the agreement between experimental and theoretical spinodal temperatures becomes quite satisfactory.

The Ising Hamiltonian described in the earlier work is used here as well: It consists of nearest-neighbor pair, triangle, and tetrahedron effective cluster interactions with values respectively chosen as 3.3155ε, -0.1119ε, and -0.1741ε per cluster. The scaling factor ε is adjusted to achieve the best overall fit. Here, however, the configurational entropy is treated in the tetrahedron-octahedron[5] (TO) and quadruple-tetrahedron[7] (QT) approximations. This work represents the first time the latter approximation has been used to calculate transition temperatures of the ordered Cu-Au phases.

Results of past and present calculations are listed in Table I. Although similar fits to the experimental[8] transition temperatures are obtained in each case, the values of ΔT for the three stoichiometric ordered phases decrease markedly as the level of CVM approximation increases. In particular, for the Cu_3Au phase studied by Ludwig *et al.*,[1] the calculated values of ΔT are successively 172, 30, and 30 K for the T, TO, and QT cluster approximations, respectively. It thus appears that ΔT has stabilized, at least for Cu_3Au and $CuAu_3$, at about the level at which the TO approximation is reached.

Transition temperatures of the nearest-neighbor fcc Ising model in zero field, as calculated with the CVM,[5,7] converge to high-temperature-expansion results[9] as the level of approximation is increased. In particular, the QT calculations agree to within 0.2% and 1.25% (Ref. 7) of the expansion results for the first-order antiferromagnetic and second-order ferromagnetic transitions, respectively. For this reason, we believe that the calculated values of ΔT will not change significantly for larger cluster calculations and the ordering spinodal temperature can therefore be defined uniquely in the limit of large cluster calculations.

TABLE I. Calculated and experimental (Refs. 1, 3, and 8) transition temperatures (in K) and (100)-ordering spinodal temperatures in the Cu-Au system.

		Approximation			
Phase		T	TO	QT	Expt.
Cu_3Au	T_{tr}	663	663	663	663
	T_{sp}	491	633	633	629
	ΔT	172	30	30	34,[a] 24.2[b]
CuAu	T_{tr}	687	679	677	683
	T_{sp}	581	622	638	
	ΔT	106	57	39	
$CuAu_3$	T_{tr}	495	493	492	473
	T_{sp}	367	472	471	
	ΔT	128	21	21	

[a]Reference 1. [b]Reference 3.

In summary, by increasing the level of approximation in a CVM calculation of the spinodal temperature of Cu_3Au beyond that originally considered in Ref. 4, we obtain a value of $\Delta T = 30$ K for Cu_3Au which is in excellent agreement with the experimental values of 34 K (Ref. 1) and 24.2 K (Ref. 3).

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