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Band theory of the Cu_3Au and $CuAu_3$ order-disorder transformations

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A band theoretical model for the Cu_3Au and $CuAu_3$ order-disorder transformations is presented based on an extended cluster–Bethe-lattice method electronic theory and the cluster-variation configurational-entropy approximation. A single *s*-band tight-binding Hartree Hamiltonian is solved self-consistently for the electronic configurations of single atoms embedded in an effective medium in the presence of nearest-neighbor short-range-order correlations. The functional dependence of the ordering energy and the temperature dependences of long- and short-range order and internal energy are compared with the Ising theory and experimental data.

The order-disorder phase transitions of the Cu-Au system have been of considerable experimental and theoretical interest. Experimentally it is known that the ordered phases of both Cu_3Au and $CuAu_3$ are of $L1_2$ symmetry, but that the first-order phase transition to a disordered state of cubic symmetry is decidedly more pronounced[1] in Cu_3Au ($T_c = 663$ K) than in $CuAu_3$ ($T_c = 473$ K). The Cu_3Au transition has been probed via diffuse x-ray scattering,[2,3] specific heat,[4] heats of formation,[5,6] optical,[7,8] Mössbauer,[9] and photoemission[10] measurements. It has been the consensus of these experiments that the variations of the Cu_3Au electronic structure with order are small. The $CuAu_3$ alloy requires long annealing times compared with Cu_3Au. This has inhibited as detailed a study of ordered $CuAu_3$ as of Cu_3Au, although diffuse x-ray scattering,[11] calorimetric,[6,12] and photoemission studies[10] of $CuAu_3$ have been performed. Theoretically, band-structure calculations[8,13] of Cu_3Au, as well as those of the pure elements, have been used to interpret the order dependence of Cu_3Au optical spectra in terms of band folding and Fermi-level gaps.

Theories of the thermodynamics of the alloys have been based on the Ising model. The most successful of these utilize the cluster-variation expression[14] for the configurational entropy of the alloys. It has been shown[15] that, within the tetrahedron approximation for this entropy, the reduced temperature (T/T_c) dependence of the Cu_3Au long-range order (LRO) and internal energy are in good agreement with experiment when site interactions are limited to nearest-neighbor pairs. If these interactions are taken to be concentration and order independent, as is usually the case, then the model predicts identical thermodynamics for Cu_3Au and $CuAu_3$. Van Baal was the first to point out[16] that the use of four-body nearest-neighbor interactions, together with the same entropy approximation, can correctly account for the observed transition-temperature disparity. It could not be argued, however, that this mechanism was necessarily the only one which could produce the observed asymmetry in the phase diagram.

In a previous work[17] we have described a band theory for order-disorder transformations. The theory calculates the LRO and short-range-order (SRO) dependence of the alloy internal energy using an extended cluster–Bethe-lattice method electronic theory. The configurational entropy contribution to the free energy is derived using the cluster-variation method. A model free energy is then minimized with respect to the order parameters at each temperature to determine the thermodynamics. In an application to the CuAu order-disorder transformation the band model was in quantitative agreement with experiment for the reduced temperature dependences of the LRO, SRO, and internal energy. In general the agreement was better than that of an Ising model that used the same entropy function but the classical pair-interaction energy. The calculated transition temperature was 555 K compared with the experimental value of 683 K. No effort was made to fit the input parameters of the electronic theory to improve agreement with experiment.

In this work we report results of further applications of our model to the Cu_3Au and $CuAu_3$ alloys. Except as noted, the electronic theory and all input parameters to the calculation are the same as those used for CuAu. Both the internal energies and the configurational entropies were calculated as a function of a single SRO parameter σ taken to be the bulk average of the nearest-neighbor SRO.

Since the symmetry of both ordered states is the same, both alloys have the same configurational entropies at a given value of σ. The value of σ can range between zero in the random alloys to $-\frac{1}{3}$ in the $T = 0$ ordered alloys. The SRO dependence of the entropy was determined by holding

σ fixed, while maximizing the entropy expression of the cluster-variation tetrahedron approximation with respect to all other correlations. This resulted in all included correlations becoming parametrized functions of σ. As in the case of the $L1_0$ structure of CuAu, the LRO drops discontinuously to zero for $|\sigma|$ less than some critical value, thus forcing a first-order transition when the internal energy depends only on σ.

The tight-binding Hartree Hamiltonian included as a basis a single s orbital per site. The d electrons were neglected since we believed the ordering energies to be primarily related to density of states changes near the Fermi level. This assumption is not inconsistent with the previously mentioned experimental conclusions concerning the order dependence of the electronic structure of the alloys. The Hartree interactions and hopping matrix elements were taken to be charge-transfer independent and limited to nearest neighbors. The internal energies of the alloys were calculated as a function of σ by embedding single Cu and Au atoms in an effective medium and calculating self-consistent electronic configurations. The ordering energy at each value of σ was calculated as the difference between the total internal energy $E_T(\sigma)$ and that of the random alloy $E_T(0)$. The reader is referred to our previous calculation[17] on CuAu for further details.

We compare our results with those previously reported[15] for an Ising model that uses the same entropy function but the classical pair-interaction energy. Such a model has an internal energy which depends linearly on the single variable σ of our model. Recall that this model does not distinguish between Cu_3Au and $CuAu_3$.

The calculated ordering energies of the two alloys are virtually identical in the present band model. The reason for this result will be discussed after a full comparison of the band- and Ising-model predictions. The SRO dependence of this ordering energy is shown in Fig. 1. The shape of curve is reminiscent of the one calculated for CuAu. For small σ the curve is linear, which means both the band and Ising models predict qualitatively the same high-temperature thermodynamics for the alloys. Near the $\sigma = -\frac{1}{3}$ regime the ordering energy of the band theory exhibits a nonlinearity, which does not allow any overall fit of the curve to Ising-like behavior. As was the case for CuAu, a nonlinearity also exists in the σ dependence of the self-consistent charge transfer.

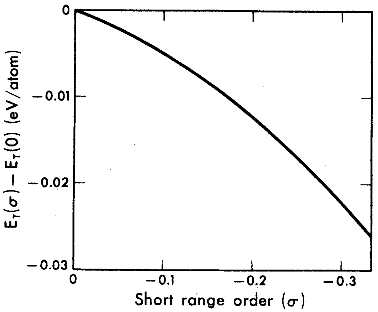

FIG. 1. Short-range-order dependence of the ordering energies of Cu_3Au and $CuAu_3$ in the band model. Differences between the curves are not visible on this scale.

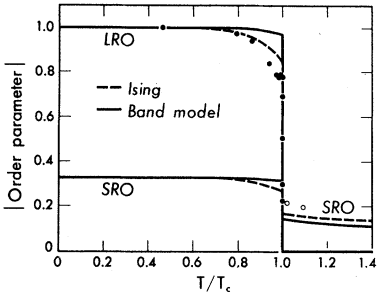

FIG. 2. Temperature dependences of the Cu_3Au LRO and SRO in the band model compared with the Ising model: LRO x-ray data (dots), and SRO x-ray data (circles).

Minimization of the alloy free energy determines the first-order transition temperatures to be ~467 K in both alloys. This value is in excellent agreement with the experimental value of 473 K for $CuAu_3$, but is quite low when compared with the observed value of 663 K for Cu_3Au. Since LRO data[2] are available only for Cu_3Au, we plot the temperature-dependent LRO and SRO in Fig. 2 as a function of the reduced temperature T/T_c. The Ising predictions are also shown for comparison. Two aspects of the figure suggest that the curvature of the ordering energy curve might actually be positive rather than negative as in the present model, or zero as in the Ising model. First, the

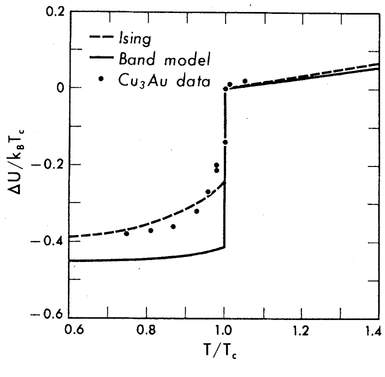

FIG. 3. Temperature dependence of the Cu_3Au heat of transformation in the band model compared with the Ising-model results and experimental data (dots). The discontinuity at T_c measures the latent heat.

discontinuity of the LRO at T_c is measured to be smaller than either theoretical prediction; and second, the Cu_3Au SRO at $T > T_c$ is measured[3] to be larger than either theoretical prediction. This conclusion rests, of course, on the assumption that the ordering energy depends only on σ and that the entropy approximation is accurate. This idea is also supported, however, by a comparison of theory and experiment[5] for the temperature dependence of the Cu_3Au internal energy. Figure 3 shows the T/T_c dependence of the normalized internal energy,

$$\Delta U/k_B T_c = [E_T(\sigma(T)) - E_T(\sigma(T_c))]/k_B T_c .$$

The positions of the two theoretical curves are qualitatively the same as they were in the CuAu calculation. The Ising theory fits the low-temperature data quite well but overestimates the latent heat of transformation at T_c. The band-theory curve is almost flat below T_c due to the curvature of the ordering energy curve, and the predicted latent heat is overestimated by a factor of almost 3. A slight positive curvature of the ordering energy curve would again bring theory into better agreement with experiment.

The band theory does represent an improvement over the Ising theory in the predictions for the theoretical ratios of the transition temperatures of $CuAu_3$ and CuAu to that of Cu_3Au. The experimental ratios are 0.71:1.03:1, while the Ising prediction is 1:0.98:1 and the band-theory prediction is 1.01:1.20:1. While both theories fail to distinguish between the $L1_2$ alloys, only the band theory succeeds in predicting the $L1_0$ structure of CuAu to have the highest transition temperature.

The negligible differences between our theoretical results for Cu_3Au and $CuAu_3$ are a result of the input parameters. The ordering energies would have been equal for all σ if the input band widths of Cu and Au had been equal. Our input band widths were not equal but their difference was not large enough to produce any significant asymmetry. This is because the parameter measuring the relative strength of the disorder-related scattering is δ/W, where δ is the difference between the centers of gravity of the s bands in pure Cu and pure Au and W is a typical band-width. Since the band is half filled and the Hartree parameters are site independent, there will only be significant differences between the ordering energies when $|W_{Au} - W_{Cu}|$ is of the order of δ. We would need $W_{Au} < W_{Cu}$ and $|W_{Au} - W_{Cu}| \gg \delta$ to produce the observed ratio of the Cu_3Au transition temperature to that of $CuAu_3$. Our input bandwidths were obtained from band-structure calculations. An accurate knowledge of these bandwidths was not necessary for the CuAu calculation, although it was important that they were about equal and both much greater than δ. In distinguishing between Cu_3Au and $CuAu_3$, their difference was crucial.

If changes in atomic volume had been taken into account, there would have been a concentration dependence of the hopping matrix elements. Assuming an exponential decay of the s wave functions centered at each site, a fit to the atomic wave functions[18] predicts that the ratio $t_{Cu\text{-}Cu}/t_{Au\text{-}Au}$ is approximately independent of concentration, even though both $t_{Cu\text{-}Cu}$ and $t_{Au\text{-}Au}$ decrease with increasing Au concentration. This effect by itself gives $CuAu_3$ a larger ordering energy than Cu_3Au, since for $\delta/W \ll 1$ the ordering energy decreases with increasing W.

Another assumed symmetry within our model is the equality of the intrasite Hartree parameters. Clearly there are considerable differences between the ionic cores located at the Cu and Au sites which, together with the above volume effects, suggest that this assumption may not be wholly justified.

Table I summarizes the quantitative effects of relaxing the above-mentioned symmetries in our input parameters. When the intra-atomic Hartree parameters were scaled by the lattice constants of Au and Cu to give $U_{Au} = 2.66$ eV and $U_{Cu} = 3$ eV, all transition temperatures were shifted almost uniformly upward. An *ad hoc* reduction of the input Au bandwidth to 8 eV did give Cu_3Au a larger ordering energy than $CuAu_3$ as expected. In neither case, however, did the shape of the ordering energy curves change enough to prevent the transition temperatures for alloys of the same symmetry from quite accurately scaling with the ordering energy. Though it would have been possible to fit our input parameters to most of the observed properties of the three Cu-Au compounds, the simplicity of the theoretical model and certain aspects of the experimental work suggest that such a procedure is not really warranted.

Our results lead us to suggest that a change in atomic volume is the main cause of the difference between the critical temperatures of Cu_3Au and $CuAu_3$. Though this effect tends to lower the Cu_3Au transition temperature in our model rather than raise it, there are other factors to consider. The most important of these is the contribution of the d electrons to Fermi-level properties through s-d hybridization. It is well known[19] that this hybridization is responsible for a sizeable fraction of the cohesive energy of the noble metals and that the trends in the compressibilities of the transition metals are tied to the filling of the d band. To account fully for the volume (i.e., concentration) dependence of the ordering energies, a calculation involving the s and d bands together with

TABLE I. Summary of Cu-Au theoretical results.

Method	Quantity	Cu_3Au	CuAu	$CuAu_3$
Experiment	T_c	663 K	683 K	473 K
Unadjusted input	Ordering energy	0.026 eV	0.039 eV	0.026 eV
	T_c	464 K	555 K	467 K
Decreased Au band width	Ordering energy	0.031 eV	0.033 eV	0.022 eV
	T_c [a]	~555 K	~470 K	~394 K
Decreased Au Hartree parameter	Ordering energy	0.030 eV	0.045 eV	0.030 eV
	T_c	541 K	628 K	530 K
Ising model	Ordering energy [b]	0.375	0.5	0.375
	T_c [b]	0.4811	0.4733	0.4811

[a] Estimates based on scaling only.

[b] In units of the pair-interaction parameter $W = 2V_{ab} - V_{aa} - V_{bb}$.

a more sophisticated scheme for determining the matrix elements will be necessary. A volume-variation effect has been discussed previously[20] in connection with the nearest-neighbor pairwise Ising model. By assuming the pair interactions to vary as r^{-6}, as in the rare gases, the Ising critical-temperature ratios change from 1:0.98:1 to 0.69:0.82:1. When compared with the experimental ratios 0.71:1.03:1, it is obvious that the theoretical ratio $T_c(CuAu_3):T_c(Cu_3Au)$ is within 2% of the experiment, but on the other hand the theoretical ratio $T_c(CuAu):T_c(Cu_3Au)$, which was only 5% too low without the correction, now becomes 21% too low. We note that the assumption of a Thomas-Fermi screened Coulomb interaction, with a screening length appropriate to Cu, produces the same ratios. Thus, although the volume effect should be significant, there seems to be no straightforward way of including it in the pair-interaction model. The Ising model with four-body interactions is able to avoid consideration of this effect by an *ad hoc* fitting of the interactions to the proper transition temperature ratios.[16]

Clapp and Moss[21] have extracted from high-temperature diffuse x-ray scattering, and by means of mean-field theory, a single effective ion-ion interchange energy

$$W(r) \equiv 2V_{ab}(r) - V_{aa}(r) - V_{bb}(r),$$

which is of infinite range and fits well all three alloys Cu_3Au, CuAu, and $CuAu_3$. It has not yet been possible, however, to include such a long-range volume-dependent interaction in an Ising theory valid near the transition temperature. A mean-field theory has been however formulated[22]; its extrapolation to low temperatures yields a Bragg-William model, with only long-range order and its attendant second-order transition. Even though this is patently incorrect, this theory yields transition temperatures ratios of 0.67:0.92:1. If we extract the values of Clapp and Moss for nearest neighbors only and apply it to the cluster-variation tetrahedron approximation, we obtain ratios of 0.19:0.47:1.

Our band theory includes only nearest-neighbor correlations, but the topology of the ion-ion interactions is not limited to pairs and the range is effectively infinite. It has the advantage of utilizing the cluster-variation method to determine realistic thermodynamic properties for all ranges of temperature. An extension of the theory to define effective pair interaction in the random alloy may allow the model also to be used in predicting high-temperature diffuse scattering patterns.

The characteristic shape of the ordering energy functions is related to the cluster size we have chosen. The slope of the curve depends on the rate at which changes occur in the vicinity of the Fermi level with changing SRO. Since the ordered structure cannot be fully perceived through only nearest-neighbor SRO correlations, the curvature of the ordering energy function is dependent on the cluster size used in the calculation. Larger-cluster calculations which average over higher-order correlations would probably decrease the slope of the curve near $\sigma = -\frac{1}{3}$ and might change the overall curvature. A classical strain-energy argument for the ordering energy predicts a minimum of the ordering energy function at $\sigma = -\frac{1}{3}$, since this is the stable structure at $T = 0$.

In summary, we have shown that a band model for the SRO dependence of the Cu_3Au and $CuAu_3$ ordering energies predicts a transition temperature in excellent agreement with the observed value for $CuAu_3$. Like the analogous Ising model, and contrary to experiment, the band model also predicts very similar ordering temperatures for $CuAu_3$ and Cu_3Au. Our band model predicts, in agreement with experiment and contrary to the Ising model, that the transition temperature of CuAu is higher than those of $CuAu_3$ and Cu_3Au.

A scaling of the band-theory predictions to a reduced temperature scale showed the Ising model to be in better agreement with SRO, LRO, and internal energy data for Cu_3Au. It was concluded that the neglect of *s*-*d* hybridization and volume effects are probably responsible for the discrepancy between the present results and the observed differences between Cu_3Au and $CuAu_3$. The use of larger clusters in the calculation would more accurately perceive the rate at which the ordered structure is approached with changing SRO, and should bring the band-model predictions of temperature-dependent properties more in line with experiment. Future theoretical work on order-disorder phenomena should focus on such matters.

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