PHYSICAL REVIEW B VOLUME 18, NUMBER 6 15 SEPTEMBER 1978

Band theory for order-disorder phase transformations: CuAu

R. C. Kittler and L. M. Falicov

Department of Physics, University of California, Berkeley, California 94720

(Received 2 May 1978)

We present a band theory for the internal energy of binary alloys which undergo order-disorder transformations. The general method involves the self-consistent solution of a tight-binding Hartree Hamiltonian in the presence of both long- and short-range-order correlations through the use of an extended cluster–Bethe-lattice method. A complete scheme for the derivation of the alloy thermodynamics is obtained by coupling the electronic theory to the cluster-variation combinatorial theory for the alloy configurational entropy. The theory is applied to the study of the CuAu order-disorder transition and comparisons are made to existing data and Ising models.

I. INTRODUCTION

Theoretical interpretation of order-disorder phase transformations have been based for the most part on various approximations to the classical Ising model.[1] The theories involve assumptions regarding the extent of multisite correlations and the manner in which the correlations determine the alloy free energy. Since the aim of the theories is to describe the temperature dependence of phase stability and of macroscopic variables such as the specific heat, it is important that the assumptions be grounded in first-principles calculations whenever possible.

Considerable effort has been devoted to improving combinatorial theories for the configurational entropy contribution to the alloy free energy. Recently Kikuchi[2] has developed a theory for a series of increasingly-higher-order approximations to the entropy which has come to be known as the cluster-variation (CV) method. The level of approximation depends on the highest-order multisite correlation to be considered. In a prescribed fashion the theory seeks to correct for the inconsistencies in counting which are necessarily present when only a finite level of correlations is taken into account. In the single-site and pair approximations the theory reduces to the well-known Bragg-Williams and Bethe approximations, respectively. Due to the ease of including higher-order correlations the CV theory has been widely applied to the determination of alloy phase diagrams[3] and to the study of ferromagnetic transitions in the bulk[4] and at phase boundaries.[5] We shall make use of the CV results in determining all necessary configurational entropies.

In principle the alloy internal energy is the total energy of the electron-ion system. One approach to constructing this term is to make chemical bonding or perturbation theory arguments towards its expression as the sum of pair interaction energies. While these arguments lead to theories which work well for alloys of simple metals[6] it is well known that for alloys of more complex elements, such as those of the transition metal series, the total energy cannot be written as the sum of pair energies.[7] This is due to the strongly itinerant character of the electron wave functions.

Despite these arguments the pair interaction model with an interaction range limited to nearest neighbors only has been quite valuable in understanding such complex phase diagrams as that of the Cu-Au alloy.[8-10] This suggests that although the total energy is not rigorously the sum of pair interactions, the ordering energy can quite effectively be modeled as such. This success, however, does not overshadow some ambiguities in the theory. Since the use of concentration-independent pair interactions leads to phase diagrams symmetric in the concentration, it is necessary to go beyond this approximation if the asymmetries of many phase diagrams are to be understood. Two straightforward solutions are to make the pair interactions concentration dependent or to retain the concentration independence and include higher-order multisite interactions. (The latter was used by Van Baal[9] and others[3] in their applications to CuAu.) Although the two methods are distinct within the classical Ising model, no clear argument exists for choosing one over the other.

A microscopic electronic theory for the concentration and correlation dependent ordering energy avoids the ambiguities connected with generalizing Ising calculations. Thus far, the efforts in this direction[11] have involved the use of coherent-potential[12] band models. The bulk of the theories are concerned with model binary alloys in which only long-range-order (LRO) correlations exist. Althought no concentration dependent studies have been made, at a fixed concentration the theories predict that the LRO functional dependence of the ordering energy is the same as in the classical

Bragg-Williams Ising model. Results for order-disorder theories in alloys having short-range-order (SRO) correlations have not been reported, although a generalized perturbation theory encompassing both LRO and SRO has been introduced.[13] Studies of electronic spectra of binary alloys which include short-range-order properties have, on the other hand, been extensively done.[14-18]

In this work we describe a band theory for the ordering energy which incorporates both LRO and SRO. The ordering energy is derived from a tight-binding Hartree Hamiltonian using a generalization[14] of the cluster–Bethe-lattice method (CBLM).[15] This is a real space approach in which the bulk density of states is derived from a configurational average over the local densities of states at the central site of a cluster of atoms embedded in an effective medium. The effective medium is chosen to have a Bethe lattice or Cayley tree topology which preserves the coordination number of the lattice but has no rings of bonds. The LRO and SRO correlations determine the branching ratios of the tree or equivalently the local environments within the effective medium.

The theory and its application are described in the remaining sections of the paper. The sections are organized as follows. In Sec. II we describe the electronic theory for the ordering energy and its use in predicting the thermodynamics of the alloy. In Sec. III we describe an application of the theory at a fixed concentration to the particularly well-studied CuAu alloy and compare its predictions to those of the classical Ising model. Lastly, in Sec. IV we present a summary and conclusions.

II. BAND THEORY OF THE PHASE TRANSITION

The internal energy of the alloy is the total energy of the electron-ion system. We choose as the Hamiltonian a tight-binding Hartree model with inter- and intrasite electron-electron Coulomb interactions. This model incorporates the essential features required for a self-consistent treatment of charge transfers and is relatively easy to solve using real space techniques. In the multiband case it may be written as

$$H=\sum_{i\sigma n}\epsilon_{in\sigma}n_{in\sigma}+\sum_{\substack{ij\\ nm\sigma}}t_{in,jm}c^{\dagger}_{in\sigma}c_{jm\sigma}+E_I-E_{ee}\,, \qquad (1)$$

where

$$\epsilon_{in\sigma}=\epsilon^{0}_{in\sigma}+U_{in}\langle n_{in-\sigma}\rangle+\sum_{\substack{m\\ m\neq n}}V_{in,im}\langle n_{im}\rangle + \sum_{\substack{jm\\ j\neq i}}V_{in,jm}\langle n_{jm}\rangle\,, \qquad (2)$$

$$E_I=\sum_{i>j}\frac{Z_iZ_j}{|\vec{R}_i-\vec{R}_j|}\,, \qquad (3)$$

and

$$E_{ee}=\frac{1}{2}\sum_{in\sigma}(\epsilon_{in\sigma}-\epsilon^{0}_{in\sigma})\,\langle n_{in\sigma}\rangle\,. \qquad (4)$$

In these equations $c^{\dagger}_{in\sigma}$, $c_{in\sigma}$, and $n_{in\sigma}$ are creation, destruction, and number operators for localized Wannier states, i and j are site indices, n and m are band indices, σ is a spin index, $n_{in}=n_{in\uparrow}+n_{in\downarrow}$, and Z_i is the core charge on the i^{th} ion. The first two terms in (1) include the electron-ion interactions and may be solved separately for the electronic density of states. The third term represents the ion-ion interaction and the fourth term corrects for the overcounting of the electron-electron interactions by the first term. All other symbols (ϵ^{o}, t, U, and V) are energy parameters.

For a specific configuration of ions and a temperature T, calculation of the local densities of electronic states and the electrostatic energy of the ions determines the internal energy. The calculation of the local densities of states $N_{in\sigma}(\omega)$ should be done self-consistently since in principle the electron density affects not only the thermally averaged occupation $\langle n_{in\sigma}\rangle$ but also the hopping matrix elements $t_{in,jm}$ and Coulomb integrals U_{in} and $V_{in,jm}$. Assuming that this self-consistency is achieved the occupations are given by

$$\langle n_{in\sigma}\rangle=\int_{-\infty}^{\infty}\frac{N_{in\sigma}(\omega)\,d\omega}{\exp[(\omega-\mu)/k_BT]+1}\,, \qquad (5)$$

where the chemical potential μ is determined through the relation

$$\sum_{in\sigma}\langle n_{in\sigma}\rangle=\sum_i Z_i\,. \qquad (6)$$

The total internal energy E_T can be written in terms of the occupations and the total density of states $N(\omega)=\sum_{in\sigma}N_{in\sigma}(\omega)$ as

$$E_T=E_H-E_{ee}+E_I\,, \qquad (7)$$

where

$$E_H=\int_{-\infty}^{\infty}\frac{N(\omega)\omega\,d\omega}{\exp[(\omega-\mu)/k_BT]+1}\,. \qquad (8)$$

The free energy of the alloy is determined by minimizing a model free-energy function over the space of possible electron-ion configurations. These configurations may be classified by the values of certain order parameters $\{\alpha_l\}$ which measure multisite correlations, e.g., long-range order, short-range order, three-body correlations, etc. For an A_xB_{1-x} alloy at temperature T we write the free energy $\mathcal{F}(T,x)$ as

$$\mathcal{F}(T,x)=\min_{\alpha_l}F(T,x;\alpha_l)\,. \qquad (9)$$

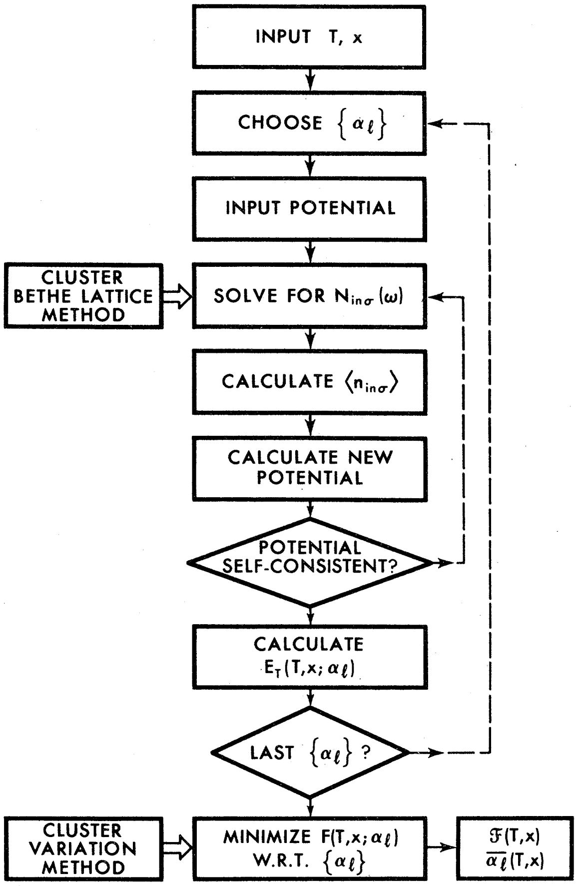

FIG. 1. Block diagram indicating the basic steps in achieving a self-consistent electronic theory of the alloy ordering energy and in determining the alloy thermodynamics.

where

$$F(T,x;\alpha_l)=E_T(T,x;\alpha_l)-TS(x;\alpha_l). \tag{10}$$

The function $S(x;\alpha_l)$ is the entropy associated with the class of configurations labeled by $\{\alpha_l\}$ at compositon x, and $E_T(T,x;\alpha_l)$ is the average energy of the class $\{\alpha_l\}$, which has a temperature dependence through the occupation probabilities, Eqs. (3)–(8). The temperature and concentration dependence of the equilibrium value of the order parameters $\{\bar{\alpha}_l\}$ is given implicitly through the relation

$$\mathcal{F}(T,x)=F(T,x;\bar{\alpha}_l). \tag{11}$$

We have as yet placed no restriction on the nature of the order parameters α_l but, in order to obtain a manageable theory, we now limit $\{\alpha_l\}$ to include only LRO and SRO, i.e., only single-site and pair correlations.

A schematic of the free-energy calculation is shown in Fig. 1. The two major loops correspond to achieving a self-consistent electron density for a given set of $\{\alpha_l\}$ and to the calculation of the internal energy over a narrow mesh in the $\{\alpha_l\}$ parameter space. We use CBLM to calculate the local densities of states $N_{in\sigma}(\omega)$. For a review of this method and its generalization to the inclusion of LRO and SRO the reader is referred to Appendix A. When the internal energy has been determined over a narrow $\{\alpha_l\}$ mesh, or over a series of special $\{\alpha_l\}$ points which facilitate a reasonable interpolation scheme, the trial free energy $F(T,x;\alpha_l)$ is constructed using the cluster-variation approximation for the entropy. Once $\mathcal{F}(T,x)$ is obtained by minimization, the thermodynamic quantities of interest—specific heat, internal energy, entropy—can be calculated for direct comparison with experiment.

III. APPLICATION TO CuAu

The phase diagram of the CuAu alloy[19] is rich in order-disorder phenomena with phase transitions at Cu_3Au, CuAu, and $CuAu_3$. At temperatures below 385°C the stable structure of the CuAu alloy is that of $L1_0$ symmetry. This is a layerlike structure (CuAu I) where the (001) planes of a tetragonally distorted fcc lattice are alternately Cu and Au. Between 385 and 410°C a long-period superlattice (CuAu II) is present in a direction parallel to the planes. At 410°C there is a first-order phase transition to an fcc disordered phase. The order-disorder transformation at 410°C has been observed in x-ray diffraction,[20] direct reflectivity,[21] Mössbauer spectra,[22] and heats of formation[23] measurements.

Theoretical interpretation of the CuAu order-disorder phase transition has been based on the Ising model. Shockley's Bragg-Williams approximation included LRO correlations only, and incorrectly predicted the transition to be of second order.[24] Later Li developed a quasichemical model[25] which included four-site correlations—the so-called tetrahedron approximation. The transition was predicted to be of first order but the complete phase diagram showed a solubility range which was much too narrow. The most realistic phase diagrams have been obtained by Golosov,[8] Van Baal,[9] and Kikuchi[10] using the CV expression for the entropy in the tetrahedron approximation. We henceforth refer to their Ising approximation as GBK model.

In what follows we apply the theory of Sec. II to determine a band model for the CuAu transition. The ordering energy is calculated as a function of a single SRO parameter σ which is the bulk average of the SRO over the various sublattices. The entropy is derived in the CV tetrahedron approximation in Appendix B as a function of this single variable σ by contracting the long-range order and higher-order correlations. At each temperature the model free energy is minimized with respect to σ to obtain the equilibrium properties. We compare our results to those of the GBK model which uses the same entropy contribution to the free energy but the classical ordering energy.

We choose for the Hamiltonian (1) a simple form that gives sensible densities of states near the Fermi level at all possible orders, since we believe this to be the primary cause of the ordering energy. The model neglects effects of the *d* electrons and includes as a basis a single *s* orbital per site. The Hartree interactions are taken to be site independent and limited to nearest neighbors. Since Mössbauer experiments[22] and Pauling electronegativities suggest that charge transfers are small, we take the Hartree parameters and hopping matrix elements as charge-transfer independent. A similar model was shown by Rudnick and Stern[26] to incorporate most of the important features necessary for a study of self-consistent screening of charged impurities by conduction electrons.

With these approximations charge-transfer effects enter the Hamiltonian only through the single-site electron energy levels:

$$\epsilon_\mu = \epsilon_\mu + U\Delta n_\mu + 2V(Z_\mu \Delta n_\mu + \zeta_\mu \Delta n_\nu), \tag{12}$$

where μ labels a Au (Cu) atom, ν a Cu (Au) atom, ϵ_μ^0 the electron energy level in pure μ material, U and V the Hartree parameters, Δn_μ and Δn_ν the charge transfers, and Z_μ (ζ_μ) the number of μ (ν) atoms in the first shell surrounding a μ atom.

The configurational averages of Z_μ and ζ_μ, denoted by $\overline{Z}_\mu$ and $\overline{\zeta}_\mu$, are simply related to the SRO through

$$\overline{Z}_\mu = 6(1+\sigma), \quad \overline{\zeta}_\mu = 6(1-\sigma), \tag{13}$$

where σ can range between zero in the random alloy and $-\frac{1}{3}$ in CuAu I at $T=0$. The averages quantities $\overline{Z}_\mu$ and $\overline{\zeta}_\mu$ are related to the branching ratios of the Cayley-tree effective medium[14] through

$$Z_{\mu\mu} = Z_{\mu\nu} = \tfrac{11}{12}\overline{Z}_\mu, \quad \zeta_{\mu\mu} = \zeta_{\mu\nu} = \tfrac{11}{12}\overline{\zeta}_\mu. \tag{14}$$

Given the Hamiltonian and the branching ratios the properties of the effective medium for a given SRO can be determined independently of the cluster configuration.

To minimize the difficulty of achieving self-consistency we choose the local densities of states to be those for single atoms embedded in the effective medium, i.e., we choose a cluster of one atom. With only two different types of sites, i.e., Au and Cu atoms in their average environments, each sum over sites in Sec. II involves just two terms. We take the $T=0$ limit in the calculation of (5) and (8), since order-disorder phenomena occur at temperatures small compared to the normal band Fermi-Dirac temperature.

The tight-binding parameters were fitted when possible to atomic and bandstructure data. This procedure allowed CBLM to interpolate between known limits of the electronic properties. The energy difference between the spectroscopic 6*s* levels[27] of Cu and Au was used as the $\epsilon_{\mathrm{Au}}^0 - \epsilon_{\mathrm{Cu}}^0$ difference. The Cu-Cu and Au-Au hopping matrix elements were chosen to reproduce calculated[28,29] *s* bandwidths of Cu and Au and their geometric mean was set equal to the Cu-Au hopping parameter. Following Rudnick and Stern,[26] we chose the parameter U to be a sizeable fraction of the *s* bandwidths but small enough to prevent the ground state from being spin ordered.[30] We have taken $U=3$ eV and $V=0.56$ eV. The values of the input parameters are summarized in Table I.

The local densities of states were determined using the self-consistency requirement that the charge transfer differs by less than 10^{-4} between consecutive iterations. The resulting total densities of states for the two extremes of the allowed SRO range are shown in Fig. 2. Van Hove-like singularities are not present in the density of states of the ordered alloy because of the lack of crystalline periodicity inherent in the CBLM. The lower band edge for the ordered alloy occurs at an energy slightly lower than that of the random alloy, but the main differences between the two curves occur near the centers of the bands. Whereas the density of states of the random alloy is symmetric about zero, the curve for the ordered alloy displays an asymmetric two-peaked structure. The asymmetry is due to the difference in the Au-Au and Cu-Cu hopping matrix elements, while the dip is a consequence of the SRO correlations. The densities of states for intermediate SRO evolve smoothly between these two limits.

TABLE I. Input parameters for the CuAu calculations.

Matrix element	Value (eV)
$\epsilon_{\mathrm{Cu}}^0 - \epsilon_{\mathrm{Au}}^0$	1.50
Au bandwidth	14.42
Cu bandwidth	15.62
$t_{\text{Au-Au}}$	1.09
$t_{\text{Cu-Cu}}$	1.18
$t_{\text{Au-Cu}}$	1.13
U	3.00
V	0.56

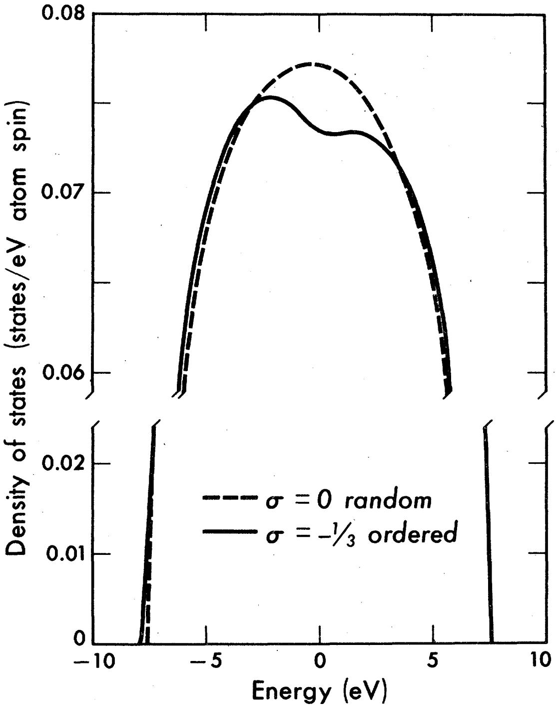

FIG. 2. Total density of states of the CuAu alloy in the s-band model. The two extremes of the SRO range occur at the $\sigma = 0$ random limit and the $\sigma = -\frac{1}{3}$ ordered limit. The curves have been normalized to a single state/(atom spin).

The SRO dependence of the charge transfer at the Au atoms is shown in Fig. 3. As opposed to previous band theories[11] for alloys which include only LRO correlations, the charge transfer is not linear in the order parameter. The maximum charge transfer is ~0.23 electron/atom and is consistent with the small value assumed in choosing the model.

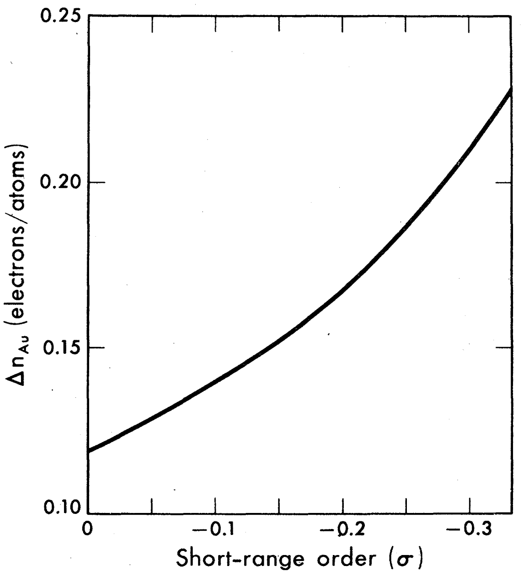

FIG. 3. Self-consistent charge transfer at a Au atom as a function of the SRO correlations.

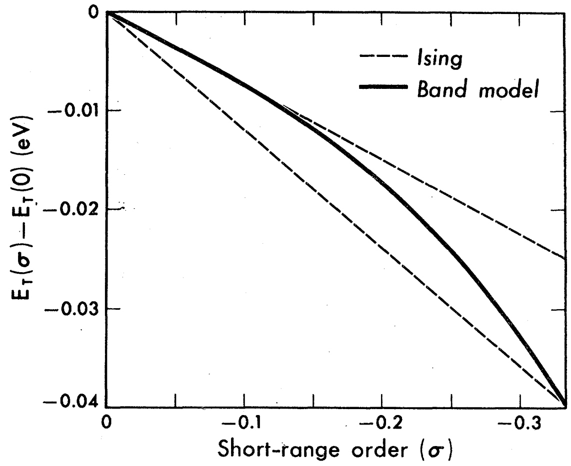

FIG. 4. Ordering energy of the CuAu alloy as calculated in the band model as a function of the SRO. The two dashed lines are possible linear fits to the Ising theory.

The alloy thermodynamics depends on only those contributions to the total internal energy which are order dependent. This enhances the validity of our simple model and provides for further simplifications within the model by allowing us to avoid the calculation of the ion-ion term (3). Within our point-ion model the ion-ion term is independent of ionic arrangement since all core charges are equal. If screening effects were taken into account we would still expect the SRO dependence of this term to be negligible since the variation of the density of states with order is small.

The results for the SRO dependence of the alloy internal energy are shown in Fig. 4. The two dotted lines are possible fits to the linear dependence always assumed by the Ising model: one fits the small σ regime while the other fits the curve over the whole range. Since our band theory yields linear behavior for small σ, it also gives qualitatively the same high-temperature thermodynamics as the Ising model. The band theory result exhibits a characteristic nonlinearity with increasing SRO which does not allow any overall fit of the curve to Ising-like behavior.

We might interpret this nonlinearity in terms of order-dependent pair interactions through the use of the Ising expression for the internal energy:

$$[E_T(\sigma) - E_T(0)]_{\mathrm{Ising}} = -\tfrac{3}{2} W_0 \sigma \,. \qquad (15)$$

Here W_0 is related to the nearest-neighbor pair-interaction energies V_{AA}, V_{AB}, and V_{BB} through

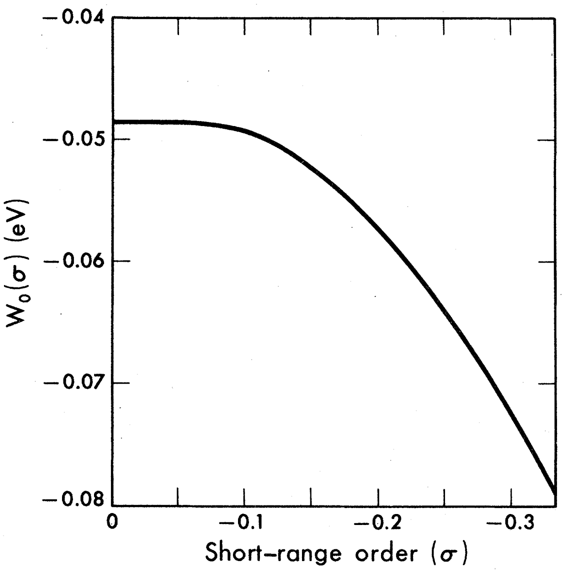

FIG. 5. SRO dependence of the pair interaction parameter $W_0 = 2V_{AB} - V_{AA} - V_{BB}$ which would be necessary for the Ising and band models to predict the same SRO dependence of the ordering energy.

$$W_0 = 2V_{AB} - V_{AA} - V_{BB} < 0 \tag{16}$$

The functional behavior of W_0 which yields the band theory internal energy is shown in Fig. 5. Since W_0 is simply related to the derivative of the internal energy curve of Fig. 4 the value of W_0 is constant only near the disorder limit $\sigma \to 0$. Outside of this region W_0 is noticeably influenced by the amount of correlation present in the alloy and can vary in magnitude by as much as 60%.

The band theory result for the ordering energy $E_T(\sigma) - E_T(0)$ together with the CV entropy expression in the tetrahedron approximation predict a first-order phase transition at 555°K. The existence of the transition and its order are mandated by the entropy function and would occur for any model which uses an internal energy dependent only on the SRO (see Appendix B). The experimental value of the transition temperature is 683°K. The relatively small discrepancy (19%) is consistent with the small disparity[23] between the experimental (0.041 eV/atom) and theoretical (0.030 eV/atom) values for the difference between the internal energies at $T = 700$°K and $T = 298$°K. In light of these small differences we analyze the temperature-dependent quantities in terms of the reduced temperature T/T_c.

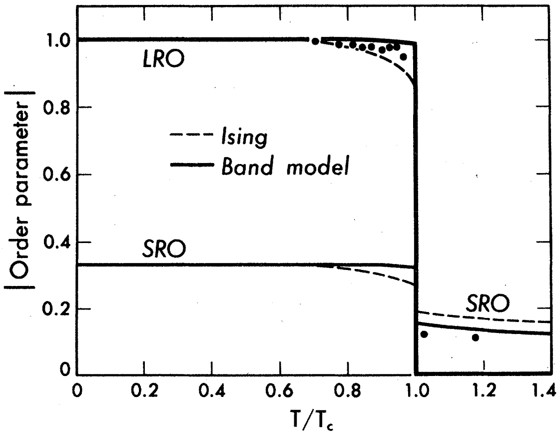

FIG. 6. Temperature dependences of the CuAu LRO and SRO in the band model compared to those of the GBK Ising model and the x-ray data (shown as dots). The LRO drops discontinuously to zero at T_c and a discontinuity occurs in the SRO.

The temperature dependences of the equilibrium LRO and SRO together with the predictions of the GBK model and the x-ray data of Roberts[20] are shown in Fig. 6. Our model predicts that the LRO drops to only 0.991 at $T = T_c$, just below the transition, compared to the GBK value of 0.847 and Robert's estimate of 0.97. The higher value of the present theory is due to the nonlinearity of the internal energy curve near $\sigma = -\frac{1}{3}$. Although the LRO x-ray data are not accurate enough to act as a critical test of the theory, when they are coupled with the SRO data an overall comparison seems to favor our theory over the GBK predictions. Note that the SRO data near T_c above the transition agrees better with the lower value of (−0.155) given by the present theory than with the GBK prediction of (−0.188). Clearly, however, more SRO data are needed to make an adequate comparison.

We define a heat of transformation ($\Delta U/k_B T_c$) as the difference ΔU between the internal energies of the alloy at temperature T and T_c normalized by $k_B T_c$. This heat of transformation is plotted in Fig. 7 and compared with the GBK results and heat of formation data.[23] Our theory agrees more closely in magnitude with the data than GBK at low T but fails to predict the rapid rise near T_c and hence overestimates the latent heat of transformation. The small slope of the curve below T_c is due to the near constancy of the SRO for these temperatures and the large latent heat at T_c to the large discontinuity in the SRO there. The data do not distinguish between the two theories above T_c.

The results of the CuAu calculation are dependent on the choice of both the Hartree parameters U and V and the cluster size. Studies with similar Hartree Hamiltonians suggest that a variation of U by up to 100% changes the ordering energy by less than an order of magnitude.[11,31] Since the choice of any reasonably sized U does not affect the qualitative order dependence of the density of states, such a variation would lead to a simple scaling of the

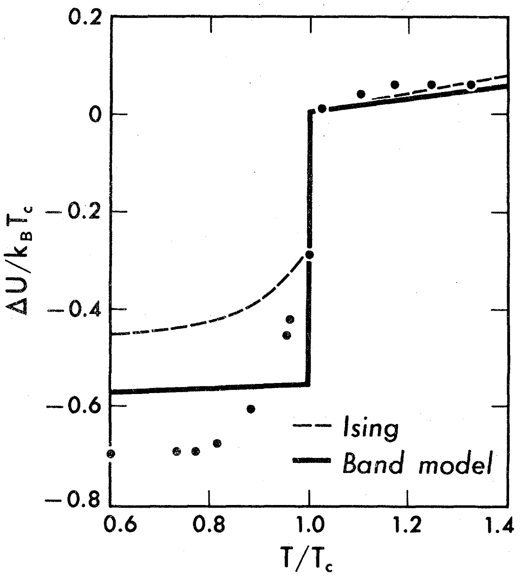

FIG. 7. Temperature dependence of the heat of transformation in the band model compared to that of the GBK Ising model and the experimental data (shown as dots). The discontinuity at T_c measures the latent heat.

$E_T(\sigma)$ curve, leaving the reduced temperature dependences unchanged. The magnitudes of U and V are comparable to those used in other theories.[11,26,31,32] The use of larger clusters would more realistically account for the geometry of the lattice but would also introduce numerical problems in the attainment of self-consistent results and in the necessity of including higher-order correlations.

IV. SUMMARY AND CONCLUSIONS

We have introduced a band-theory method for calculating the ordering energy of a binary alloy. We include both long- and short-range order. A complete scheme for the derivation of the alloy thermodynamics was obtained by coupling the electronic theory for the ordering energy to the CV combinatorial theory for the configurational entropy of the alloy.

The theory was applied to study the order-disorder transition of CuAu. The band model predicts a SRO dependence to the ordering energy different from that assumed in Ising theories. Both the band theory and the GBK model predict first-order transitions and qualitatively the same temperature dependences of the order parameters and heat of transformation. A detailed comparison with experimental results, however, favors the present theory over previous Ising models. This is very encouraging in light of the simple electronic theory used and reflects the fact that the driving forces behind the order-disorder transformation are primarily Fermi-level effects. Improvements in the theoretical model could be achieved by including higher-order correlations and screening effects, by taking account of the d electrons as well as s-d hybridization, and by increasing the cluster size.

Overall, the theoretical results obtained for CuAu seem to contain no spurious aspects. Their good agreement with experiment should encourage further applications of the theory.

APPENDIX A: CBLM ELECTRONIC THEORY

The CBLM is here briefly reviewed and extended to include LRO, as well as SRO. For further details the reader is referred to Refs. 14 and 15. The object of CBLM is to provide a theory for the local densities of states in a bulk alloy by embedding finite clusters of atoms in an effective medium. For a given cluster configuration the local density of states for a site i within the cluster, band n and arbitrary spin is given by

$$N_{in}(\omega) = -(1/\pi)\,\mathrm{Im}\langle in\,|\,(\omega - H - \Sigma)^{-1}\,|\,in\rangle\,, \tag{A1}$$

where H is the Hamiltonian for the bare cluster and Σ is a self-energy which takes the coupling to the effective medium into account. In CBLM, Σ is diagonal in the site index and its nonzero elements occur only for those sites on the boundary of the cluster. For such a site we can write the self-energy Σ_{ii} as a sum over the contributions due to each nearest-neighbor link between the boundary atom and the effective-medium atoms:

$$\Sigma_{ii} = \sum_{(j\beta)} \Delta_{ij}^{\alpha\beta} \tag{A2}$$

where i labels an atom A or B on the α sublattice at the boundary, j an atom on the β sublattice in the effective medium, and $\Delta_{ij}^{\alpha\beta}$ the self-energy contribution due to this link.

The $\Delta_{ij}^{\alpha\beta}$ can be determined self-consistently using a Green's-function technique.[14] They are simply related to the transfer functions $t_{ji}^{\beta\alpha}$ described in our previous work through

$$\Delta_{ij}^{\alpha\beta} = V_{ij}\,t_{ji}^{\beta\alpha}\,, \tag{A3}$$

where $V_{ij} = \langle i\,|H|\,j\rangle$. Analogous to the transfer function derivation we have

$$\Delta_{ij}^{\alpha\beta} = V_{ij}\left(\omega - U_i - \sum_{\gamma} \left(Z_{ij}^{\alpha\beta\gamma}\,\Delta_{ij}^{\gamma\alpha} + \zeta_{ij}^{\alpha\beta\gamma}\,\Delta_{\bar{i}i}^{\gamma\alpha}\right)\right)^{-1} V_{ji}\,, \tag{A4}$$

where $U_i = \langle i\,|H|\,i\rangle$ and $\bar{i}$ is the species different from i.

In (A4), $Z_{ij}^{\alpha\beta\gamma}$ ($\zeta_{ij}^{\alpha\beta\gamma}$) gives the average number of like (unlike) atoms; this refers to i-site α-sublattice atom, connected to a γ sublattice further down a Cayley tree and to a j atom β sublattice in the previous step of the Cayley tree hierarchy. With more than one band the Δ's, V's, and U's all become matrices. The $Z_{ij}^{\alpha\beta\gamma}$ and $\zeta_{ij}^{\alpha\beta\gamma}$ are easily related to the bulk order parameters.

APPENDIX B: SRO DEPENDENCE OF THE ENTROPY

We wish to determine the entropy for the $L1_0$ phase of an $A_{0.5}B_{0.5}$ alloy as a function of the SRO only. Consider the CV entropy in the tetrahedron approximation for an arbitrary concentration. Let α, β, γ, and δ be the four sublattices of the fcc-like structure and i label either an A or a B atom. Further, let x_i^α be the probability of an i atom occupying an α sublattice site with $y_{ij}^{\alpha\beta}$ and $z_{ijkl}^{\alpha\beta\gamma\delta}$ (or simply z_{ijkl}) the corresponding pair and tetrahedral probabilities. Sum rules require that

$$\sum_{ijkl} z_{ijkl}=1, \quad \sum_{kl} z_{ijkl}=y_{ij}^{\alpha\beta}, \quad \sum_{j} y_{ij}^{\alpha\beta}=x_i^\alpha \tag{B1}$$

The CV entropy can be expressed in terms of these variables as[2]

$$\frac{S}{k_B N}=6\left(\frac{1}{6}\sum_{(\alpha\beta)}\sum_{ij}\mathcal{L}(y_{ij}^{\alpha\beta})\right)-5\left(\frac{1}{4}\sum_{\alpha}\sum_{i}\mathcal{L}(x_i^\alpha)\right)$$
$$-2\left(\sum_{ijkl}\mathcal{L}(z_{ijkl})\right)-1, \tag{B2}$$

$$\text{where } \mathcal{L}(x)\equiv x\ln x - x. \tag{B3}$$

We wish to maximize S with respect to the independent parameters z_{ijkl} subject to the constraints that the concentration and the SRO remain fixed, and the sum rules be satisfied. The SRO is expressed in terms of the z_{ijkl} as

$$\sigma = 1 - p_{AB}/x(l-x), \tag{B4}$$

$$p_{AB}=\frac{1}{12}\sum_{ijkl} g_{ijkl} z_{ijkl}, \tag{B5}$$

where p_{AB} is the A-B bond probability, x is the concentration of A atoms, and g_{ijkl} is the number of A-B bonds in the $ijkl$ configuration. The factor of $\frac{1}{12}$ acts to normalize the sum since there are 12 different nearest-neighbor links in each tetrahedron. Lagrange multipliers allow as to eliminate constraints by maximizing

$$\Phi \equiv S/k_B N - \lambda f - \gamma g, \tag{B6}$$

where

$$f \equiv \sum_{ijkl} z_{ijkl} - 1,$$
$$g \equiv \sum_{ijkl} g_{ijkl} z_{ijkl} - 12x(1-x)(1-\sigma). \tag{B7}$$

Differentiation with respect to z_{ijkl} gives

$$\frac{\partial\Phi}{\partial z_{ijkl}} = 0 = \ln Y_{ijkl} - \frac{5}{4}\ln X_{ijkl}$$
$$- 2\ln z_{ijkl} - \lambda - \gamma g_{ijkl}, \tag{B8}$$

where

$$Y_{ijkl} \equiv y_{ij}^{\alpha\beta} y_{ik}^{\alpha\gamma} y_{il}^{\alpha\delta} y_{jk}^{\beta\gamma} y_{jl}^{\beta\delta} y_{kl}^{\gamma\delta}, \tag{B9}$$

$$X_{ijkl} = x_i^\alpha x_j^\beta x_k^\gamma x_l^\delta. \tag{B10}$$

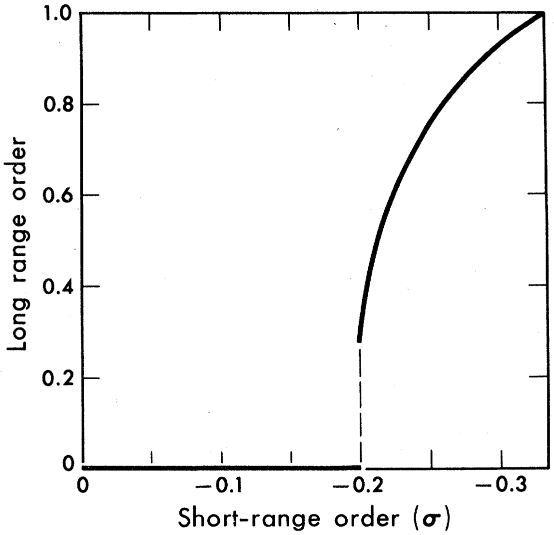

FIG. 8. LRO in the CV tetrahedron approximation as a parametrized function of the SRO. The LRO is zero for $|\sigma| < 0.199$ and jumps to a value of 0.284 at the discontinuity.

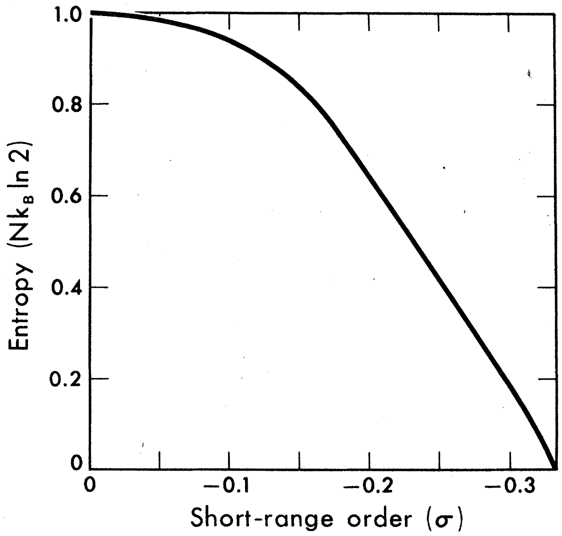

FIG. 9. Entropy in the CV tetrahedron approximation as a function of the SRO. A small discontinuity in slope at $\sigma_c = -0.199$ is not visible on this scale.

The solution of (B8) gives

$$z_{ijkl}=\exp[\tfrac{1}{2}(-\lambda-\gamma g_{ijkl})](Y_{ijkl})^{1/2}(X_{ijkl})^{-5/8}. \quad \text{(B11)}$$

These $2^4=16$ equations corresponding to the 16 z's in (B11) together with the two constraints (B7) $f=g=0$ give us 18 equations in 18 unknowns. To solve them we utilize the natural-iteration[3,10] technique.

When the concentrations of A and B atoms are equal and the symmetry is that of the $L1_0$ phase, the solution is considerably simplified. The equivalence of certain sublattices reduces the number of independent z's from 16 to 6. Maximization of the function Φ in (B6) results in the six z's and hence all correlations being parameterized in terms of σ. The parametrized LRO function is shown in Fig. 8. When $|\sigma|<|\sigma_c|=0.199$ the maximum of Φ exists in a region of parameter space associated with zero LRO. For $|\sigma|>|\sigma_c|$ a secondary maximum in the region of finite LRO discontinuously becomes an absolute maximum of Φ. This discontinuous jump in the parameter space trajectory is reflected in a small discontinuity in the slope of the entropy curve at σ_c. Aside from this feature the entropy function is a smooth function of the SRO (Fig. 9).

It is important to note that the discontinuity in the LRO necessitates the occurrence of a first-order phase transition in any model which uses the CV entropy in the tetrahedron approximation and an internal energy with only SRO dependence.

ACKNOWLEDGMENT

This work is supported in part by the NSF through Grant No. DMR78-03408.

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[1] For a review see H. Sato, in *Physical Chemistry*, edited by W. Jost, (Academic, New York, 1970), Vol. 10, p. 549.

[2] R. Kikuchi, Phys. Rev. 81, 988 (1951).

[3] R. Kikuchi and D. de Fontaine, Natl. Bur. Stand. *Phase DiagramWorkshop* (U. S. GPO, Washington, D.C., to be published); R. Kikuchi, Acta Metall. 25, 195 (1977); R. Kikuchi, D. de Fontaine, M. Murakami, and T. Nakamura, *ibid.* 25, 205 (1977).

[4] S. K. Aggarwal and T. Tanaka, Phys. Rev. B 16, 3963 (1977); M. Kurata, R. Kikuchi, and T. Watari, J. Chem. Phys. 21, 434 (1953).

[5] J. W. Cahn and R. Kikuchi, J. Phys. Chem. Solids 27, 1305 (1966).

[6] V. Heine and D. Weaire, Solid State Phys. 24, 249 (1970).

[7] J. Friedel, in *Physics of Metals*, edited by J. M. Ziman, (Cambridge U. P., London, 1969), p. 349.

[8] N. S. Golosov, L. E. Popov, and L. Y. Pudan, J. Phys. Chem. Solids 34, 1149 (1973); 34, 1159 (1973).

[9] C. M. van Baal, Physica (Utr.) 64, 571 (1973).

[10] R. Kikuchi, J. Chem. Phys. 60, 1071 (1974).

[11] N. Natta and P. Villemain, Solid State Commun. 10, 137 (1972); M. Plischke and D. Mattis, Phys. Rev. B 7, 2430 (1973); F. Brouers, J. Giner, and J. van der Rest, J. Phys. F 4, 214 (1974); J. Giner, F. Brouers, F. Gautier, and J. van der Rest, *ibid.* 6, 1281 (1976).

[12] P. Soven, Phys. Rev. 156, 809 (1967).

[13] F. Ducastelle and F. Gautier, J. Phys. F 6, 2039 (1976).

[14] R. C. Kittler and L. M. Falicov, J. Phys. C 9, 4259 (1976).

[15] F. Yndurain, J. D. Joannopoulos, M. L. Cohen, and L. M. Falicov, Solid State Commun. 15, 617 (1974); F. Yndurain and L. M. Falicov, *ibid.* 17, 1545 (1975); L. M. Falicov and F. Yndurain, Phys. Rev. B 12, 5664 (1975).

[16] P. Bloom and D. Mattis, Phys. Rev. B 15, 3633 (1977).

[17] C. T. White and E. N. Economou, Phys. Rev. B 15, 3742 (1977).

[18] D. G. Hall and J. S. Faulkner, Phys. Rev. B 15, 5850 (1977).

[19] M. Hansen, *Constitution of Binary Alloys* (McGraw-Hill, New York, 1958).

[20] B. W. Roberts, Acta Metall. 2, 597 (1954).

[21] W. R. Scott and L. Muldawer, Phys. Rev. B 14, 4426 (1976).

[22] P. G. Huray and L. D. Roberts, Phys. Rev. B 4, 2147 (1971).

[23] R. L. Orr, J. Luciat-Labry, and R. Hultgren, Acta Metall. 8, 431 (1960).

[24] W. Shockley, J. Chem. Phys. 6, 130 (1938).

[25] Y. Y. Li, J. Chem. Phys. 17, 447 (1949).

[26] J. Rudnick and E. A. Stern, Phys. Rev. B 7, 5062 (1973).

[27] C. E. Moore, *Atomic Energy Levels*, (U.S. GPO, Washington, D.C., 1958).

[28] G. A. Burdick, Phys. Rev. 129, 138 (1963).

[29] N. E. Christensen and B. O. Seraphin, Phys. Rev. B 4, 3321 (1971).

[30] J. Hubbard, Proc. R. Soc. A 281, 401 (1964); N. F. Mott, Rep. Prog. Phys. 33, 881 (1970).

[31] F. Gautier, J. van der Rest, and F. Brouers, J. Phys. F 5, 1884 (1975).

[32] M. Cyrot, Solid State Commun. 20, 467 (1976).