Atomistic Landau Theory of Ordering and Modulated Phases in Cu-Au Alloys

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We present a Landau theory derived from an alloy Hamiltonian based on a quantum mechanical description of cohesion in metallic systems. This Landau theory, obtained by making a mean-field approximation, provides an excellent description of the ordering transitions in CuAu, Cu_3Au, and $CuAu_3$, including the sequence of transitions from the disordered to the modulated CuAu II phase to the low-temperature CuAu I phase.

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The alloys of Cu and Au have been the subject of numerous experimental and theoretical investigations [1,2]. These alloys undergo ordering transitions to the CuAu- or Cu_3Au-type structures and modulated phases appear extensively [1,3]. These features make Cu-Au a prototype order-disorder system reflecting the full range of complexity encountered in the phase diagrams of intermetallic alloys. Since the stability of alloys is determined by the electrons that bind the atoms together, it is a challenge to show that a classical Hamiltonian, based on electronic structure, can give rise to such diversity of structure.

In the present work, we start with an atomistic Hamiltonian and construct a Landau theory for the Cu-Au alloys. The free-energy functional is *explicitly* calculated by making a mean-field approximation to the Hamiltonian. Recent Monte Carlo simulations on small systems using this Hamiltonian exhibited the correct ordering trends [4]. The construction of a Landau theory extends the scope of this approach beyond purely numerical experiments to a complete theoretical approach which can be applied to alloys in general.

The most spectacular achievement of the atomistic Landau theory is the prediction of a modulated phase with the CuAu II symmetry in a narrow temperature range between the disordered and CuAu I phases. The modulated phase arises because of competing terms in the Hamiltonian leading to a negative gradient term in the free-energy functional, an effect that could not have been deduced from any symmetry arguments. Similarly, the CuAu I and CuAu II transitions are predicted to be first order because of a subtle coupling between lattice distortions and alloy configurations which drives the coefficient of the fourth-order term negative. We also find a pronounced asymmetry between the Cu_3Au and $CuAu_3$ transitions, in agreement with experiments. These phenomena depend on the details of the interactions and, although one could have phenomenologically constructed free-energy functionals to describe each of these transitions separately, all the transitions are seen to be simultaneously described by a Hamiltonian based on the electronic properties of Cu and Au.

The standard model for the Cu-Au alloy, an Ising model on a fixed fcc lattice [5], has a long history [2,5–7]. Ising parameters obtained from first-principles electronic structure calculations [7–9] have indicated a crucial concentration dependence of the Ising interactions [8]. Mean-field theories derived from these fixed-lattice models, including the ones obtained from first-principles calculations, are incapable of providing an adequate description of the observed phase diagrams and it has been assumed, because of the frustrated nature of the fcc lattice, that improving the statistical model would be the key to getting the correct phase diagram. Although Monte Carlo simulations and the cluster variation method [2,7] are correct for almost all aspects of the Cu-Au phase diagram [2,5,8], some crucial issues remain unresolved. Most noteworthy among these are the appearance of the modulated phases, and the lattice distortions accompanying the ordering transitions. In this Letter, we show that the microscopic Hamiltonian for the Cu-Au alloys captures both these aspects of the phase diagram, and does so *even within the mean-field approximation.*

The important feature is the construction of the Hamiltonian from a quantum mechanical description of cohesion in metals, without assuming some form for the interactions *a priori.* An *ab initio* electronic structure calculation does not lend itself to this procedure since cohesive energies are calculated only for ordered periodic solids or the completely random alloy, which necessitates fitting by an assumed form [8,9] or expanding about the disordered alloy [10,11]. An alternative approach to the construction of a classical alloy Hamiltonian is the effective medium theory (EMT) of cohesion in solids [12] which lies between an *ab initio* approach and a completely phenomenological one.

The EMT derived from density functional theory [13] is a variational approach based on a particular ansatz for the form of the electron density, which has been shown to be extremely good in comparison with self-consistently calculated electron densities [14]. The EMT expression for the binding energy of the Cu-Au alloys, discussed in detail in Ref. [4], has two key components, the cohesive energy $E_{c,Z}(\bar{n})$ and the primarily electrostatic term $E_{es}(\bar{n})$ [12]. The function $E_{c,Z}$ exhibits a single minimum at a characteristic electron density which depends on the atomic number Z, and the atom can minimize its energy by seeking an environment with this density. The

embedding density $\bar{n}$ at a site depends on the alloy configuration and the interatomic distances. The configuration can be specified by the Ising variables $\{\zeta_i\}$ which describe the occupancy of a site i by a Cu or a Au atom. These are the only variables in a fixed-lattice Ising model. The EMT Hamiltonian depends, in addition, on the positions of atoms. For the sake of simplicity, we will focus on only those changes of the lattice which can be represented by changes in lattice parameters. This reduces the positional degrees of freedom to three independent lattice constants. It is possible to describe the ordered superstructures and the modulated structures of CuAu and Cu_3Au within this restricted space.

The classical alloy Hamiltonian is the EMT binding energy written as a function of the variables $\{\zeta_i\}$, and the lattice parameters $\{a_\mu\}$, $\mu=1,2,3$:

$$H=\sum_i E_{c,Z_i}(\bar{n}_i(\{\zeta_i\},\{a_\mu\})) + \sum_i \alpha_i[\bar{n}_i(\{\zeta_i\},\{a_\mu\})-\bar{n}_i^{\rm fcc}(\{\zeta_i\},\{a_\mu\})]\,. \quad (1)$$

The summations are over all lattice sites, and the second summation represents the electrostatic term $E_{\rm es}$, which is a measure of the electrostatic interaction of atom i with the tails of the electron density from the neighboring atoms, and is constructed to be zero for a pure metal in a perfect fcc structure [12]. The function $E_{c,Z}$ includes many-body interactions because it is nonlinear in the embedding density. The cohesive function is primarily sensitive to the variables $\{a_\mu\}$, whereas the electrostatic term is sensitive to the Ising variables ζ_i [4]. The parameters characterizing $E_{c,Z}$ and $E_{\rm es}$ can be determined by performing self-consistent calculations of an atom in a homogeneous electron gas. Calculations of ground-state properties of Cu, Au, and Cu-Au alloys by this procedure show that although this *ab initio* EMT gives a good description of trends in ground-state properties, the absolute values are not in very good agreement with experimental measurements [4]. To obtain the Hamiltonian which is best suited for studying phase diagrams within the EMT framework, the parameters were obtained by fitting to cohesive properties of the *pure* metals. In addition, one parameter per metal was adjusted, *without changing the description of the pure metals,* to reproduce the formation energy of CuAu [4]. This EMT Hamiltonian provides an excellent description of ground-state properties such as lattice constants and formation energies [4], and Monte Carlo simulations were shown to correctly describe the finite temperature transitions to CuAu I, Cu_3Au, and $CuAu_3$ [4]. These results are significant, considering that only one ground-state alloy property and no finite-temperature properties were used in the fitting.

A mean-field approximation leads to a free energy which depends on the concentration variables, $\{c_i\}=\{\langle\zeta_i\rangle\}$, and the lattice parameters. The Landau free-energy functional is constructed by minimizing this free energy with respect to the lattice parameters for a given value of the order parameter. The variables c_i can be expressed in terms of the order parameter η and the parameters f_μ as

$$c_i=c+\eta\sum_\mu f_\mu \exp(i\mathbf{k}_\mu\cdot\mathbf{R}_i)\,, \quad (2)$$

where c is the average concentration, $\mathbf{R}_i$ denotes the coordinate of site i, and the ordering vectors are $\mathbf{k}_1=(2\pi/a_1,0,0)$, $\mathbf{k}_2=(0,2\pi/a_2,0)$, and $\mathbf{k}_3=(0,0,2\pi/a_3)$.

The ordered CuAu structures are described by $f_1=f_2=0$, $f_3=\frac{1}{2}$, the Cu_3Au structure by $f_1=f_2=f_3=-\frac{1}{4}$, and the $CuAu_3$ structure by $f_1=f_2=f_3=\frac{1}{4}$. We study, in detail, the Landau theory of phase transitions at the three stoichiometric concentrations, and have not attempted, in this work, to draw any conclusions about the topology of the complete phase diagram.

The uniform ordered phase, CuAu I, has a face-centered-tetragonal structure compared to the fcc structure in the disordered phase. Figure 1(a) shows the free-energy function, $F(\eta)$, optimized with respect to the lattice parameters. It is clear that the CuAu I phase appears through a first-order transition. The numerical results can be represented very well by a functional form with a negative quartic term, and no cubic term:

$$F(\eta)=F(\eta=0)+|a|(T-T_0)\eta^2-|u|\eta^4+|v|\eta^6\,. \quad (3)$$

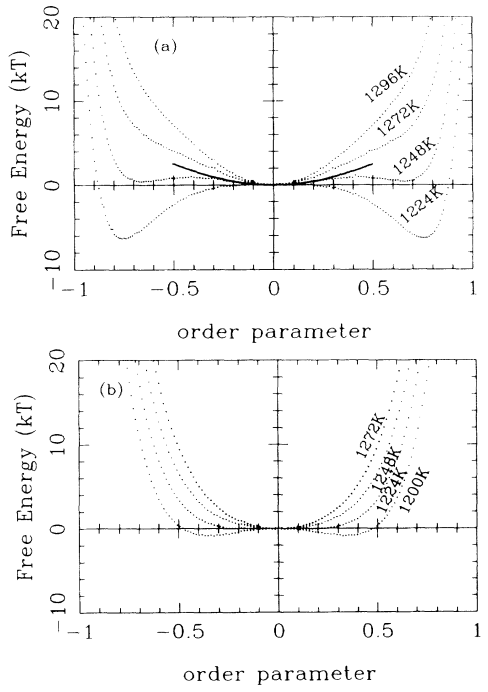

FIG. 1. (a) Calculated free-energy curves for CuAu at various temperatures. Each point represents a calculation. The solid line shows the free-energy curve for a modulated structure with $q_v=2\pi/10a$, at $T=1272$ K. (b) Free energy curves for CuAu *with cubic symmetry imposed.*

TABLE I. Parameters for the Landau free-energy functional of unmodulated phases: $F-F_0=a(T-T_0)\eta^2+b\eta^3+u\eta^4+v\eta^6$. For the modulated phases of CuAu, the coefficients of the gradient terms were found to be $|e|(2\pi/a_2)^2=306kT$, and $|f|(2\pi/a_2)^4=2346kT$.

	a (kT)	T_0 (K)	b (kT)	u (kT)	v (kT)
CuAu	0.5	1219	0	−63	73
Cu_3Au	0.5	1245	−237	283	0
$CuAu_3$	0.5	640	−200	160	0

The coefficients are presented in Table I. The absence of the cubic term could have been predicted by symmetry; however, the sign of the quartic term, which is responsible for making the transition first order, is not derived from symmetry.

To investigate the role of the tetragonal distortion in the CuAu phase transition, a similar calculation was performed with the lattice forced to be cubic (all a_μ equal to a). These results for F are shown in Fig. 1(b). The fourth-order term is positive in this case and the transition is second order. These observations imply that the coupling to the tetragonal distortion plays a decisive role in the CuAu I transition by changing the coefficient of the quartic term from positive to negative and underlines the importance of including these couplings in describing phase transitions in real alloys. Such a change in sign arising from coupling to lattice strain had been conjectured and derived phenomenologically many years ago [15,16]. As expected for a mean-field theory, the transition temperatures obtained from the Landau theory are higher than experiments and our EMT-based Monte Carlo results which were very close to the experimental values [4,17].

The scenario for the Cu_3Au and the $CuAu_3$ transitions is very different. The transitions are predicted to be first order because of the *cubic* term in the free-energy function. This is dictated by symmetry rather than by details of the Hamiltonian. The lattice remains cubic in the ordered phases. There is a pronounced asymmetry between Cu_3Au and $CuAu_3$, as is evident from the values quoted in Table I. This asymmetry is also predicted by Ising models with concentration-dependent interactions [7,8].

To construct a Landau theory of the CuAu II phase, one needs to examine the gradient terms in the free-energy functional. This was done by expanding the free energy in terms of η_q, the Fourier components of $\eta(i)$, for various modulation vectors $\mathbf{q}$. Since the CuAu II structure has a modulation along a direction perpendicular to the ordering direction [3], the first set of modulation vectors was chosen to be along such a direction (say y), and $F(\eta_q)$ was constructed for different magnitudes of q. It was seen that the coefficient of the quadratic term, $a(q)$, is smaller for finite q than for $q=0$ [cf. Fig. 1(a)], and has a minimum at a finite q. The free-energy functional deduced from these calculations and adopting a continuum formulation is

$$F(\eta)=F_0+\int d\mathbf{r}[|a|(T-T_0)\eta^2-|u|\eta^4+|v|\eta^6-|e|(\partial\eta/\partial y)^2+|f|(\partial^2\eta/\partial y^2)^2]. \quad (4)$$

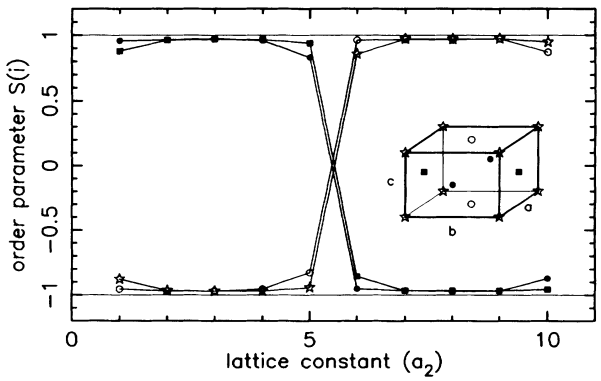

FIG. 2. Plot of $S_i=1-2c_i$ as a function of lattice spacing, for the four fcc sublattices showing the appearance of the CuAu II phase in the Monte Carlo simulations. The temperature is just below the simulation result for $T_c^{II}\simeq 630$ K. The results for the lattice constants of this structure are $a_1=7.37$ a.u., $a_2=7.34$ a.u., $a_3=7.01$ a.u.

The parameters appear in Table I. A functional with negative gradient terms leads to modulated structures [18], and was constructed, phenomenologically, by McMillan to explain the CuAu II phase [19]. Considering a purely sinusoidal modulation [19], the free energy can be minimized analytically. We find a *first-order* transition from the disordered to a modulated phase with the CuAu II symmetry at $T_c^{II}=T_0+42$ K, and another *first-order* transition from the modulated, CuAu-II-like phase to the CuAu I phase at $T_c^{I}=T_0+26$ K. The modulation vector for this purely sinusoidal modulation remains fixed at $q=\sqrt{e/2f}\simeq 0.25(2\pi/a_2)$. This value should vary with composition since the minimum of $a(q)$ is expected to depend upon the concentration. The experimentally measured periodicity of the CuAu II phase at the 50-50 composition is $q\simeq 2\pi/10a_2$. We expect these quantitative results to change upon inclusion of higher harmonics. An examination of $a(q)$ for $\mathbf{q}$ along the ordering direction shows that the minimum is at $q=0$, and therefore, only a one-dimensional modulated structure is stable at this composition. The prediction of the modulated structures is a clear indication that EMT captures the crucial competing interactions in Cu-Au alloys. Additional evidence for this comes from our Monte Carlo simulations [17], showing ordering into the orthorhombic CuAu II structure. The variation of the order parameter $\eta(i)$, shown in Fig. 2, clearly demonstrates a long-period superstructure with a period of $10a_2$.

The CuAu II phase has been commonly attributed to

Fermi-surface-driven instabilities [20]. In EMT, details of the Fermi surface are described by one-electron energy terms [12], left out of the Cu-Au Hamiltonian since they are expected to be small [12]. Our results show that the competition between E_c and E_{es} leads to the modulated phase. In the CuAu I phase, the Cu and Au planes are under strain since the preferred lattice constants of pure Cu and pure Au are very different. This difference is precisely what is responsible for the tetragonal distortion. The strain can be further minimized in the CuAu II structure. However, the distortion of the Ising order parameter costs energy through the E_{es} term. This competition, reflected in the Landau theory through the appearance of the negative gradient terms, leads to the CuAu II phase existing in a *narrow temperature range.*

In conclusion, a mean-field Landau theory based on a microscopic Hamiltonian has been shown to be remarkably successful in describing the ordering transitions in Cu-Au; notably the disordered → CuAu II → CuAu I transitions. This is the first nonphenomenological approach that has led to the description of this transition sequence. Our analysis underscores the need to derive model Hamiltonians from a microscopic viewpoint, reinforces the role of elastic energies in determining phase stability [8], and suggests that the *fixed-lattice* Ising model is too impoverished a model to describe Cu-Au alloys.

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