

Cu-Au, Ag-Au, Cu-Ag, and Ni-Au intermetallics: First-principles study of temperature-composition phase diagrams and structures

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The classic metallurgical systems—noble-metal alloys—that have formed the benchmark for various alloy theories are revisited. First-principles fully relaxed general-potential linearized augmented plane-wave ~LAPW! total energies of a few ordered structures are used as input to a mixed-space cluster expansion calculation to study the phase stability, thermodynamic properties, and bond lengths in Cu-Au, Ag-Au, Cu-Ag, and Ni-Au alloys. ~i! Our theoretical calculations correctly reproduce the tendencies of Ag-Au and Cu-Au to form compounds and Ni-Au and Cu-Ag to phase separate at $T=0$ K. ~ii! Of all possible structures, Cu_3Au ($L1_2$) and CuAu ($L1_0$) are found to be the most stable low-temperature phases of $\text{Cu}_{1-x}\text{Au}_x$ with transition temperatures of 530 K and 660 K, respectively, compared to the experimental values 663 K and ' 670 K. The significant improvement over previous first-principles studies is attributed to the more accurate treatment of atomic relaxations in the present work. ~iii! LAPW formation enthalpies demonstrate that $L1_2$, the commonly assumed stable phase of CuAu_3 , is *not* the ground state for Au-rich alloys, but rather that ordered ~100! superlattices are stabilized. ~iv! We extract the nonconfigurational ~e.g., vibrational! entropies of formation and obtain large values for the size-mismatched systems: $0.48 k_B/\text{atom}$ in $\text{Ni}_{0.5}\text{Au}_{0.5}$ ($T=1100$ K!), $0.37 k_B/\text{atom}$ in $\text{Cu}_{0.141}\text{Ag}_{0.859}$ ($T=1052$ K!), and $0.16 k_B/\text{atom}$ in $\text{Cu}_{0.5}\text{Au}_{0.5}$ ($T=800$ K!). ~v! Using 8 atom/cell special quasirandom structures we study the bond lengths in disordered Cu-Au and Ni-Au alloys and obtain good qualitative agreement with recent extended x-ray-absorption fine-structure measurements.

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I. INTRODUCTION: CHEMICAL TRENDS IN NOBLE-METAL ALLOYS

Noble-metal alloys are, experimentally, among the most studied intermetallic systems.¹⁻²⁴ In addition, the Cu-Au system has been considered the classic paradigm system for applying different theoretical techniques of phase diagram and phase stability calculations.²⁵⁻⁶³ Most notably, this system has been considered as the basic test case for the classic Ising-Hamiltonian statistical-mechanics treatment of alloys.²⁵⁻³² More recently, noble-metal binary alloys have been treated theoretically via empirical fitting of the constants in Ising Hamiltonians,²⁵⁻³⁴ semiempirical interatomic potentials,³⁵⁻⁴⁷ and via first-principles cluster expansions.⁴⁸⁻⁵⁵ The essential difference in philosophy between the classical application of Ising models to CuAu ~Refs. 25-30 and 33! and more modern approaches based on the density functional formalism⁶⁴ is that in the former approach the range and magnitudes of the interactions are postulated at the outset ~e.g., first or second neighbor pair interactions!, while the latter approaches make an effort to determine the interactions from an electronic structure theory. However, despite recent attempts,⁴⁸⁻⁵⁴ it is still not clear whether the noble-metal alloys can be essentially characterized as systems with short-range pair interactions or not.

Now that first-principles cluster expansion approaches^{65,66} have advanced to the stage where both $T=0$ ground state structures and finite-temperature thermodynamic quantities can be predicted without any empirical information, it is interesting to take a *global look* at the noble-metal alloy family. Table I summarizes some of the salient

features^{1-4,14,15,18,67-69} of the four binary systems Cu-Au, Ag-Au, Cu-Ag, and Ni-Au. We included the relative lattice constant mismatch $\Delta a/\bar{a} = 2|a_A - a_B|/a$

TABLE I. Major physical properties of Ag-Au, Cu-Ag, Cu-Au, and Ni-Au alloys. We give constituent size mismatches $D\bar{a}/\bar{a} = 2(a_A - a_B)/(a_A + a_B)$, electronegativity differences on the Pauling scale -Ref. 68! Dx , mixing enthalpies of the disordered alloys at the equiatomic composition, $DH_{\text{mix}}(x = \frac{1}{2})$, signs of the nearest-neighbor Ising interaction, J_2 , order-disorder transition temperatures -or miscibility gap temperatures for Cu-Ag and Ni-Au! $T_c(x = \frac{1}{2})$, and excess entropies of solid solutions, $DS_{\text{tot}}^{\text{form}} - DS_{\text{ideal}}$. All phases are fcc based.

System	$D\bar{a}/\bar{a}$ ^a	Dx ^b	$DH_{\text{mix}}(x = 1/2)$ -meV/atom!	J_2	Low- T phases ^g	$T_c(x = \frac{1}{2})$ -K!	$DS_{\text{tot}}^{\text{form}} - DS_{\text{ideal}}$ ^g (k_B /atom!)
Cu-Au	12%	0.64	-91 ^c	>0	$L1_2, L1_0, L1_2\text{-?!}$	683 ^g	+0.04
Ag-Au	0%	0.61	-				

-iv! The amount $DS_{XS} = DS_{\text{tot}}^{\text{expt}} - DS_{\text{ideal}}$ by which the measured entropy² $DS_{\text{tot}}^{\text{expt}}$ deviates from the ideal configurational entropy $DS_{\text{ideal}} = k_B x \ln x + (1-x) \ln(1-x)$ is unexpectedly large in Cu-Ag and Ni-Au, indicating a large non-configurational entropy of formation.

Other interesting facts about the noble-metal binary intermetallics include the following.

-v! Despite numerous studies,^{1-4,7,8,10-12} the structure of the ordered phases in Au-rich Cu-Au is not well established yet. It is often assumed¹⁻⁴ that the stable Au-rich low-temperature phase is CuAu_3 in the $L1_2$ structure, but direct experiments^{7,8,10} below the order-disorder transition temperature $T_c(x = \frac{3}{4}) \sim 500$ K are difficult because the diffusion rates are very low and even the best ordered samples contain significant disorder. Possible further thermodynamic transformations at lower temperatures may be kinetically inhibited.

-vi! The trends in bond lengths vs composition are non-trivial. Traditionally, all coherent-potential-approximation-based theories⁷⁰⁻⁷² of intermetallic alloys have assumed that the nearest-neighbor bond lengths are equal, $R_{AA} = R_{AB} = R_{BB}$, and proportional to the average lattice constant. Recent theories⁷³⁻⁷⁵ suggested, however, that bond lengths relax in the alloy to new values, and this has a significant effect on the electronic structure.^{53,76,77} Recent extended x-ray-absorption fine-structure -EXAFS! experiments on NiAu -Ref. 23! and CuAu -Ref. 24! show distinct $R_{AA} \neq R_{AB} \neq R_{BB}$ bond lengths, which need to be explained.

In this work we will analyze the above-mentioned trends in terms of a first-principles mixed-space cluster expansion,^{65,66} based on modern local density approximation -LDA! total energy calculations. We reproduce the observed trends -i! -vi! in ordering preferences, mixing enthalpies DH_{mix} , transition temperatures T_c , and interatomic bond lengths. In addition, we predict new, and to our knowledge hitherto unsuspected, ordered phases in Au-rich Cu-Au alloys.

II. BASIC IDEOLOGY AND METHODOLOGY

There are many problems in solid state physics that require knowledge of the total energy $E(\mathcal{S})$ of a lattice with N sites as a function of the occupation pattern \mathcal{S} of these sites by atoms of types A and B . This information is needed, for example, in the ground state search problem,⁷² where one seeks the configuration with the lowest energy at $T=0$ K. $E(\mathcal{S})$ is also needed for calculating the temperature- and composition-dependent thermodynamic functions and phase diagrams of an $A_{1-x}B_x$ alloy.

A direct, quantum-mechanical calculation of the total energy $E_{\text{direct}}(\mathcal{S}) = \langle \mathcal{C} | \hat{H} | \mathcal{C} \rangle$ -where \mathcal{C} is the electronic ground state wave function and \hat{H} is the many-electron Hamiltonian! is possible only for a limited set of configurations \mathcal{S} . This is so because -i! the computational effort to solve the Schrödinger equation for a single configuration scales as the cube of the number of atoms per unit cell, so that only small unit cells can be considered, -ii! there are 2^N configurations, and -iii! for each configuration, one has to find the atomic relaxations $\mathbf{d}\mathbf{u}_{\text{min}}(\mathcal{S})$ which minimize the total energy. Consequently, one searches for a ‘‘cluster expansion’’ -CE! that accurately reproduces the results of a direct, quantum-mechanical -e.g., LDA! calculation,

$$E_{\text{CE}}(\mathcal{S}) \approx E_{\text{direct}}(\mathcal{S}), \quad \text{-i!}$$

without the unfavorable scaling of the computational cost with the size of the unit cell.

In designing a cluster expansion, there are few choices of independent parameters. For example, one could choose to obtain a cluster expansion for the volume- (V -) dependent equation of state $E_{\text{direct}}(\mathcal{S}, V)$ -see, e.g., Refs. 52, 78, and 79# or to find a cluster expansion for the energy at the volume $V_{\text{min}}(\mathcal{S})$ that minimizes $E_{\text{direct}}(\mathcal{S}, V)$. We choose the latter possibility. Furthermore, for each configuration \mathcal{S} , we wish to reproduce the total energy corresponding to the fully re-

laxed cell shape and atomic positions $\mathbf{d}\mathbf{u}_{\min}(\mathbf{s})$. In other words, we choose to represent

$$E_{\text{CE}}(\mathbf{s}) = E_{\text{direct}}(\mathbf{s}; \mathbf{d}\mathbf{u}_{\min}(\mathbf{s}); V_{\min}(\mathbf{s})) \quad (2)$$

Note that by focusing on the equilibrium energy of each configuration, we give up the possibility of studying non-equilibrium geometries -e.g., bond lengths- and equations of state. Instead, for each occupation pattern \mathbf{s} , we can find the total energy $E(\mathbf{s})$ of the atomically relaxed and volume-optimized geometry.

The best-known cluster expansion is the generalized Ising model in which the equilibrium total energy of an *arbitrary* configuration \mathbf{s} is expanded in a series of basis functions defined as pseudospin products on the crystal sites:

$$E(\mathbf{s}) = J_0 + \sum_i J_i S_i + \dots$$

is singular. Physically, the nonanalyticity of $J_{\text{pair}}(\mathbf{k})$ is caused by long-range interactions via macroscopic elastic strain and cannot be reproduced using finite-ranged real-space pair interactions, but must be accounted for explicitly in reciprocal space. If the singularity is neglected, then as explained in Ref. 65, the cluster expansion fails not only for long-period ($n \rightarrow \infty$) superlattices $A_n B_n$, but also for those short-period ($n > 2$) superlattices which have not been explicitly included in the constraint, Eq. 21. We emphasize that although the contribution of $J_{\text{CS}}(\mathbf{k})$ to the formation energy is nonzero only in size-mismatched systems, it is not related to the atomic relaxation energy for a particular structure S in any simple way -except if S itself is a long-period superlattice!.

The singularity in $J_{\text{pair}}(\mathbf{k})$ is similar to the singularity in the dynamical matrix $D_{ab}(k, \mathbf{k}, \mathbf{u}, \mathbf{k})$ of polar crystals in the long-wavelength limit,⁸³ caused by long-range electrostatic interactions via macroscopic electric field. In lattice dynamics, $D_{ab}(k, \mathbf{k}, \mathbf{u}, \mathbf{k})$ is expressed as a sum of regular and singular parts, $D_{ab}(k, \mathbf{k}, \mathbf{u}, \mathbf{k}) = D_{ab}^{\text{sing}}(k, \mathbf{k}, \mathbf{u}, \mathbf{k}) + D_{ab}^{\text{reg}}(k, \mathbf{k}, \mathbf{u}, \mathbf{k})$, where $D_{ab}^{\text{reg}}(k, \mathbf{k}, \mathbf{u}, \mathbf{k}) \sim \text{analytic as } \mathbf{k} \rightarrow 0$ is due to short-range force constants. The singular part $D_{ab}^{\text{sing}}(k, \mathbf{k}, \mathbf{u}, \mathbf{k})$ gives rise to LO/TO splitting of the zone-center optical frequencies ν_G in polar crystals, and also leads to a directional dependence of $\nu_G(\hat{k})$ in uniaxial crystals -e.g., CuPt-type GaInP_2). These phenomena cannot be reproduced by any set of finite-ranged microscopic force constants, but have to be calculated explicitly using the macroscopic Maxwell equations.⁸⁴

In summary, we seek to find a function $E_{\text{CE}}(S)$ which accurately reproduces the LDA total energies $E_{\text{LDA}}(S, \mathbf{u}_{\text{min}}(S); V_{\text{min}}(S)) \approx E_{\text{LDA}}(S)$ at the atomically relaxed geometry and equilibrium volume of configuration S . The function $E_{\text{CE}}(S)$ we consider includes composition- and volume-independent interactions, so as to maintain maximum similarity with the classical Ising model. The number

potential and electronic charge density terms are calculated in all space and included in the Hamiltonian matrix. Core states are treated fully relativistically and recalculated in each self-consistency iteration. The wave equation for the valence states includes all relativistic effects except the spin-orbit interaction; i.e., they are treated scalar relativistically. The FLAPW method is the most accurate all-electron method, superior to the methods employing overlapping atomic spheres @atomic-sphere approximation -ASA!# and/or shape approximations to the potential.

We use the Wigner exchange-correlation functional.⁸⁹ As a check, we have performed several calculations using the Perdew-Zunger⁹⁰ parametrization of the Ceperley-Alder⁹¹ functional and the generalized gradient approximation of Perdew and Wang.⁹² We find -see Sec. IV A 1! that the various exchange-correlation functionals change the enthalpies of formation of ordered Cu-Au compounds by a negligible amount -less than 2 meV/atom!.

The total energies of the ordered structures and end-point constituents are obtained keeping all computational parameters exactly equal. Specifically, we always use the same basis sets ($RK_{\max}=9$), charge density cutoffs ($RK_{\max}=19$), muffin-tin radii $R_{\text{Au}}=2.4a_0$, $R_{\text{Ag}}=R_{\text{Cu}}=R_{\text{Ni}}=2.2a_0$, maximum difference in the angular momenta in the nonspherical Hamiltonian terms ($l_{\max}=4$), maximum angular momenta in the nonspherical charge densities and potentials inside the muffin-tin spheres ($l_{\max}=8$), and equivalent \mathbf{k} point sets⁹³ in the evaluation of Brillouin zone integrals. When the unit cell vectors of the ordered compound permit, we choose a \mathbf{k} mesh equivalent to the 60 special points $8 \times 8 \times 8$ fcc mesh. Several structures -e.g., those of A_2B or AB_2 stoichiometry! have reciprocal unit cell vectors which are incommensurate with the $8 \times 8 \times$

are several important *qualitative* differences between the behavior in Fig. 2 and that predicted by the harmonic elasticity. First, $q(a_s, \hat{G})$ strongly depends on the substrate lattice constant, while the harmonic $q_{\text{harm}}(\hat{G})$ does not. Second, the harmonic expression gives a definite order of $q(\hat{G})$ as a function of the direction; i.e., either $\sim 100!$ is the softest and then $\sim 111!$ *must* be the hardest, or vice versa. This order does not hold for large deformations. For instance, $\sim 201!$ becomes the softest direction for $a_s \ll a_0$ and $\sim 110!$ is the hardest for $a_s \gg a_0$ in Cu. Finally, $q(100)$ exhibits a particularly dramatic softening for $a_s \gg a_0$, which has important consequences for the constituent strain energy and stability of superlattices along this direction.⁹⁶

The above-mentioned properties of q_{Cu} can be described by generalizing Eq. ~17! for g to higher Kubic harmonics and strain-dependent expansion coefficients:

$$g_{\sim a_s}, \hat{G}! = \sum_{l=0}^{l_{\text{max}}} b_{l\sim a_s}! K_{l\sim \hat{G}}!, \quad \sim 18!$$

which has the property that in the harmonic limit ($a_s \rightarrow a_0$) all expansion coefficients with angular momenta higher than 4 tend to zero, reproducing g_{harm} from Eq. ~17!. Due to the cubic symmetry, only terms with $l=0,4,6,8,10,12, \dots$ enter in this expansion. A detailed discussion of the nonlinear epitaxial strain properties of elemental metals will be given in a separate publication.⁹⁶

We have taken $l_{\max}=10$, which gives five composition-dependent fitting coefficients determined from a fit to the directly calculated values (Eq. 14) for six principal directions. The characteristic errors of this fit at the equiatomic composition are 1–2 meV/atom. Equation 19 is then used in Eqs. 11 and 12.

C. Constructing the cluster expansion

Once we have a closed-form expression for the equilibrium constituent strain energy $DE_{CS}(\mathbf{s})$ and a set $\$DH^{LDA}(\mathbf{s})\%$ of $T=0$ formation enthalpies, we determine the unknown cluster interactions of Eq. 10 in the following two-step process.

First, the total energies of all structures from Table III are used in the fit to investigate the behavior of the root-mean-square (rms) error D_{rms} of the fit, Eq. 13, as a function of the number of real-space pair and multibody interactions. Reciprocal-space CE allows one to add pair interactions systematically in the order of increasing intersite separation, up

to any number of near-neighbor shells. The \mathbf{k} -space smoothness criterion in Eq. 13 automatically selects optimally short-ranged interactions and chooses physically important pair interactions which are essential to produce a good fit to the directly calculated LDA energies. The dependence of the rms error on the number of pair and multibody interactions is shown in Fig. 4. Figure 4-a) is obtained by fixing the number

of the overall fit. It is retained in the CE only if D_{rms} decreases considerably. During the fitting process, we also monitor the overall stability of the CE, as measured by a

constituent size mismatch between Cu and Au. The pair interactions are slowly decaying in Cu-Ag and Ni-Au, too.

The calculated multibody interaction energies are shown in Fig. 6. J_1 is the point interaction, J_3 , K_3 , N_3 , ... are triplets and J_4 , K_4 , and L_4 are four-point clusters in increasing order of interatomic separation -see Lu *et al.*⁵⁴ for a full description of the clusters!. Figure 6 illustrates the importance of the multibody terms in our Hamiltonian.

D. Finding the $T=0$ ground states and $T>0$ properties

Having parametrized the configurational energies in terms of the mixed-space cluster expansion, Eq. ~10!, we can use it

with established statistical methods to predict various structural properties: $T=0$ ground states, order-disorder transition temperatures, configurational entropies, free energies, phase

ally identical! energies. We explore many equally spaced compositions with an interval $\Delta x=0.05$. The number of possible configurations for each x is $N_{\text{conf}}=N!/(xN)!(N(1-x))!$.

The configurational entropy of the disordered alloys at finite T is computed from the energy vs temperature curves obtained by cooling the system from very high $\sim T=\infty$ temperatures. The following thermodynamic formula gives the configurational entropy at temperature T :

$$DS_{\text{conf}}(T) = DS_{\text{ideal}} + E(T)/T - k_B \int_0^b E(b) db, \quad (20)$$

where $b=1/k_B T$ and $DS_{\text{ideal}}=k_B [x \ln x + (1-x) \ln(1-x)]$ is the configurational entropy of an ideal solid solution.

IV. RESULTS

A. $T=0$ ground states

1. Ground states of Cu-Au

Figure 7 shows the calculated $T=0$ ground state lines of Cu-Au and Ag-Au which were obtained from simulated annealing quenches of a $16 \times 16 \times 16$ system. In Cu-Au, we find the $L1_2$ \sim Cu_3Au and $L1_0$ \sim CuAu !

can be calculated either with the help of the fast Fourier transform (FFT) or evaluated directly taking advantage of the special method described in Ref. 87. The latter is much more economical: If the total number of sites in the simulation box is N , a full FFT has to be done only once after approximately every \sqrt{N} accepted spin flips, which makes the whole computational effort for this special method scale as $N^{1.5}$.

A simulation box of $N=4096$ atoms ($16 \times 16 \times 16$) is used to calculate all thermodynamic properties presented in this paper. The transition temperatures are computed by cooling the system from high temperatures and monitoring the discontinuities in the average energy and peaks in heat capacity. To eliminate possible hysteresis effects, the resulting low-temperature configurations are gradually heated up past the transition point. The former process provides the lower bound on the transition temperature T_1 , while the latter gives the upper bound T_2 . The heating and cooling rates are such that T_1 and T_2 differ by no more than 20 K, an insignificant uncertainty compared to the inaccuracies of the LDA calculations and the fit errors of the cluster expansion. Here 1000 flips/site and a temperature decrease of 2% for each Monte Carlo step are usually sufficient, although in a few cases the results are checked using 2000 flips/site and 0.5% temperature change.

Zero-temperature ground states are found by cooling the system to $T=0$ and checking whether the energy of the final configuration lies on the convex hull. This process is repeated for several random number seeds and starting temperatures, always yielding configurations with similar usu-

these calculations using the Perdew-Zunger⁹⁰ parametrization of the Ceperley-Alder⁹¹ LDA functional, as well as the generalized gradient approximation (GGA) of Perdew and Wang,⁹² and found insignificant (about 2 meV/atom) changes in the formation enthalpies. Inclusion of the spin-orbit interaction in the second variation procedure¹⁰⁴ changed the formation enthalpy of $L1_0$ (CuAu) by only 3.7 meV/atom (from -48.2 to -51.9), indicating that it is not important for the energetics of Cu-Au. This conclusion is in line with the findings of Ref. 105 that the spin-orbit interaction influences the band structure but has little effect on equilibrium lattice properties. Therefore, we conclude that *state-of-the-art first-principles density functional calculations do not predict $L1_2$ to be a stable $T=0$ ground state of $CuAu_3$* . It is possible that van der Waals interactions, omitted by the LDA and important for large, polarizable atoms such as Au, can affect the formation energies and hence the ground states of Cu-Au.

We next analyze the possibility that the correct $T=0$ ground state around $x=\frac{3}{4}$ is not $L1_2$ as has been assumed in the literature before. Although most compilations¹⁻⁴ of binary alloy phase diagrams give $L1_2$ as the stable structure of $CuAu_3$, the experimental evidence^{7,8,10} seems inconclusive because of the difficulties in obtaining equilibrated long-range ordered samples. X-ray studies⁸ have found superlattice peaks consistent with the cubic $L1_2$ structure, but only very broad low-order reflections have been observed. These superlattice lines could not be sharpened by any heat treatment.⁸ It is not clear to us if the x-ray reflections can be reindexed according to some other non- $L1_2$ phase. It is also possible that at elevated ($T \sim 500$ K) temperatures $L1_2$ is stabilized by the entropy (configurational and vibrational), while another transformation to the low-energy structure should occur but is kinetically inhibited below 500 K. The biggest experimental obstacles to verifying our predictions seem to be low diffusion rates below the ordering temperature of $CuAu_3$, $T_c \sim 500$ K.

Next we discuss the experimental signatures of the new LDA ground state structures. $MoSi_2$ -type $b2$ $CuAu_2$ has a superlattice reflection at $(\frac{2}{3}00)$, but the $CuAu_3$ (100) superlattice has reflections at (100) and $(\frac{1}{3}00)$. These reflections also manifest themselves in the predicted atomic short-range order of the disordered alloys (for details see Ref. 103).

2. Ground states of Ag-Au, Cu-Ag, and Ni-Au

The ground state line of Ag-Au is shown in Fig. 7-b), exhibiting $L1_2$ (Ag₃Au), $L1_0$ (AgAu), and $L1_2$ (AgAu₃) stable low-temperature phases. Experimentally, these alloys are known to be completely miscible,²⁻⁴ and there are several indications⁶⁹ that they are 82[(caectAg)81.8362(belo)Tj] 6.9X398re Tf 1.Ag st

TABLE IV. Calculated mixing enthalpies of disordered $\text{Cu}_{1-x}\text{Au}_x$ alloys compared with the values obtained by other studies and experimental measurements (in meV/atom). FLAPW is the full-potential linearized augmented plane wave method; LMTO, linearized muffin-tin-orbital method; KKR, Korringa-Kohn-Rostoker multiple scattering method; ASA, atomic-sphere approximation; CPA, coherent potential approximation; CWM, Connolly-Williams cluster expansion; MSCE, mixed-space cluster expansion used in this study; ‘‘Rel.,’’ incorporating atomic relaxations; and ‘‘Unrel.,’’ neglecting atomic relaxations.

Composition	Expt. ^f	This study	Wei <i>et al.</i> ^a	Amador and Bozzolo ^b	Terakura	Ruban	Weinberger
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C. Order-disorder transition temperatures

Order-disorder transitions have been investigated at compositions ($x = \frac{1}{4}, \frac{1}{2}, \frac{2}{3},$ and $\frac{3}{4}$) using the Monte Carlo simulation technique described in Sec. III D. The resulting transition temperatures T_c are given in Table V. All transitions are found to be first order, involving discontinuities in the energy and correlation functions. At $x = \frac{1}{4}$ we find a transition from the disordered state to long-range ordered $L1_2$ Cu_3Au at $T_c = 530$ K, which is only 130 K lower than the experimentally observed transition temperature. For the equiatomic alloy at $x = \frac{1}{2}$ the calculated and experimental transition temperatures agree to a few degrees kelvin. However, we do not find the CuAu II phase which exists in a narrow temperature range between 658 K and 683 K. This phase is stabilized by the free energy differences between $L1_0$ and long-period superstructures of $L1_0$ which are as small as 1 meV/atom (Ref. 56) and therefore beyond the accuracy of self-consistent LDA calculations.

For $x = \frac{3}{4}$ we obtain a sequence of transformations, the first one occurring at $T = 750$ K from the disordered $A1$ phase to a coherent two-phase mixture of $b2$ and $A1$. Then a subsequent transition at $T = 635$ K takes CuAu_3 into the long-range ordered (100) superlattice which is predicted to be the stable $T = 0$ ground state at that composition (see Sec. IV A 1). The calculated transition at $x = \frac{2}{3}$ goes straight into the $b2$ phase at $T = 735$ K. Therefore, a two-phase $b2$

+ $A1$ field is predicted to exist at temperatures somewhere between 635 K and 730 K and around $x = \frac{3}{4}$. These predictions reflect the LDA. As stated in Sec. IV A 1, corrections to the LDA might be significant.

D. Nonconfigurational entropy

The effect of the nonconfigurational entropy (electronic, vibrational, etc.) on the alloy phase stability has recently attracted considerable interest.^{106–116} For instance, it has

been suggested¹⁰⁸⁻¹¹⁵ that there are large differences in the vibrational *entropies of ordering* $S_{\text{ordered}}^{\text{vib}} - S_{\text{disord}}^{\text{vib}}$, which should manifest themselves in shifts of the order-disorder transition temperatures. There is another important class of thermodynamic properties where the vibrational entropy may play a role and which has often been overlooked. Namely, it is the *entropy of formation* with respect to the pure constituents, defined in analogy with DH in Eq. 4!:

$$DS_{\text{tot}}^{\text{form}}(A_{1-x}B_x, T) = S(A_{1-x}B_x, T) - (1-x)S(A, T) - xS(B, T), \quad (21)$$

where $S(A, T)$ is the total entropy of the pure constituent A at temperature T . It is often assumed that the configurational entropy is the dominant contribution to $DS_{\text{tot}}^{\text{form}}(A_{1-x}B_x, T)$

the interatomic potential curves, which are rapidly hardening upon compression and softening upon expansion. However, our results for R_{AA} at $x = \frac{3}{4}$ and

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