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Brief Reports

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Order-disorder transition in Cu_3Au: A combined molecular-dynamics and cluster-variation-method approach

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The order-disorder transition in Cu_3Au has been investigated using a combined molecular-dynamics and cluster-variation-method approach. These techniques allow an accurate estimate of, respectively, the configuration-dependent enthalpy and the configurational entropy. Vibrational entropy has also been included in the calculations. The transition temperature is accurately reproduced. The behavior of long-range and short-range order parameters is consistent with the hypothesis that the disordering process occurs via the creation of out-of-step domains.

Several alloys exhibit an order-disorder transition at temperatures T_c well below the melting temperatures T_m. The low-temperature phase is characterized by an ordered arrangement of the atomic species on the lattice sites, while the high-temperature state is characterized by a random arrangement of atoms. While the phase with the lowest enthalpy is stable at $T=0$ K, the competition between enthalpy and entropy determines the occurrence of structural transitions at higher temperatures.

This class of systems has been extensively studied by means of thermodynamic models[1-3] and in the frame of the calculation of phase diagrams.[4] The relation between these two approaches has been carefully investigated by Sanchez, de Fontaine, and Teitler.[5]

The task of building the free-energy functional required for the theoretical description of structural phase transitions is accomplished via the development of a model of atomic interactions together with accurate approximation schemes for the configurational as well as for the other contributions to the system entropy. The cluster variation method [CVM (Refs. 6 and 7)] is a very efficient way to compute the configurational entropy of an atomic system in terms of probability distribution variables assigned to each configuration of a cluster: for a given structure, different levels of approximations can be obtained varying the size of the largest cluster included in the calculation. The free-energy models based on CVM have concentrated, so far, only on the calculation of the ordering energy contribution, either using simple Ising Hamiltonians,[7] pair potential schemes,[8] or the coherent-potential approximation.[9] Recently, a theoretical approach based on *ab initio* calculations has been introduced to derive an empirical potential for the expression of the ordering energy.[10]

The purpose of this work is to integrate the CVM prescription with a formulation of the system enthalpy which allows for a proper treatment of the local volume and elastic relaxation (neglected by simpler models[7] or included in global form[8,9]). This is accomplished using molecular-dynamics (MD) simulations with a many-body-potential scheme. In the same framework, thus we have also accounted for vibrational contributions to internal energy (through temperature dependence) and entropy. The only experimental input to this procedure derives from a fit of our potential to the system properties at $T=0$ K.

The present study is focused on Cu_3Au which exhibits a first-order disordering transition with a measured latent heat of transition $\Delta H(T_c)=12$ meV/atom.[11] Cu_3Au, when chemically ordered, has the cubic $L1_2$ structure (Au atoms on the cell corners and Cu atoms at the center of the faces) which, at high temperature, transforms to an fcc structure with Au and Cu atoms randomly distributed over the cell sites. The $L1_2$ structure naturally defines four sublattices: three of them, containing Cu atoms, are equivalent, while the fourth contains Au atoms. We label 1, 2, and 3 the Cu sublattices and 4 the Au sublattice.

Starting from a cubic lattice with N sites occupied according to the $L1_2$ structure with the stoichiometry $c_{Au}=0.25$ and $c_{Cu}=0.75$, the equilibrium behavior of the system at constant temperature and pressure is defined by the minimum value of the Gibbs free energy $G=H-TS$, where H is the system enthalpy and S the total entropy, including[12] a configurational part S_c, a vibrational contribution S_v, and an electronic term S_{el}.

We have attempted to express these terms as a function of a suitable set of independent variables. The CVM allows us to write the configurational entropy S_c in terms of the probability of arranging the different atomic species on a set of lattice point clusters. It has been shown[7] that, for the fcc lattice, the CVM tetrahedron approximation (i.e., where short-range order is characterized by the probability distribution of tetrahedra) provides an accurate description of the $L1_2$ ordering processes in binary alloys. In this approximation, S_c can be written as

$$S_c/N=-k_B\{\tfrac{5}{4}\Sigma_{ijk}[\mathcal{L}(p_i)+\mathcal{L}(p_j)+\mathcal{L}(p_k)+\mathcal{L}(q_l)]-\Sigma_{ijkl}[\mathcal{L}(y_{ij})+\mathcal{L}(y_{ik})+\mathcal{L}(y_{jk})+\mathcal{L}(x_{il})+\mathcal{L}(x_{jl})+\mathcal{L}(x_{kl})] +2\Sigma_{ijkl}\mathcal{L}(w_{ijkl})\}\ , \tag{1}$$

where $\mathcal{L}(x)=(x\ln x-x)$, p_α is the concentration of atomic species α ($\alpha=1$ for Cu and 2 for Au) in one of the three equivalent sublattices (1–3), q_α is the concentration of α in sublattice 4, $x_{\alpha\beta}$ is the concentration of α-β pairs between sublattices 14, 24, and 34, $y_{\alpha\beta}$ is the concentration of α-β pairs between the equivalent sublattices 12, 13, and 23 and w_{ijkl} is the concentration of tetrahedra having the configuration *ijkl* (in this case *ijkl* refers to the sublattices 1234 in this order). These variables are linked by a series of consistency relationships ($y_{ij}=\Sigma_{kl}w_{ijkl}$, $p_i=\Sigma_j y_{ij}$, etc.) which, together with the normalization condition $\Sigma_{ijkl}w_{ijkl}=1$, define the w_{ijkl}'s as the only independent variables.[7]

The main aim of the present approach is to write an explicit expression for the enthalpy and the vibrational entropy of the system as functions of the CVM variables without making recourse to any Ising-like Hamiltonians, as those proposed by Sanchez and co-workers[4,10] for pair potentials. To this purpose the enthalpy of our $\mathrm{Cu_3Au}$ model system has been calculated, by means of MD simulations, in a large number of thermodynamic states taking advantage of the most recent many-body potentials developed for the modeling of metallic systems.[13,14] Each state is characterized by the system temperature T and by the values of the long-range η (Bragg-Williams) and short-range σ (Bethe) order parameters which, in turn, are defined as $\eta=(q_2-c_{\mathrm{Au}})/(1-c_{\mathrm{Au}})$ and $\sigma=(n_{\mathrm{AuCu}}-9)/\,3$, where q_2 is the probability of finding an Au atom on sublattice 4 and n_{AuCu} is the average number of Au—Cu bonds per Au atom.

From the set $\{H_i,\eta_i,\sigma_i,T_i\}$ resulting from MD simulations, a phenomenological thermodynamic expression for the system enthalpy has been written as

$$H(\eta,\sigma,T)=H_0+c_pT +B_0(1+B_1\eta^2+B_2\sigma+B_3\eta T+B_4\sigma T)\ . \tag{2}$$

This expression takes the desired form writing η and σ in terms of the CVM variables appearing in Eq. (1):

$$\eta=\tfrac{1}{6}\Sigma_{ijkl}H_{ijkl}w_{ijkl}\ , \tag{3}$$

$$\sigma=\tfrac{1}{6}\Sigma_{ijkl}K_{ijkl}w_{ijkl}\ , \tag{4}$$

where

$$H_{ijkl}=h_{ij}+h_{ik}+h_{il}+h_{jk}+h_{jl}+h_{kl} \tag{5}$$

and $h_{\alpha\beta}=(-1)^\beta$ if $\beta=i,j,k$ or $h_{\alpha\beta}=(-1)^{\beta+1}$ if $\beta=l$. Furthermore,

$$K_{ijkl}=k_{ij}+k_{ik}+k_{il}+k_{jk}+k_{jl}+k_{kl}\ , \tag{6}$$

where $k_{\alpha\beta}=5-8\delta_{\alpha\beta}$ (δ is the Kronecker delta).

An approximate procedure for writing the vibrational entropy per atom S_v using the same CVM variables is as follows. In the quasi-harmonic approximation S_v can be written as[15]

$$S_v=k_B\int_0^{\omega_{\max}}\left[-\ln\left[2\sinh\frac{h\omega}{2k_BT}\right] +\frac{h\omega}{2k_BT}\coth\left[\frac{h\omega}{2k_BT}\right]\right]g(\omega)d\omega\ , \tag{7}$$

where $g(\omega)$ is the phonon spectrum of the system in a given phase. Using the matrix of force constants derived from the same potential used for MD simulations,[13,14] the $g(\omega)$ of the fully ordered $L1_2$ phase (at $\eta=\sigma=1$) can be calculated. Concerning phases at different η and σ, the fully disordered system ($\eta=\sigma=0$) can be described by means of the "virtual crystal method,"[16] which replaces the disordered system with an equivalent monoatomic system with masses and force constants resulting from stoichiometric averages. We have arbitrarily chosen to describe the dependence of S_v on η by means of a simple power law of the type

$$S_v(\eta,T)=S_v(1,T)+\Delta S_v(1-\eta^m)\ , \tag{8}$$

with $m=0,1,2$ which interpolates the calculated values,

$$S_v(1,T)=0.22\ \mathrm{meV/K}+T5.82\times10^{-4}\ \mathrm{meV/K^2}\ ,$$

and $\Delta S_v=-0.0103$ meV/K, independent of temperature.

In addition to configurational and vibrational terms, one should also include the contribution S_{el} due to electronic excitations. In the low-temperature approximation, the electronic contribution to the system entropy is proportional to the density of states (DOS) at the Fermi level $n(\epsilon_F)$ as $S_{\mathrm{el}}=\frac{1}{3}k_B^2\pi^2Tn(\epsilon_F)$. The difference of electronic entropy between the fully ordered and the fully disordered state, evaluated from the DOS as described above, contributes to the difference of free energy in the two states at $T=700$ K an amount $T\Delta S_{\mathrm{el}}=4\times10^{-4}$ eV/atom (Ref. 17) in agreement with the value deduced from the measured electronic specific heat.[11] This value is about two orders of magnitude smaller than the other entropic contributions to the free energy and as such has been neglected in the calculations which follow. Therefore, the final form of our free-energy functional is

$$G(w_{ijkl})=H(w_{ijkl})-T[S_c(w_{ijkl})+S_v(w_{ijkl})]\ , \tag{9}$$

where in the right-hand side of Eq. (9) we have inserted the enthalpy and the entropy as functions of the CVM variables according to Eqs. (3) and (4).

The model system used for enthalpy MD simulations and for setting up the system dynamical matrix, is an assembly of $N=500$ atoms (125 Au and 375 Cu) arranged in the $L1_2$ structure. Usual periodic boundary conditions have been imposed to minimize size effects. The cohesive energy E_c of the system is derived from a many-body potential derived from a second moment approximation of a tight-binding model[13,14]:

$$E_c=\sum_{i=1}^{N}\left[\sum_{j=1}^{N}A_{\alpha\beta}e^{-p_{\alpha\beta}(r_{ij}/r_0^{\alpha\beta}-1)}-\left\{\sum_{j=1}^{N}\xi_{\alpha\beta}^2e^{-2q_{\alpha\beta}(r_{ij}/r_0^{\alpha\beta}-1)}\right\}^{1/2}\right], \tag{10}$$

where $r_0^{\alpha\beta}$ is the nearest-neighbor distance in the pure metals if $\alpha=\beta$ or in the alloy if $\alpha\neq\beta$. $A_{\alpha\beta}$, $\xi_{\alpha\beta}$, $p_{\alpha\beta}$, and $q_{\alpha\beta}$ are adjustable parameters whose values (listed in Table I) have been determined to reproduce, at $T=0$ K, the experimental values of cohesive energy and elastic constants, and the structural stability of the ordered phase.[14] The potential has been truncated up to and including fifth neighbors. Simulations have been carried out in the Nosé-Parrinello-Rahman (constants N, P, and T) ensemble, making use of a fifth-order predictor-corrector algorithm to integrate the equations of motion, with a time step of 10^{-15} s.

To check the model capability to reproduce the system properties, isobaric heating of the disordered phase has been performed and the melting temperature of the simulated Cu_3Au system has been located at $T_m=1420$ K which has to be compared with the experimental value of 1233 K (Ref. 11) shown in Fig. 1. It is to be noted that melting temperature as deduced by MD simulations defines the system mechanical instability temperature, which is the upper limit of the thermodynamical melting.[18] Several thermodynamic quantities have then been calculated and successfully compared with the experimental data (from Ref. 11, in parentheses), as the latent heat of melting $\Delta H(T_m)=0.09$ eV/atom (0.12 ± 0.01), the thermal dilation coefficient $\alpha=5.4\times10^5$ K^{-1} (4.9×10^{-5}), and the low-temperature specific heat $c_p=2.57\times10^{-4}$ eV K^{-1} $atom^{-1}$ (2.5×10^{-4}).

Evaluation of the enthalpy values from MD simulations is as follows. Starting from the ordered phase at a given temperature, a suitable number of antisite defects corresponding to a given value of η is introduced in the system, which is then left free to relax for 5×10^5 time steps at constant pressure ($P_{ext}=0$) and temperature. This procedure is repeated several times using different antisite configurations (i.e., with the same value of η but with different values of σ) at a number of temperatures ranging from 300 to 1000 K, for a total of about 100 points. The fit to the MD data has been performed using several functional forms until the best agreement was obtained with the use of Eq. (2), with the following parameters ($H_0=E_c=3.6345$ eV and c_p fixed at the calculated value): $B_0=21.795$ meV, $B_1=0.5014$, $B_2=-1.46$, $B_3=1.28\times10^{-4}$ K^{-1}, and $B_4=2.15\times10^{-4}$ K^{-1}. The precision of the fit is in the range 1–3 % on the whole set of MD data.

TABLE I. Potential parameters used in the calculations.

	A (eV)	ξ (eV)	p	q	r_0 (Å)
Au-Au	0.2061	1.790	10.229	4.036	2.884
Cu-Cu	0.0855	1.224	10.960	2.278	2.556
Au-Cu	0.1539	1.5605	11.05	3.0475	2.642

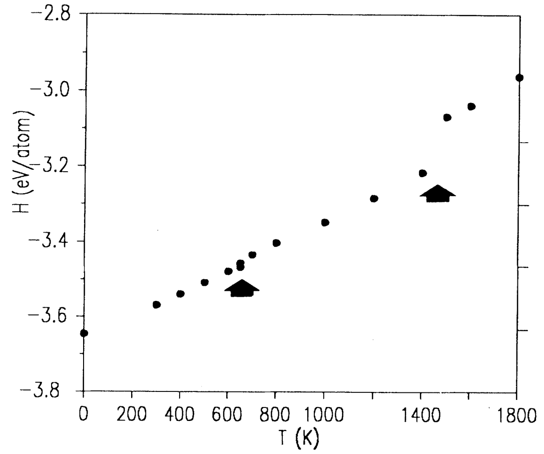

FIG. 1. Enthalpy as a function of temperature for Cu_3Au. Arrows mark the order-disorder transition ($T_c=635$ K) and the melting temperature ($T_m=1420$ K) of our model system.

The equilibrium value of the free energy is obtained from a minimization of Eq. (9) with respect to the configurational variables w_{ijkl} using the natural iteration scheme (NI), first proposed by Kikuchi.[7] Equation (9) is minimized with two constraints arising from the normalization of the w_{ijkl}'s and from the requirement of a fixed concentration. For each value of T and for the correct stoichiometry of the system the equilibrium values of η and σ have been evaluated from Eqs. (3) and (4) inserting the values of the w_{ijkl}'s deduced according to the above procedure. The dependence of η on temperature is shown in Fig. 2, where the experimental points[19] have been reported for comparison. In this figure, we show the calculated equilibrium value of η as a function of T for different η dependences of the vibrational entropy. One observes that if the contribution of S_v is neglected altogether [$m=0$ in Eq. (8)] the transition occurs at a temperature lower than experimentally observed, while, if

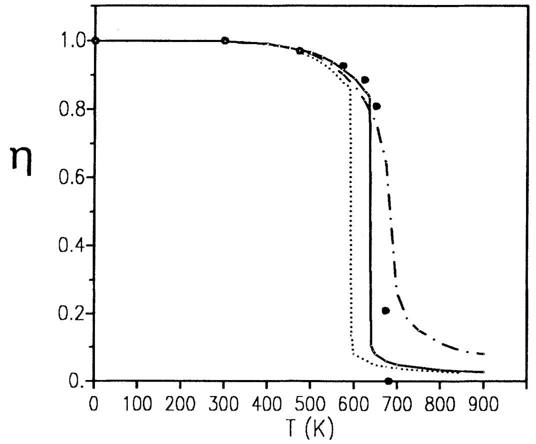

FIG. 2. Equilibrium values of the long-range order parameter η calculated for three values of m in Eq. (9). Full dots: experimental points (Ref. 19); dotted line: $m=0$; dash-dotted line: $m=1$; full line: $m=2$.

one chooses $m=1$, the transition is markedly rounded off, thus losing a typical signature of the first-order character of the transformation. The best agreement with experiment is obtained with the choice $m=2$, which is able to reproduce accurately both the sharpness and the scale of the transition temperature. Precursor effects concerning the behavior of η for $T<T_c$, are also evident. With increasing temperature, η decreases slowly from 1 to 0.85 before going abruptly to 0. This feature, typical of first-order transitions, is in quantitative agreement with the experiment where the same phenomenon occurs at $\eta \sim 0.80$. The estimated transition temperature is $T_c=635$ K ($T_c^{\exp}=663$ K). The latent heat of the transition has been evaluated as $\Delta H(T_c)=10$ meV/atom.

The dependence of S_v on the short-range order parameter σ is not taken into account by the present calculations. This could be one of the main limits of our approach considering that the behavior of σ with temperature reveals some interesting features of the transition, as shown in Fig. 3. Before the transition, σ is close to the value given by the formula $\sigma=\eta^2$ (random distribution of defective regions) while, after the transition—that is, at $\eta=0$—σ first takes a value of about 0.45 and then decays very slowly. This behavior agrees with theoretical and phenomenological models[20,21] which are based on the relation of the short-range order parameter with bond energy, lattice dilation, and composition. The meaning of this feature is extremely interesting as far as the disordering mechanism is concerned. Actually, a value of σ definitely larger than η^2 reveals a tendency of the system to keep the highest possible number of Au—Cu bonds. It is then presumable that the transition proceeds with the creation of out-of-step domains which, although destroying the long-range sequences, preserve to a large extent the short-range order. If the disorder were established through a random occupation of sites, the value of σ should have been vanishingly small. Only at very high temperatures (much higher than the system melting temperature) does the model predict vanishing values for the short-range order parameter.

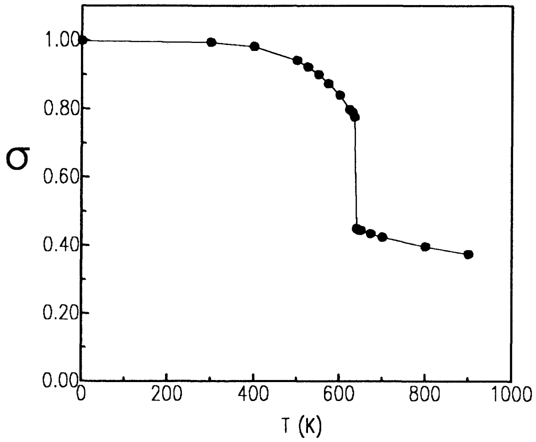

FIG. 3. Equilibrium values of the short-range order parameter σ calculated with $m=2$.

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