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First-principles theory of vibrational effects on the phase stability of Cu-Au compounds and alloys

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The importance of vibrational effects on the phase stability of Cu-Au alloys is investigated via a combination of first-principles linear response calculations and a statistical mechanics cluster expansion method. We find that (i) the logarithmic average of the phonon density of states in ordered compounds is lower than in the pure constituents, thus leading to positive vibrational entropies of formation and to negative free energies of formation, stabilizing the compounds and alloys with respect to the phase separated state. (ii) The vibrational free energy is lower in the configurationally random alloy than in ordered ground states, which leads to lower order-disorder transition temperatures. (iii) The random alloys have larger thermal expansion coefficients than ordered ground states, and therefore the vibrational entropy difference between the random and ordered states is a strongly increasing function of temperature. However, (iv) due to the associated increase in the static internal energy, the effect of thermal expansion on the free energy (and thus on the phase diagram) is only half that of the entropy alone. [S0163-1829(98)50534-6]

The thermodynamics of alloy phase diagrams is decided by the interplay between the configurational (conf) enthalpy (H) and entropy (S), and by the vibrational (vib) contributions:[1]

$$G=(H_{\mathrm{conf}}-TS_{\mathrm{conf}})+(H_{\mathrm{vib}}-TS_{\mathrm{vib}}). \tag{1}$$

Configurational effects reflect the different occupation patterns of the statically relaxed, but nonvibrating lattice sites by the atoms of type A and B. The occupation of site i by one of these types of atoms is conveniently labeled by a spin variable $\hat{S}_i=\pm 1$. These configurational degrees of freedom can be treated via ''first-principles statistical mechanics'' [2] by expanding the quantum-mechanically calculated $T=0$ formation enthalpies ΔH_{conf} in a generalized Ising-like cluster expansion (CE)

$$\Delta H_{\mathrm{conf}}(\{\hat{S}_i\})=J_0^{\mathrm{conf}}+J_1^{\mathrm{conf}}\sum_i \hat{S}_i+\frac{1}{2}\sum_{i,j} J_{ij}^{\mathrm{conf}}\hat{S}_i\hat{S}_j + \frac{1}{3!}\sum_{i,j,k} J_{ijk}^{\mathrm{conf}}\hat{S}_i\hat{S}_j\hat{S}_k+\cdots, \tag{2}$$

determining the effective pair $\{J_{ij}^{\mathrm{conf}}\}$, three-body $\{J_{ijk}^{\mathrm{conf}}\}$ and higher interactions from self-consistent electronic-structure total energy calculations, and finding the configurational entropy and free energy by subjecting the CE Hamiltonian [Eq. (2)] to Monte-Carlo simulations. This approach has produced a wealth of information on phase diagrams, short-range order, and ground states in metal and semiconductor alloys.[2] On the other hand, the effect of vibrations on alloy phase stability has only been recently studied experimentally,[3–5] and accurate first-principles investigations are very scarce.[6]

In general, the vibrational contribution to the free energy may have two distinct effects: (i) change in the stability of an alloy or ordered compound A_mB_n in configuration σ with respect to the solid constituents $A+B$, and (ii) change in the stability of an ordered compound with respect to the random alloy at the same composition. The first effect is quantified by considering the vibrational free energy of formation with respect to the pure constituents:

$$\Delta G_{\mathrm{vib}}^{\mathrm{form}}(\sigma,T)=G_{\mathrm{vib}}(\sigma,T) -[(1-x)G_{\mathrm{vib}}(A,T)+xG_{\mathrm{vib}}(B,T)]. \tag{3}$$

The second effect is described by the ''vibrational free energy of ordering'':

$$\delta G_{\mathrm{vib}}^{\mathrm{ord}}(\sigma,T)=G_{\mathrm{vib}}(\sigma,T)-G_{\mathrm{vib}}^{\mathrm{rand}}(x,T), \tag{4}$$

where $G_{\mathrm{vib}}^{\mathrm{rand}}(x,T)$ is the vibrational free energy of the random alloy. In what follows, we also consider vibrational entropies S_{vib} and configurational enthalpies H_{conf} of formation (ordering), defined in analogy with Eq. (3) [Eq. (4)]. In the quasiharmonic approximation the vibrational free energy G_{vib} can be obtained from the phonon density of states $g_\sigma(\nu,a_T)$ of configuration σ (denoting a given occupation pattern $\{\hat{S}_i\}$) at a zero-pressure lattice constant a_T via[8]

$$G_{\mathrm{vib}}(\sigma,T)=k_BT\int d\nu\; g_\sigma(\nu,a_T)\,\ln\left[2\sinh\frac{h\nu}{2k_BT}\right]. \tag{5}$$

At temperatures higher than the characteristic Debye temperature, $H_{\mathrm{vib}}=3k_BT$, and therefore the structural dependence of $G_{\mathrm{vib}}(\sigma,T)$ is entirely due to $S_{\mathrm{vib}}(\sigma,T)$. The basic expectations regarding the effects of vibrations on the alloy phase stability are:

(i) *Formation free energies* $\Delta G_{\mathrm{vib}}^{\mathrm{form}}$: If the phonon spectrum of the compound is redshifted (blueshifted) with respect to the weighted average of the constituents, then $\Delta G_{\mathrm{vib}}^{\mathrm{form}}<0$ ($\Delta G_{\mathrm{vib}}^{\mathrm{form}}>0$). Previous studies[9–12] have shown that in *phase-separating* alloys such as GaP-InP,[9] Cu-Ag,[10,11] or Ni-Cr[12] (where $\Delta H_{\mathrm{conf}}^{\mathrm{form}}>0$) one often finds a vibrational stabilization of compounds ($\Delta G_{\mathrm{vib}}^{\mathrm{form}}<0$), leading to increased solubilities and lower miscibility gap temperatures. It is still an open question whether in *compound-forming* systems (e.g., Cu-Au) the vibrational effects would lead to increased ($\Delta G^{\mathrm{form}}_{\mathrm{vib}}<0$ and $\Delta S^{\mathrm{form}}_{\mathrm{vib}}>0$) or decreased ($\Delta G^{\mathrm{form}}_{\mathrm{vib}}>0$ and $\Delta S^{\mathrm{form}}_{\mathrm{vib}}<0$) thermodynamic stability, although it has been found that $\Delta S^{\mathrm{form}}_{\mathrm{vib}}>0$ in Cd-Mg.[13]

(i) *Ordering free energy* $\delta G^{\mathrm{ord}}_{\mathrm{vib}}$: this quantity affects the order-disorder transition temperature T_c determined by the equality of free energies of both phases at the transition point, $\delta H^{\mathrm{ord}}_{\mathrm{conf}}(T_c)-T_c\,\delta S^{\mathrm{ord}}_{\mathrm{conf}}(T_c)+\delta G^{\mathrm{ord}}_{\mathrm{vib}}(T_c)=0$. It can be shown[14] that the transition temperature is given approximately by

$$T_c \approx T_{c,\mathrm{conf}}\left(1+\frac{\delta S^{\mathrm{ord}}_{\mathrm{vib,h}}+\Delta_{\mathrm{qh}}/2}{\delta S^{\mathrm{ord}}_{\mathrm{conf}}}\right)^{-1}, \tag{6}$$

where $T_{c,\mathrm{conf}}=\delta S^{\mathrm{ord}}_{\mathrm{conf}}/\delta H^{\mathrm{ord}}_{\mathrm{conf}}$ is a ‘‘purely configurational’’ transition temperature calculated without vibrations, and $\Delta_{\mathrm{qh}}=\delta S^{\mathrm{ord}}_{\mathrm{vib,qh}}-\delta S^{\mathrm{ord}}_{\mathrm{vib,h}}$ is a quasiharmonic (qh) correction due to thermal expansion, which usually increases the lattice constant a_T and decreases the phonon frequencies entering Eq. (5). Equation (6) shows that in a *harmonic* crystal where Δ_{qh} is negligible, phonon softening in the disordered phase would lower the transition temperature by a factor $\delta S^{\mathrm{ord}}_{\mathrm{vib}}/\delta S^{\mathrm{ord}}_{\mathrm{conf}}$. Since $\delta S^{\mathrm{ord}}_{\mathrm{conf}}$ is bound from above by the ideal mixing entropy $-k_B[x\ \ln x+(1-x)\ln(1-x)]\leqslant 0.69k_B/\mathrm{atom}$, even a relatively small $\delta S^{\mathrm{ord}}_{\mathrm{vib}}\propto 0.1k_B$ could lower T_c by a significant amount. Indeed, experimental values of $\delta S^{\mathrm{ord}}_{\mathrm{vib}}=0.14\pm 0.05k_B$ for $\mathrm{Cu_3Au}$ have led to the expectation of a large lowering of T_c. However, if much of $\delta S^{\mathrm{ord}}_{\mathrm{vib}}$ is contributed by anharmonicity, then by Eq. (6) the effect of vibrations on T_c is smaller by a factor of 2 than that suggested by the harmonic analysis. In fact, if $\Delta_{\mathrm{qh}}\gg\delta S^{\mathrm{ord}}_{\mathrm{vib,h}}$ (as found,[15,16] e.g., in $\mathrm{Ni_3Al}$), then the vibrational entropy increases rapidly with temperature and the harmonic estimate based on the measured *total* entropy $\delta S^{\mathrm{ord}}_{\mathrm{vib}}=\delta S^{\mathrm{ord}}_{\mathrm{vib,h}}+\Delta_{\mathrm{qh}}$ would be incorrect. Many previous studies[15–17] have focused on the vibrational entropy, not on the vibrational free energy, and therefore have not considered this connection between vibrational free energy and order-disorder transition temperature.

We have previously[18] calculated the configurational energies of the Cu-Au system using the local density approximation (LDA), and extracted $\{J^{\mathrm{conf}}_{ij\ldots}\}$ by inverting Eq. (2). These interactions were used in Monte Carlo simulations to obtain the configurational entropy. In the present work we calculate the phonon dispersion curves $\{\nu_{n\mathbf{k}}(a,\sigma)\}$ of a set of ordered configurations $\{\sigma\}$ from the first principles using density-functional linear response theory.[7] These frequencies are then used in Eq. (5) to evaluate the vibrational free energy. Since a direct linear response calculation of $g(\nu)$ for the random alloy is currently not feasible, we obtain $\Delta G^{\mathrm{rand}}_{\mathrm{vib}}$ from a cluster expansion similar to Eq. (2), namely:

$$\Delta G^{\mathrm{form}}_{\mathrm{vib}}(\{\hat S_i\},T)=J^{\mathrm{vib}}_0(T)+J^{\mathrm{vib}}_1(T)\sum_i \hat S_i+\frac{1}{2}\sum_{i,j} J^{\mathrm{vib}}_{ij}(T)\hat S_i\hat S_j+\frac{1}{3!}\sum_{i,j,k} J^{\mathrm{vib}}_{ijk}(T)\hat S_i\hat S_j\hat S_k+\cdots. \tag{7}$$

We determined $\{J^{\mathrm{vib}}_{ij\ldots}(T)\}$ from fitting to directly calculated $\Delta G^{\mathrm{form}}_{\mathrm{vib}}$ of six ordered configurations $\{\sigma\}=\{$fcc Cu, $L1_2(\mathrm{Cu_3Au})$, $L1_0(\mathrm{CuAu})$, $L1_1(\mathrm{CuAu})$, $L1_2(\mathrm{CuAu_3})$, fcc Au$\}$, and calculated via Eq. (7) the vibrational free energies of the disordered and short-range ordered alloys. The accuracy of this procedure depends on the convergence of the cluster expansion: although our predictions for the random alloys are probably less accurate than the values for ordered compounds, comparison with the experimental estimates of $\Delta S^{\mathrm{form}}_{\mathrm{vib}}$ and $\delta S^{\mathrm{ord}}_{\mathrm{vib}}$ (see below) show that it correctly captures the essential effects. The alloy phase diagram and T_c’s have then been obtained in Monte Carlo calculations using the full Ising Hamiltonian given by the sum of configurational [Eq. (2)] and vibrational [Eq. (7)] terms.

The phonon spectra were obtained using the density-functional perturbation theory[7] implementation in a plane-wave basis set. We used equivalent **k**-point meshes[19] for both electron and phonon Brillouin-zone summations, designed to ensure maximum error cancellation in the energy and entropy differences between different structures. Electronic (phonon) states were calculated on grids equivalent to 85 (10) irreducible **k** points for the fcc structure. The harmonic phonon frequencies were calculated at the equilibrium $T=0$ local-density approximation (LDA) lattice parameter determined by $\partial E_{\mathrm{conf}}(a,\sigma)/\partial a=0$. Anharmonic effects were treated in the quasiharmonic approximation[8] by explicitly calculating the phonon mode Grüneisen parameters $\gamma_{n\mathbf{k}}(\sigma)=\partial\ln\nu_{n\mathbf{k}}(a,\sigma)/\partial\ln a$ and finding the lattice parameter that minimized the sum of the static internal energy and vibrational free energy. To determine the vibrational interaction energies $\{J^{\mathrm{vib}}_{ij\ldots}\}$ of Eq. (7) we calculated $\{G_{\mathrm{vib}}(\sigma,T)\}$ directly from Eq. (5) for a set of ordered structures $\{\sigma\}$, and mapped these free energies onto Eq. (7). We included vibrational cluster interactions corresponding to five figures (J_0—empty cluster, J_1—point cluster, J_2—nearest neighbor (NN) pair, K_2—second NN pair, and J_3—NN triangle).

The calculated phonon frequencies, thermal expansion coefficients, and thermodynamical functions of ordered compounds are in excellent agreement with the available experimental results.[14] Table I lists the vibrational entropies $\Delta S^{\mathrm{form}}_{\mathrm{vib}}$ and free energies $\Delta G^{\mathrm{form}}_{\mathrm{vib}}$ of formation at $T=800$ K, calculated both without the thermal expansion (harmonic approximation) and with it (quasiharmonic approximation). For comparison, we also give the configurational formation enthalpies $\Delta H^{\mathrm{form}}_{\mathrm{conf}}$. We see the following:

(i) All calculated $\Delta S^{\mathrm{form}}_{\mathrm{vib}}(\sigma,T)$ are positive, indicating that the vibrational entropy favors compound formation over phase separation. This means that the frequencies deciding vibrational entropy are lower in compounds than in the constituents, and thus the appropriate force constants are softer. Note that the bulk moduli (often used to estimate S_{vib} in simple models[21]) are not good indicators of this trend, as they represent merely the hydrostatic response. Indeed, LDA calculations find that the bulk modulus of $\mathrm{CuAu_3}$ is larger than that of either Cu or Au,[22] showing that hydrostatically the compound is stiffer than its constituents.

(ii) Comparison of $\Delta S^{\mathrm{form}}_{\mathrm{vib}}(L1_0)=0.121\ k_B/\mathrm{atom}$ and $\Delta S^{\mathrm{form}}_{\mathrm{vib}}(L1_1)=0.261\ k_B/\mathrm{atom}$ at the same volume $V=14.81$ Å and ideal $c/a=1$ ratio shows that most of the large difference in the vibrational formation entropies is purely ‘‘configurational,’’ i.e., it is *not* caused by a volume difference between these phases.[20] This is in contrast to Althoff *et al.*[15] who find that most of the difference between

TABLE I. Formation vibrational entropies ($\Delta S_{\mathrm{vib}}^{\mathrm{form}}$) and free energies ($\Delta G_{\mathrm{vib}}^{\mathrm{form}}$) per atom for ordered Cu-Au compounds and the perfectly random alloy in the harmonic (h) and quasi-harmonic (qh) case. We also give the calculated formation enthalpies $\Delta H_{\mathrm{conf}}^{\mathrm{form}}$, average Grüneisen parameters $\overline{\gamma}$, and the change in the lattice parameter due to thermal expansion, $\Delta a(T)=a_{\mathrm{eq}}(T)-a_{\mathrm{eq}}(T=0)$. All results are given for $T=800$ K. Random alloy properties have been obtained from a cluster expansion.

Structure	$\Delta H_{\mathrm{conf}}^{\mathrm{form}}$ (meV/at.)	$\Delta S_{\mathrm{vib,(h)}}^{\mathrm{form}}$ (k_B/at.)	$\Delta G_{\mathrm{vib,(h)}}^{\mathrm{form}}$ (meV/at.)	$\Delta S_{\mathrm{vib,(qh)}}^{\mathrm{form}}$ (k_B/at.)	$\Delta G_{\mathrm{vib,(qh)}}^{\mathrm{form}}$ (meV/at.)	$\overline{\gamma}$	$\Delta a(T)$ (Å)
fcc Cu	0.0	0.0	0.0	0.0	0.0	1.87	0.034
Cu_3Au ($L1_2$)	−37.3	0.099	−7.0	0.201	−9.3	2.46	0.049
Random $Cu_{0.75}Au_{0.25}$	+2.6	0.150	−10.5	0.284	−13.7	2.48	0.050
CuAu ($L1_0$)	−48.2	0.117	−8.3	0.209	−10.4	2.74	0.049
CuAu ($L1_1$)	+32.5	0.314	−21.9	0.584	−28.4	3.07	0.064
Random $Cu_{0.50}Au_{0.50}$	+1.6	0.209	−14.6	0.390	−18.9	2.91	0.057
$CuAu_3$ ($L1_2$)	−17.3	0.137	−9.6	0.258	−12.1	3.14	0.053
Random $Cu_{0.25}Au_{0.75}$	+5.4	0.165	−11.5	0.305	−14.8	3.15	0.054
fcc Au	0.0	0.0	0.0	0.0	0.0	3.11	0.047

ordered and disordered states in Ni_3Al is due to the larger volume in the disordered state.

(iii) The value of the vibrational entropy of formation of $L1_2$ $\Delta S_{\mathrm{vib}}^{\mathrm{form}}=+0.07\pm0.03\ k_B$/atom extracted from experiment by Bogdanoff and Fultz[23] for ordered Cu_3Au at room temperature agrees well with our calculated $\Delta S_{\mathrm{vib,(h)}}^{\mathrm{form}}(L1_2)=+0.1\ k_B$/atom. Furthermore, the calculated vibrational entropy difference $\delta S_{\mathrm{vib}}^{\mathrm{ord}}$ between the perfectly ordered $L1_2$ and disordered states of Cu_3Au at $T=300$ K is found to be $+0.06\ k_B$/atom (see Fig. 1), which is slightly below the lower limit of the value $+0.14\pm0.05\ k_B$/atom suggested by the experimental study of Nagel, Anthony, and Fultz.[5] Finally, combining their measured $\delta S_{\mathrm{vib}}^{\mathrm{ord}}=\Delta S_{\mathrm{vib}}^{\mathrm{form}}(L1_2)-\Delta S_{\mathrm{vib}}^{\mathrm{form}}(\mathrm{random})=0.14\ k_B$/atom with the measured $\Delta S_{\mathrm{vib}}^{\mathrm{form}}(L1_2)=+0.07\ k_B$/atom, gives $\Delta S_{\mathrm{vib}}^{\mathrm{form}}(\mathrm{random})=0.21\pm0.08\ k_B$/atom, which should be compared with our calculated $\Delta S_{\mathrm{vib,(h)}}^{\mathrm{form}}(\mathrm{random})=+0.15\ k_B$/atom (Table I). This comparison gives a measure of the accuracy of our cluster expansion.

(iv) Thermodynamically averaged Grüneisen parameters $\overline{\gamma}$ (given in the last column of Table I) are higher in the disordered $Cu_{1-x}Au_x$ phases than in ordered ground states $L1_2$ and $L1_0$. Therefore, the thermal expansion $\Delta a(T)$ is larger in the disordered phase and its phonon frequencies soften more rapidly with increasing temperature.

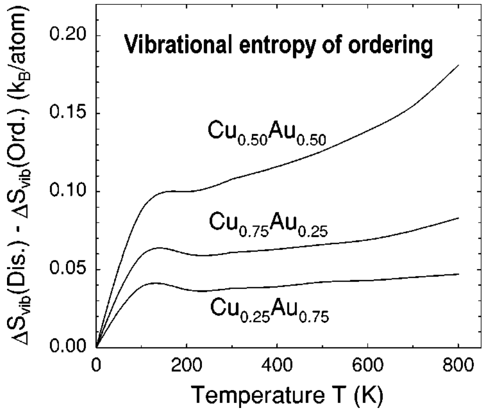

FIG. 1. T dependence of the vibrational entropy difference between the perfectly ordered and disordered states.

(v) Comparison of the harmonic $\Delta S_{\mathrm{vib,(h)}}^{\mathrm{form}}$ and quasiharmonic $\Delta S_{\mathrm{vib,(qh)}}^{\mathrm{form}}$ in Table I shows that the thermal expansion contributes ≈50% to the total vibrational formation entropies at $T=800$ K. Thermal expansion also causes a strong temperature dependence of the vibrational entropy of ordering $\delta S_{\mathrm{vib}}^{\mathrm{ord}}$ (see Fig. 1) at high temperatures ($T\geqslant200$ K) due to larger Grüneisen parameter in the disordered phase. This is in agreement with the conclusions of Refs. 15 and 16, but in contrast to the result of van de Walle *et al.*[6] for Ni_3Al.

(vi) Figure 2 summarizes the free energies of $Cu_{0.50}Au_{0.50}$ on three levels of calculation: (a)–(b) configurational degrees of freedom only, (c) configurational+harmonic vibrational degrees of freedom, and (d)–(e) configurational +quasiharmonic vibrational degrees of freedom. (a) At $T=0$ K, the formation enthalpy $\Delta H_{\mathrm{conf}}^{\mathrm{conf}}$ of the ordered $L1_0$ phase is $\delta H_{\mathrm{conf}}^{\mathrm{ord}}=50$ meV/atom higher than of the random alloy. (b) At $T=800$ K (above the order-disorder transition) the configurational entropy ΔS_{conf} stabilizes the disordered phase, bringing its free energy below the ordered $L1_0$ state. (c) The harmonic vibrational entropy further stabilizes the disordered phase over $L1_0$, and (d) the contribution of thermal expansion to the vibrational entropy term (going from $\Delta S_{\mathrm{vib}}^{\mathrm{harm}}$ to $\Delta S_{\mathrm{vib}}^{\mathrm{q\text{-}harm}}$) doubles the effect due to the harmonic

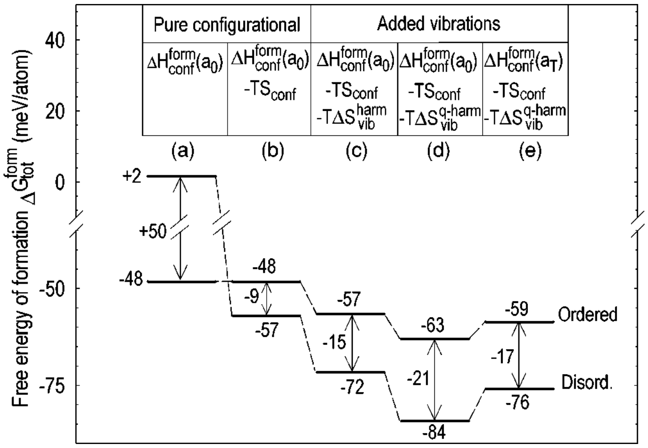

FIG. 2. The calculated vibrational and configurational free energies of the disordered $Cu_{0.5}Au_{0.5}$ and ordered CuAu ($L1_0$) phases at $T=800$ K.

TABLE II. Effect of vibrations on the calculated transition temperatures in Cu-Au.

		T_c (K)		
Composition	Transition	No vibrations	With vibrations	Expt.
$x=0.25$	fcc→$L1_2$	530	455	663
$x=0.50$	fcc→$L1_0$	660	560	683/656
$x=0.75$	fcc→$\beta 2+A1$	750	660	≈500[a]

[a] Current compilations of phase diagrams list $L1_2$ as the stable $T=0$ phase of CuAu_3, while LDA predicts that Au-rich (100) superlattices are more stable.

entropy term alone. (e) However, since the volume expansion imposes an energetic penalty $\Delta H_{\mathrm{conf}}^{\mathrm{form}}(a_T)-\Delta H_{\mathrm{conf}}^{\mathrm{form}}(a_0)$, the total effect of thermal expansion on the ordering free energy $\delta G_{\mathrm{tot}}^{\mathrm{ord}}$ is much smaller than that suggested by the change in the quasiharmonic vibrational entropy term (only -2 meV/atom opposed to -6 meV/atom). Therefore, although the thermal expansion has a dramatic effect on the vibrational entropies, it has a much smaller effect on the free energies, and hence on the phase diagram. This important aspect of the free energy is not accounted for by studies[15–17] focusing exclusively on the vibrational entropy. Figure 2 also shows that the vibrational free energy gives a significant (≈25%) contribution to the total free energy of mixing. For instance, the calculated $\Delta G_{\mathrm{conf}}^{\mathrm{form}}$ of the disordered $\mathrm{Cu}_{0.50}\mathrm{Au}_{0.50}$ phase at $T=800$ K is -57 meV/atom [column (b)], while vibrations and thermal expansion contribute an additional -19 meV/atom [column (e)].

Our Monte Carlo simulations of the Cu-Au phase diagram using the sum of the configurational [Eq. (2)] and vibrational [Eq. (7)] Hamiltonians show that the vibrational entropy does not change the stable low-temperature phases of Cu-Au. However, it lowers the transition temperatures considerably: Table II shows that T_c's are lowered by 15% (but less than 100 K). In conclusion, we find that the atomic vibrations contribute significantly to the phase stabilities and thermodynamic functions of Cu-Au. Further studies are needed to assess the importance of vibrational effects in other alloy systems.

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