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

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~Received 8 May 1998!

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

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~e.g., Cu-Au! the vibrational effects would lead to increased ($\mathrm{D}G_{\mathrm{vib}}^{\mathrm{form}}\ ,\ 0$ and $\mathrm{D}S_{\mathrm{vib}}^{\mathrm{form}}\ .\ 0$) or decreased ($\mathrm{D}G_{\mathrm{vib}}^{\mathrm{form}}\ .\ 0$ and $\mathrm{D}S_{\mathrm{vib}}^{\mathrm{form}}\ ,\ 0$) thermodynamic stability, although it has been found that $\mathrm{D}S_{\mathrm{vib}}^{\mathrm{form}}\ .\ 0$ in Cd-Mg.[13]

~i! *Ordering free energy* $dG_{\mathrm{vib}}^{\mathrm{ord}}$: this quantity affects the order-disorder transition temperature T_c determined by the equality of free energies of both phases at the transition point, $dH_{\mathrm{conf}}^{\mathrm{ord}}(T_c)\ 2\ T_c\,dS_{\mathrm{conf}}^{\mathrm{ord}}(T_c)\ 1\ dG_{\mathrm{vib}}^{\mathrm{ord}}(T_c)\ 5\ 0$. It can be shown[14] that the transition temperature is given approximately by

$$T_c\ '\ T_{c,\mathrm{conf}}\left\{1\ 1\ \frac{dS_{\mathrm{vib,h}}^{\mathrm{ord}}\ 1\ \mathrm{D}_{\mathrm{qh}}/2}{dS_{\mathrm{conf}}^{\mathrm{ord}}}\right]^{2\,1}, \qquad \text{~6!}$$

where $T_{c,\mathrm{conf}}\ 5\ dS_{\mathrm{conf}}^{\mathrm{ord}}/dH_{\mathrm{conf}}^{\mathrm{ord}}$ is a ‘‘purely configurational’’ transition temperature calculated without vibrations, and $\mathrm{D}_{\mathrm{qh}}\ 5\ dS_{\mathrm{vib,qh}}^{\mathrm{ord}}\ 2\ dS_{\mathrm{vib,h}}^{\mathrm{ord}}$ 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 D_{qh} is negligible, phonon softening in the disordered phase would lower the transition temperature by a factor $dS_{\mathrm{vib}}^{\mathrm{ord}}/dS_{\mathrm{conf}}^{\mathrm{ord}}$. Since $dS_{\mathrm{conf}}^{\mathrm{ord}}$ is bound from above by the ideal mixing entropy $2\ k_B@x\ \ln x\ 1\ (1\ 2\ x)\ln(1\ 2\ x)\#<0.69k_B/\mathrm{atom}$, even a relatively small $dS_{\mathrm{vib}}^{\mathrm{ord}}\}\ 0.1k_B$ could lower T_c by a significant amount. Indeed, experimental values of $dS_{\mathrm{vib}}^{\mathrm{ord}}$ $5\ 0.14\ 6\ 0.05k_B$ for $\mathrm{Cu_3Au}$ have led to the expectation of a large lowering of T_c. However, if much of $dS_{\mathrm{vib}}^{\mathrm{ord}}$ 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 $\mathrm{D}_{\mathrm{qh}}@\,dS_{\mathrm{vib,h}}^{\mathrm{ord}}$ ~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 $dS_{\mathrm{vib}}^{\mathrm{ord}}\ 5\ dS_{\mathrm{vib,h}}^{\mathrm{ord}}\ 1\ \mathrm{D}_{\mathrm{qh}}$ would be incorrect. Many previous studies[15–17] have focused on the vibra-

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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 $L1_2$ D$S_{\text{vib}}^{\text{form}}$ 5 1 0.07 6 0.03 k_B/atom extracted from experiment by Bogdanoff and Fultz[23] for ordered Cu_3Au at room temperature agrees well with our calculated D$S_{\text{vib,~h!}}^{\text{form}}(L1_2)$ 5 1 0.1 k_B/atom. Furthermore, the calculated vibrational entropy difference $dS_{\text{vib}}^{\text{ord}}$ between the perfectly ordered $L1_2$ and disordered states of Cu_3Au at T 5 300 K is found to be 1 0.06 k_B/atom ~see Fig. 1!, which is slightly below the lower limit of the value 1 0.14 6 0.05 k_B/atom suggested by the experimental study of Nagel, Anthony, and Fultz.[5] Finally, combining their measured $dS_{\text{vib}}^{\text{ord}}$ 5 D$S_{\text{vib}}^{\text{form}}(L1_2)$ 2 D$S_{\text{vib}}^{\text{form}}$(random) 5 0.14 k_B/atom with the measured D$S_{\text{vib}}^{\text{form}}(L1_2)$ 5 1 0.07 k_B/atom, gives D$S_{\text{vib}}^{\text{form}}$(random) 5 0.21 6 0.08 k_B/atom, which should be compared with our calculated D$S_{\text{vib,~h!}}^{\text{form}}$(random) 5 1 0.15 k_B/atom ~Table I!. This comparison gives a measure of the accuracy of our cluster expansion.

~iv! Thermodynamically averaged Grüneisen parameters $\overline{g}$ ~given in the last column of Table I! are higher in the disordered $Cu_{1\ 2\ x}Au_x$ phases than in ordered ground states $L1_2$ and $L1_0$. Therefore, the thermal expansion D$a(T)$ is larger in the disordered phase and its phonon frequencies soften more rapidly with increasing temperature.

~v! Comparison of the harmonic

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entropy term alone. ~e! However, since the volume expansion imposes an energetic penalty $\mathrm{D}H^{\mathrm{form}}_{\mathrm{conf}}(a_T)$ $2\,\mathrm{D}H^{\mathrm{form}}_{\mathrm{conf}}(a_0)$, the total effect of thermal expansion on the ordering free energy $dG^{\mathrm{ord}}_{\mathrm{tot}}$ is much smaller than that suggested by the change in the quasiharmonic vibrational entropy term ~only 2 2 meV/atom opposed to 2 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 $\mathrm{D}G^{\mathrm{form}}_{\mathrm{conf}}$ of the disordered $\mathrm{Cu}_{0.50}\mathrm{Au}_{0.50}$ phase at $T\,5\,800$ K is 2 57 meV/atom @column ~b!#, while vibrations and thermal expansion contribute an additional 2 19 meV/atom @column ~e!#.