# Entropically Favored Ordering: The Metallurgy of $Al_2Cu$ Revisited

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The famous sequence of precipitates which form upon heat treating Al-Cu is part of nearly every metallurgical textbook. Numerous precipitation (and other) experiments have led to a long-standing belief that the energetic ground state of $Al_2Cu$ is the $\theta$ phase. Modern first-principles calculations at $T = 0$ K surprisingly predict the energy of the observed $Al_2Cu$-$\theta$ phase to be higher than that of its metastable counterpart, $\theta'$. We show that vibrational entropy reverses this energetic preference at $T \sim 150-200$ °C, resolves the apparent discrepancy between theory and experiment, and hence plays a critical (but previously unsuspected) role in the precipitation sequence.

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The accidental discovery of the phenomenon of precipitation hardening by Wilm, published in 1911 [1], was in an Al-Cu-based alloy. Craftsmen apparently knew of this effect before scientists, as a precipitation hardened Al-Cu alloy was used in the engine powering the Wright brothers' historic flight in 1903 [2]. However, the discovery of the structural cause of the hardening had to wait until the 1930s, when Guinier and Preston [3,4] independently observed Cu-rich precipitates in Al-Cu alloys. These three events highlight the pivotal role that Al-Cu has played in the understanding of precipitation hardening, a process to which many current commercial alloys are subject. The hardening process results from precipitates which are formed via thermal aging of an alloy supersaturated with solute. Upon isothermal aging the disordered Al-Cu alloy often [5] gives way first to small disk-shaped clusters of Cu atoms (called "Guinier-Preston zones" after their discoverers), then to a metastable $Al_2Cu$ phase called $\theta'$, and finally to the equilibrium $Al_2Cu$ phase, $\theta$. $Al_2Cu$ $\theta'$ is a tetragonally distorted version of the cubic fluorite ($C1$) structure, whereas $\theta$ is the $Al_2Cu$ ($C16$) phase (Fig. 1). The last transformation $\theta' \rightarrow \theta$ is particularly important since a sizable drop in alloy hardness accompanies the transformation to the equilibrium $C16$ phase. Thus, the stability of the $\theta'$ phase relative to the equilibrium $\theta$ phase is of considerable interest.

In an effort to elucidate the relative stabilities of $Al_2Cu$ in the $\theta$ and $\theta'$ structures, first-principles $T = 0$ total energy calculations were performed for both structures. A variety of methods and exchange correlation functionals were used within both the local density and generalized gradient approximations (LDA and GGA) to density functional theory (DFT): (1) the full-potential linearized augmented plane wave method (FLAPW) [6], (2) the pseudopotential method utilizing ultrasoft pseudopotentials as implemented in the Vienna *ab initio* Simulation Package (VASP) [7], and (3) norm-conserving pseudopotentials (NCPP) [8]. The seeming redundancy of these calculations was performed to ensure that the calculated energetic preference of $Al_2Cu$ is truly a prediction of DFT and not merely a peculiarity of one particular method, exchange correlation, pseudopotential, etc. Careful tests were performed to ensure that the energetics were converged with respect to **k** points (up to a $16 \times 16 \times 16$ grid was used) and basis-set cutoffs (up to $E_{\text{cut}} = 16.7$, 21.5, and 60 Ry were used in the FLAPW, VASP, and NCPP calculations, respectively). In all cases, structures were fully relaxed with respect to volume as well as all cell-internal and cell-external coordinates. One should note that observed $\theta'$ precipitates are *semicoherent* with the Al matrix; that is, they are constrained to be coherent with Al in the (100) plane, but not perpendicular to this plane. This coherency constraint results only in a small (~1.5%) tetragonal distortion of the $\theta'$ precipitates from their ideal, cubic structure. In the present work, we consider *incoherent* $\theta$ (tetragonal) and $\theta'$ (cubic) and use the nomenclature $\theta'_c$ to distinguish the ideal cubic fluorite structure from the slightly distorted structure of $\theta'$ precipitates. The calculated structural parameters (lattice constants and cell-internal positions) of $Al_2Cu$ in the $C16$ structure are shown in Table I and are in excellent

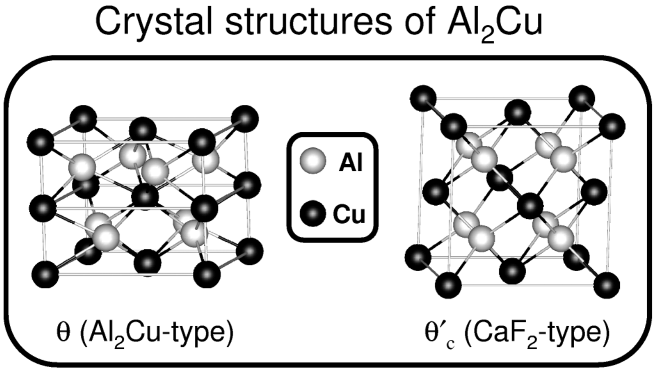

FIG. 1. The $\theta$ and $\theta'_c$ phases of $Al_2Cu$: tetragonal $C16$ and cubic fluorite $C1$, respectively.

TABLE I. First-principles calculated and experimental energetics (in meV/atom) and geometries of $Al_2Cu$ in the $\theta$ ($C16$) and $\theta'_c$ ($CaF_2$) structures. Results include a variety of first-principles methods and exchange correlations: FLAPW = full-potential linearized augmented plane wave method; US-PP = ultrasoft pseudopotential method; NCPP = norm-conserving pseudopotentials; Wig. = Wigner; CA = Ceperley-Alder; GGA = generalized gradient correction (Perdew and Wang, 1991). (A 45° rotation between the conventional cells of the observed body-centered tetragonal $\theta'$ precipitates and the undistorted $\theta'_c$ fluorite structure requires multiplying the observed $a_{\theta'}$ by $\sqrt{2}$ for direct comparison with our calculations of $a_{\theta'_c}$.)

| | Exchange | | | $Al_2Cu$-$\theta$ | | $Al_2Cu$-$\theta'_c$ | |
|---|---|---|---|---|---|---|---|
| Method | correlation | $a$ (Å) | $c/a$ | $x$ | $\Delta H(\theta)$ | $a$ (Å) | $\Delta H(\theta'_c)$ |
| FLAPW | Wig. | 6.02 | 0.800 | 0.16 | −182 | 5.74 | −207 |
| FLAPW | CA | 5.96 | 0.800 | 0.16 | −184 | 5.68 | −199 |
| US-PP | CA | 5.95 | 0.801 | 0.158 | −185 | 5.68 | −212 |
| US-PP | GGA | 6.08 | 0.803 | 0.158 | −166 | 5.78 | −209 |
| NCPP | CA | 5.93 | 0.805 | 0.159 | −196 | 5.66 | −234 |
| Expt.[a] | | 6.066 | 0.803 | 0.154 | −135, −139, −206, −245[a]<br>−164[b] | $\sqrt{2}\,a_{\theta'} = 5.725, c_{\theta'} = 5.812$ | |

[a]See Ref. [18] and references therein.
[b]Reference [17].

agreement with experiment for all calculations. Also, the calculated formation enthalpies of $Al_2Cu$ with respect to fcc-Al and fcc-Cu all fall well within the range of experimental data for this quantity. Thus, we are confident in the accuracy of the current DFT calculations.

We find the following surprising result (Table I): *Although $\theta$ is the observed stable phase of $Al_2Cu$, state-of-the-art first-principles calculations predict the $T = 0$ energy of $\theta'_c$ to be below that of $\theta$.* This energetic ordering was found consistently for *all* of the methods and exchange correlations, with the most accurate calculation (FLAPW, using the exchange-correlation functional of Ceperley and Alder [9]) yielding $E(\theta) - E(\theta'_c) = +15$ meV/atom. Therefore, we are forced to conclude that this apparent discrepancy with experiment is either a qualitative failure of LDA and GGA, or there is no discrepancy at all, and some excitation at $T \neq 0$ acts to reverse the stability of $\theta'_c$ vs $\theta$. We consider that the failure of DFT is extremely unlikely since it would represent the first such known failure in a nonmagnetic, metallic system, and also DFT calculations have recently been demonstrated to be extremely accurate in predicting Al-Cu precipitate shapes, energetics, coherency strains, and phase stability [10]. Also, in the present calculations, lattice parameters, cell-internal positions, and formation enthalpies of the $Al_2Cu$-$\theta$ compound are all in good agreement with observations. Hence, we do not consider the possibility of a DFT failure. Instead, we investigate whether thermal contributions to the free energy, such as configurational, electronic, or vibrational, might reverse the stability of $\theta$ and $\theta'_c$.

Both configurational and electronic entropies were found to contribute negligibly to the energetic preference of $\theta$ vs $\theta'_c$ at finite temperatures, and therefore we discuss these calculations only in passing: The configurational entropy was determined from a combination of antisite defect energies of $\theta$ and $\theta'_c$ (calculated from VASP using 96-atom supercells) and a first-order low-temperature expansion technique. Electronic entropies between $\theta$ and $\theta'_c$ were calculated from the difference in densities of states at the Fermi level.

To assess the magnitude of the *entropy due to vibrations* in $Al_2Cu$, we used first-principles density functional linear response theory [11,12] with NCPP [8] to calculate harmonic phonon dispersion curves of the $\theta$ and $\theta'_c$ phases. The calculated phonon densities of states (DOS) of $\theta$ and $\theta'_c$ are shown in Fig. 2. It is seen that the phonon DOS of $\theta$ has more weight in the low-frequency region between 100 and 150 $\mathrm{cm}^{-1}$. Since at high temperatures the vibrational entropy is proportional to the logarithmic moment of phonon DOS, $S_{\mathrm{vib}} \propto -\int g(\omega) \ln\omega \, d\omega$ [13], it follows that $\theta$ has a higher vibrational entropy than $\theta'_c$. We obtain a remarkably large positive value of the harmonic entropy difference [14] between $\theta$ and $\theta'_c$, $\delta S_{\mathrm{vib}}^{\theta/\theta'_c} = +0.37 k_B$/atom, demonstrating that vibrational entropy strongly favors the tetragonal $\theta$ phase over the cubic $\theta'_c$, whereas $T = 0$ energetics has the opposite tendency. At high enough temperatures, entropy wins out and the structural transition temperature between these phases can be determined from $T_c = \delta H^{\theta/\theta'_c} / \delta S_{\mathrm{vib}}^{\theta/\theta'_c}$. Using what we consider to be our most accurate result for the structural energy difference between $\theta$ and $\theta'_c$ (the FLAPW-calculated value of $\delta H^{\theta/\theta'_c} = 15$ meV/atom), we find that $\theta$ will be favored over $\theta'_c$ above $T_c \sim 200\,^{\circ}\mathrm{C}$. *Thus, the harmonic vibrational entropy reverses the relative high-temperature stability of $\theta$ and $\theta'_c$, reconciling the observed precipitation sequence with the DFT ($T = 0$ K) structural stabilities in the* Al-Cu *system.*

Analysis of the phonon dispersion of $\theta$ and $\theta'_c$ shows that the excess phonon DOS between 100 and 150 $\mathrm{cm}^{-1}$ (see Fig. 2) is due to soft transverse optical (TO) phonon modes in $\theta$. Figure 3 shows atomic displacements for the lowest optical mode phonons in both structures: in $\theta$ it is a doubly degenerate TO-phonon mode at the zone-boundary $M$-point $[00\frac{\pi}{c}]$, while in $\theta'_c$ it is a doubly degenerate

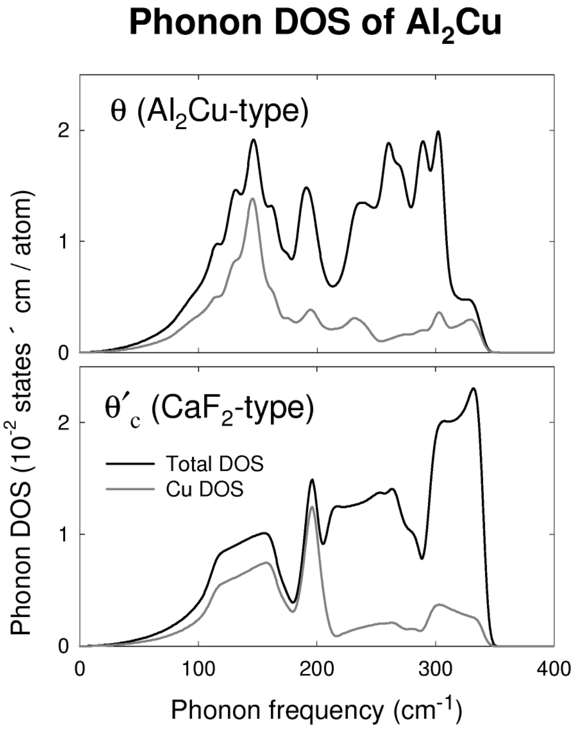

FIG. 2. First-principles calculated phonon DOS for the $\theta$ and $\theta_c'$ phases of Al$_2$Cu.

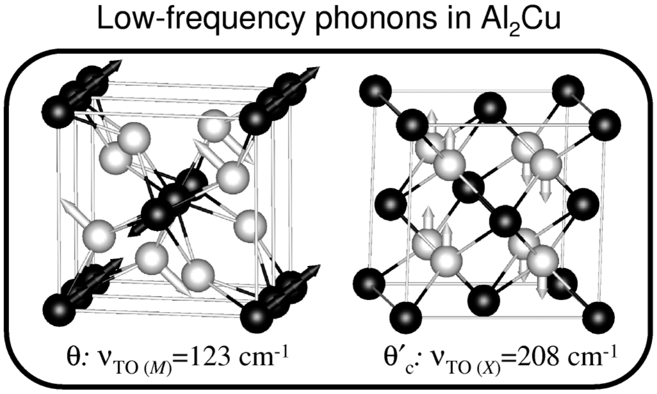

FIG. 3. Lowest-frequency optical modes in $\theta$ and $\theta_c'$ phases of Al$_2$Cu. Note that the $\theta$ phase is rotated with respect to the orientation shown in Fig. 1 for clarity. [The tetragonal (001) direction is into the page.]

TO-phonon mode at the zone-boundary $X$-point $[\frac{\pi}{a}00]$. The most noticeable difference between the two modes is in the degree of nearest-neighbor (NN) Cu-Al bond stretching. Indeed, in the TO($M$) mode of $\theta$, Cu and Al atoms move perpendicular to each other and within the (001) layers, roughly preserving all Cu-Al bond lengths. As a consequence, the frequency of this mode is rather low since it is determined by weaker bond-bending and second nearest-neighbor bond-stretching forces. In contrast, the lowest optical phonon in $\theta_c'$ [TO($X$); see Fig. 3(b)] involves large longitudinal distortions of all Cu-Al bonds and thus has a much higher frequency than the TO($M$) phonon in $\theta$. More generally, the existence of low-frequency optical phonon modes in $\theta$ is facilitated by the layered tetragonal structure of this compound, which is formed by alternate stacking of (001) planes of pure Al and pure Cu. Each Al (Cu) atom shares NN bonds with four Cu (eight Al) atoms in adjacent (001) layers [no NN bonds exist between atoms in the same (001) layer], forming buckled ...-Cu-Al-Cu-... chains along the $[1\bar{1}0]$ and $[\bar{1}10]$ directions, i.e., all NN bonds are almost parallel to one of the $(1\bar{1}0)$ or $(\bar{1}10)$ planes. This peculiar structure leads to a local site coordination which is strongly anisotropic. As a result, atomic displacements perpendicular to the buckled bonding planes cause only slight stretching of the NN Cu-Al bonds, and the associated optical phonon modes are expected to have low frequencies. Indeed, as seen from Fig. 3(a), the low-frequency TO($M$) mode of $\theta$ involves precisely such a displacement pattern. Al atoms move nearly perpendicular to the Al-Cu bonds inducing rather small changes in bond lengths. The latter are easily accommodated by small Cu displacements in the direction perpendicular to both Al displacements and $\langle 001 \rangle$. In contrast, as seen from Fig. 3(b), cubic site symmetry in $\theta_c'$ guarantees that even the lowest TO-phonon mode involves huge changes in nearest-neighbor bond lengths.

To this point, all calculations of the $\theta_c'$ phase have been performed for the undistorted, cubic fluorite structure. Observed $\theta'$ precipitates possess a small tetragonal distortion $\sim$1.5% (see Table I) due to coherency with the Al matrix along (100). We have computed the energetic effect of this coherency constraint by requiring $a_{\theta'} = a_{\mathrm{Al}}$ and allowing $c_{\theta'}$ to relax. Under these conditions, the $\theta'$ phase drops from cubic to tetragonal symmetry, and the energy is raised by $\sim$1–2 meV/atom. In terms of the analysis above, this small energy penalty would correspond to a 30°–60° reduction in the calculated $\theta/\theta'$ transition temperature, yielding $T_c \sim 150$ °C. However, one should note that the inherent inaccuracies within the LDA, GGA, and other approximations present in first-principles methods are larger than the 1–2 meV/atom of coherency strain. Therefore, the precise value of the calculated $T_c$ value should not be interpreted too strictly.

Given the large amount of experimental work devoted to the Al-Cu system, and the practical importance of this alloy, the present conclusion of a thermodynamic $\theta/\theta'$ transition in Al$_2$Cu is both important and quite unexpected. Because the predicted transition is at fairly low temperatures, a direct observation of this transition might prove difficult, due to sluggish kinetics. However, in retrospect, several pieces of experimental evidence lend support to our prediction: (1) In one of the seminal papers characterizing the precipitation sequence in Al-Cu alloys, Silcock *et al.* [15] performed long aging experiments (up to approximately one year) as a function of temperature. For long aging times, $\theta$ was the final product observed for temperatures above 190 °C. For temperatures below this, $\theta'$ was the final precipitate. Guinier [16] found $\theta$ only near 300 °C, and $\theta'$ was the final product for lower temperatures. This change in precipitate phase with temperature could be attributed to slow kinetics at lower temperatures; however, our results suggest an alternative, thermodynamic explanation. (2) Databases of thermodynamic data, optimized to observe phase diagrams, yield a formation entropy for $Al_2Cu$-$\theta$ of $\Delta S \sim -0.27 k_B$ [17], in good agreement with our calculated vibrational formation entropy of $\Delta S \sim -0.25 k_B$. (3) Although the solubility solvus of the metastable $\theta'$ is not well characterized experimentally [18], at least one estimate [19] shows that it comes into coincidence with the equilibrium solvus around 300 °C, i.e., the free energies of $\theta$ and $\theta'$ become equal around this temperature, in agreement with our calculations. The incorporation of our calculated thermodynamic data into existing databases should yield a useful and reliable solvus for $\theta'$, and promising initial results have already been obtained.

The proposed explanation for the existence of low-energy phonons in low-symmetry layered structures is quite general since it uses only geometric considerations. We suggest that vibrationally induced stabilization may, in fact, be rather common in intermetallic alloys and could account for the existence of many other "exotic" low-symmetry structures. An interesting fact indirectly supporting our hypothesis is that $C16$ is often encountered in glass-forming systems such as Fe-B and Ni-Zr, where topological disorder and vibrations are naturally expected to be important. In another technologically interesting system, Al-Sc, Asta and Ozoliņš [20] have found that an orthorombic BCr-type phase has a higher vibrational entropy than the cubic $B2$ phase of AlSc, accounting for a few observations of the former structure at high temperatures. The experimental study of vibrational entropy in metallic alloys has recently generated much interest [21], with some experimental results showing a large vibrational entropy difference between ordered and disordered phases. However, these large vibrational entropies would merely serve to alter the phase diagram (by changing transition temperature, etc.) quantitatively. What we are proposing here is that vibrational entropy can also produce qualitative changes in phase diagrams by changing the stable ordered state and its underlying structure type. Whether this effect is unique to $Al_2Cu$ or whether it has broader implications for the high-temperature structural stability of many low-symmetry intermetallic phases remains to be explored.

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