Short-range order in archetypal disordered Cu3Au: effects on thermodynamic, structural, and mechanical properties

Will Morris\textsuperscript{a}, Duane D. Johnson \textsuperscript{b,c}, and Prashant Singh\textsuperscript{b,*}

\textsuperscript{a}Department of Energy SULI program, Ames National Laboratory, Ames, Iowa 50011, USA
\textsuperscript{b}Ames National Laboratory, U.S. Department of Energy, Iowa State University, Ames, Iowa 50011, USA
\textsuperscript{c}Department of Materials Science & Engineering, Iowa State University, Ames, IA 50011, USA

Abstract

Density-functional theory based electronic-structure method was used to demonstrate the effect of chemical short-range order (SRO) on thermodynamic, structural, electronic, and mechanical properties of archetypal face-centered-cubic Cu\textsubscript{3}Au alloy. We show that SRO can be tuned to modify bonding characteristics, lattice dynamics (i.e., phonons), and electronic structure of disordered Cu\textsubscript{3}Au with direct impact on thermodynamic and mechanical properties. The formation energy of disordered phase (-34.3 meV-atom\textsuperscript{-1}) was found to increase by nearly 34 meV-atom\textsuperscript{-1} in presence of SRO (-68.2 meV-atom\textsuperscript{-1}). The vibrational entropy estimated form phonon dispersions decreases with increasing short-range order, which shows significant drop below room temperature, e.g., from 9k\textsubscript{B} at 300 K to 6k\textsubscript{B} at 100 K. The SRO shows weak effect on average mechanical properties (Bulk, Young’s, and Shear moduli), however, the directional dependence of Young’s and Shear moduli was increased substantially in presence of SRO. We established through detailed analysis of archetypal Cu\textsubscript{3}Au that ignoring SRO may lead to a skewed view of the actual properties of the disordered phase of more chemically complex alloys. More generally, our results indicate SRO can be used as a control parameter that can be tuned to achieve desirable properties.

Keywords: Short-range order, DFT, Thermodynamics, Electronic-structure, Mechanical property

Introduction

Thermally induced short-range order (SRO) in disordered alloys has direct correlation to atomic-scale chemical interactions, manifest as infinitesimal chemical fluctuations. The SRO has been widely observed in Fe-Cr, Ni-Cr, and Cu-Au based binary alloys [1-6], which has been found to have significant impact on electronic, structural, magnetic, and mechanical properties. Gerold et al. [7] argued that planarity of dislocation gliding was primarily triggered by SRO in face-centered-cubic (f.c.c.) metals, while Han et al. [8] found the role of SRO in Cu-Mn alloys driving anomalous recovery of work-hardening rates by activating planar slips. More recently, both theory and experiment have showcased the explicit role of SRO in chemically complex materials controlling electronic [9-11], mechanical [12,13], thermoelectric [14,15], and transport [16] properties. Furthermore, a recent breakthrough in direct observations of SRO [12,17,18] has confirmed prior theoretical predictions [9,19,20] and has reignited the much-needed discussion on this complex topic. The explicit demonstration of SRO and its role on changing alloy properties undoubtedly will lead to further direct investigation of this challenging topic especially due to underlying chemical and structural complexity.

Here, we choose a simple archetypal system, f.c.c. Cu\textsubscript{3}Au, a classic example in the solid-solution alloy theory, where temperature dependence of SRO has been measured [6,21]. As a prototype material, Cu\textsubscript{3}Au is often used to investigate the difference of physical properties between the ordered and disordered

*Email: psingh84@ameslab.gov
phases in both experimental and theoretical sides [22-27]. However, here, we focus on understanding the effect of chemical SRO on thermodynamic, structural, electronic, and mechanical properties using first-principles density-functional theory (DFT) of f.c.c Cu₃Au. The model DFT supercells with optimized SRO configurations were generated using Super-Cell Random APproximates (SCRAPs) method [28]. The favorable degree of ordering in disordered Cu₃Au was rationalized by finding lowering of mixing energy, which comes from increased energetic preference of unlike atoms compared to the random solid solution. A systematic investigation of SRO tunability was done to understand the effect of SRO on bonding characteristics, lattice dynamical properties (i.e., phonons) and electronic density of states of f.c.c. Cu₃Au. This study, in principle, showcase our approach to capture the effect of correlated disorder arising from SRO in chemically complex alloys.

Computational Methods

We employed first principles DFT as implemented in Vienna Ab-initio Simulation Package (VASP) [29,30] for geometrical optimization (e.g., lattice constants, volume, bond length, and bond angles) and charge self-consistency. The generalized-gradient approximation (GGA) of Perdew, Burke and Ernzerhof (PBE) was employed [31] with a plane-wave cut-off energy of 520 eV. The choice of PBE over LDA or meta-GGA [32,33] functionals is based on the work of Söderling et al. [34] and Giese et al. [35] that establishes the effectiveness of GGA functionals. The 108-atom SCRAP was optimized with energy and force convergence criteria of 10⁻⁶ eV and 10⁻⁶ eV/Å, respectively. A Monkhorst-Pack k-mesh was used for Brillouin-zone integration during structural-optimization and charge self-consistency [36].

Density-functional perturbation theory (DFPT) was used to construct force constant matrix needed to calculate lattice dynamical properties [37-40]. The phonon dispersion plots are done along the high-symmetry direction of crystal Brillouin zone [41]. We performed finite displacements of 0.03 Å for each atom along x-, y-, and z-direction in the supercell. The phonon calculations on 108 atoms SCRAPs were done on 5x5x5 k-mesh using energy convergence criteria of 10⁻⁷ eV. The bonding analysis was done using projected crystal orbital Hamilton population (pCOHP) as implemented in Local Orbital Basis Suite Towards Electronic Structure Reconstruction (LOBSTER) code. The off-site densities-of-states in COHP are weighted by respective Hamilton matrix elements to reveal bonding interactions, i.e., bonding, nonbonding, and antibonding, in the given crystalline materials, [44-46]. The mechanical properties were calculated using stress-strain method as implemented within DFT-VASP [29,30]. The Born stability criteria was utilized to determine mechanical stability through elastic moduli (Cᵦ) of f.c.c. Cu₃Au. The Young’s and shear moduli were plotted to understand the directional dependence [42,43].

Results and discussion

At temperatures above phase decomposition (or spinodal) temperature, alloys often form solid solutions with disordered arrangement of constituent elements. However, atoms in these solid solutions are not fully random, rather they show some degree of preferential atomic bias due to chemical pair interactions, i.e., SRO [1,6,47]. The Warren-Cowley SRO parameters (αᵢᵣ) in a chemically disordered alloy have a finite range given by

\[-\frac{\min (p_μp_ν)}{p_μp_ν} \leq \alpha_μν ≤ +1\]

Eq. (1)

where (p_μ, p_ν) are site probabilities of μ (ν) atom at site i (j) [1,28]. SRO can have three possibilities, (i) \(\alpha_μν < 0\) (-ve; ordering-type SRO), (ii) \(\alpha_μν = 0\) (fully disordered), and (iii) \(\alpha_μν > 0\) (+ve; clustering-
type SRO). The free energy of a high-temperature disordered phase will be higher due to absence of most favored chemical interaction among alloying elements, i.e., \( a_{ij}^{\mu \nu} = 0 \). From this definition, tuning degree of ordering can enhance (or reduce) phase stability and structural property.

The deviation from fully random determines the degree of order in disordered, chemically complex alloys. The 108-atom SCRAPs [28] was optimized with specified experimental SRO up to three shells [6,21] to mimic a homogeneously (fully) random state (\( a_{ij}^{\mu \nu} = 0 \) at 550°C) and SRO (\( a_{ij}^{\mu \nu} < 0 \) at 450°C and 405°C) as shown in Fig. 1.

Figure 1. Model 108-atom SCRAPs with optimized SRO over three shells for disordered f.c.c. Cu₃Au – (a) High T (550°C) \{\( \alpha = 0, 0 \)\}, SRO₁ (450°C) \{\( \alpha = -0.195, +0.215, +0.003 \)\}, and SRO₂ (450°C) \{\( \alpha = -0.218, +0.286, -0.012 \)\} [6].

Thermodynamic properties: Using the 108-atom SCRAPs, the structural properties (lattice constant and volume per atom) and formation energies (\( E_{\text{form}} \)) for f.c.c. Cu₃Au were calculated using DFT for the three SRO values at three temperatures, as seen in Fig. 1, along with the change in electronic density of states (DOS) at -5 eV below the Fermi energy (\( E_{\text{Fermi}} \)), discussed later in Fig. 3b. See tabulated values given in Table 1. We observed a weak change in lattice constant (0.4%) and cell volume (1.1%) with increasing SRO. However, even a small change of structural parameters shows a strong impact on phase stability (\( E_{\text{form}} \)), where the disordered phase \( E_{\text{form}} \) of -34.3 meV-atom\(^{-1}\) lowers to -63.7 and -68.2 meV-atom\(^{-1}\), respectively, for SRO₁ and SRO₂. The energy stabilization in the solid-solution phase is attributed to increased electronic excitation arising from thermally induced chemical fluctuations due to increased SRO. This is expected as ordering should energetically favor the preferential positioning of constituent elements in the alloy.

Table 1: Change in lattice constant (Å), volume (Å\(^3\)-atom\(^{-1}\)), formation energy (\( E_{\text{form}} \); meV-atom\(^{-1}\)), and density of states (States-eV\(^{-1}\)-atom\(^{-1}\)) with SRO in f.c.c. Cu₃Au.

| System [Cu₃Au] | \( a_{\text{lat}} \) | V | \( E_{\text{form}} \) | DOS [at \(-5 \text{ eV}\)] |
|----------------|------------------|---|------------------|-----------------|
|                | Å                | Å\(^3\)-atom\(^{-1}\) | meV-atom\(^{-1}\) | States-eV\(^{-1}\)-atom\(^{-1}\) |
| High T         | 3.802            | 13.739                  | -34.3            | 1.40             |
| SRO₁           | 3.791            | 13.617                  | -63.7            | 1.75             |
| SRO₂           | 3.788            | 13.597                  | -68.2            | 1.90             |

Structural properties – volume change, local lattice displacement and atomic bonding: To understand the observed changes in thermodynamic stability of disordered Cu₃Au, we investigated the change in nearest-
neighbor occupation and average bond-length with increasing SRO, as listed in Table 2. As expected, the number of Cu-Au near neighbors increased significantly (29.4\%) with increase in SRO, while like-pairs decrease for Cu-Cu (11.7\%) and Au-Au (100\%), as required by pair probability sum rule. Moreover, a more uniform distribution of Cu-Au pairs was found with increased SRO.

A random distribution of Cu/Au in disordered Cu\textsubscript{3}Au would produce a relatively large local lattice and bond distortion due to atomic-size differences and change in chemical (Cu/Au) interactions. This is also reflected through Cu-Au (2.673 Å), Cu-Cu (2.605 Å), and Au-Au (2.740 Å) bond anisotropy of the disordered phase. As follows for ordering-type SRO, the neighbor analysis indicates increased probability for Au and Cu to be a neighbor for SRO\textsubscript{1} and SRO\textsubscript{2}, see Table 2. The uniform distribution of unlike pairs is expected to reduce both bond anisotropy and local lattice distortion compared to disordered phase. Expectedly, the Cu-Au (2.625 Å), and Au-Au (2.646 Å) bond lengths become more isotropic with increasing SRO, as shown in Table 2 and Fig. 2a. To be more specific, the homoatomic pairs, i.e., Cu-Cu and Au-Au, are mostly elongated, while the unlike pairs of Cu-Au show compressed bonds. This is also expected as it is more electronically favorable for Cu to sit around Au due to increased degree of favorable ordering. The reduced average bond-length of unlike pairs is in agreement with reduced lattice constants (a\textsubscript{highT} > a\textsubscript{SRO1} > a\textsubscript{SRO2}) and volume (V\textsubscript{highT} > V\textsubscript{SRO1} > V\textsubscript{SRO2}) in Table 1.

Table 2: Change in nearest neighbors (NN) and average bond-length (BL\textsubscript{avg}) with SRO in f.c.c. Cu\textsubscript{3}Au. The optimized structural files are provided with the supplement.

|                  | NN pairs | Avg. bong length [Å] |
|------------------|----------|----------------------|
|                  | Cu-Cu | Au-Au | Cu-Au | Cu-Cu | Au-Au | Cu-Au |
| High T           | 410   | 17    | 221   | 2.605 | 2.740 | 2.673 |
| SRO\textsubscript{1} | 375   | 1     | 272   | 2.625 | 2.748 | 2.646 |
| SRO\textsubscript{2} | 362   | 0     | 286   | 2.627 | N/A   | 2.645 |
| % Change         | -11.7\% | -100\% | 29.4\% | 0.85 | N/A   | -1.02 |

Given the fully disordered phase has zero chemical correlation, i.e., \(\alpha_{\mu\nu}^{ij} = 0\) in Eq. (1). The bond anisotropy in Cu\textsubscript{3}Au is possibly driven by large lattice mismatch between Cu (1.28 Å)/Au (1.44 Å), which will be the main stabilizing factor of disordered phase. In Fig. 2a, we plot the distribution of average bond-length for Cu [atoms 1-81] and Au [atoms 82-108] for High-T (zero SRO), SRO\textsubscript{1}, and SRO\textsubscript{2} cases.
Figure 2. (a) Bond-length, and (b) local lattice distortion ($\Delta u$) with increasing SRO in f.c.c. Cu$_3$Au.

For the high-T disordered case, the bond-length distribution between Cu-Cu, Cu-Au/Au-Cu, Au-Au nearest-neighbor (NN) pairs show large fluctuations. This affirms our hypothesis that in absence of chemical SRO, the atomic-size mismatch of Cu/Au leads to local distortion that energetically stabilize the disordered phase, as also reflected in non-uniform change in bond-length in Fig. 2a. Interestingly, introducing SRO in the disordered phase decreased the large bond-lengths fluctuations in unlike Cu-Au pairs. The SRO reduces the average Au bond-length by more than 1% compared to fully disordered phase. The reduced average bond lengths in SRO phase could be attributed to enhanced charge-transfer due to increased SRO.

Ye et al [48] considered the atomic-size change by considering atoms are exactly at ideal lattices, and provide an empirical definition for the local lattice distortion (LLD) as

$$\text{LLD} = 100 \times \sqrt{\sum_{i=1}^{n} c_i (1 - r_i \bar{r})^2}$$

Eq. (2)

where $\bar{r} = \sum_{i}^{n} c_i r_i$, $c_i$ and $r_i$ are elemental composition and calculated atomic radii, $i$ is type of elements. Such LLD estimations in Eq. (2) are ambiguous as same atom type in different alloys can adopt different radii due to change in local chemical environment and local chemical interaction (different electronegativity variances).

To characterize LLD, we adopted a supercell approach to calculate the distortion by full relaxations and calculating local atomic displacement within DFT as defined by

$$\Delta u [Å] = \sum_{i} \sqrt{(x - x_1)^2 + (y - y_1)^2 + (z - z_1)^2}$$

Eq. (3)

where $(x, y, z)$ are relaxed positions and $(x_1, y_1, z_1)$ are ideal lattice positions [49]. In Fig. 2b, we plot the average atomic displacement ($\Delta u$) after full relaxation of crystallographic lattice of f.c.c. Cu$_3$Au for SRO (3 shells of neighbors) at 550°C, 450°C, and 405°C, where $\Delta u$ represents the likelihood of an atomic site to be displaced (compressed or elongated). In fully disordered Cu$_3$Au, each Cu/Au atoms have a random chemical environment that can cause lattice distortion due to difference in atomic size (1.28 and 1.44 Å) and electronegativity (1.85 and 1.92 on Allen scale) differences.

The bond-length analysis in Fig. 2a shows that SRO leads to uniform Au (Cu) bond-length distribution around Cu (Au) (Table 2). Similar behavior was found in atomic displacement, where increasing SRO has significantly reduced the $\Delta u$ variation, as shown in Fig. 2b. This suggests that increasing ordering tendency enhances the local bonding by increasing the covalency, which stabilizes the alloy as reflected through formation energy and volume change in Table 1. The idea of bond elongation or compression based on alloying elements and their intrinsic characteristic is clearly reflected through absolute lattice displacement. A significant decrease in the mean-squared atomic displacement in Fig. 2b shows that both friction stress and ability to form solid solution responsible for alloy strength can be tuned using SRO in chemically complex alloys.

Furthermore, we plot Au-Au, Cu-Cu, Au-Cu bond-lengths with respect to local atomic displacement ($\Delta u$) for High-T, SRO$_1$, and SRO$_2$ cases in Fig. 3a-c. The bond-length for high-T case in Fig. 3a shows large spatial distribution with respect to local atomic-displacement. We believe this arises purely from atomic size difference of Cu and Au in absence of local chemical interaction. However, increasing the strength of SRO,
i.e., lowering temperature, in Fig. 3b,c, shows uniform distribution of Au-Au, Cu-Cu, Au-Cu bond-lengths and displacement.

Figure 3. The change in bond-length distribution with respect to atomic displacement ($\Delta u$) for (a) high T, (b) SRO$_1$, and (c) SRO$_2$ phase of f.c.c. Cu$_3$Au.

To rationalize the thermodynamic and structural properties of solid-state materials, it is important to understand the change in charge-correlation, which could be done through change in valence-electron distribution. We used Mulliken and Löwdin analytical models [46] to assess the charge behavior in f.c.c. Cu$_3$Au as shown in Fig. 4a-c. If we carefully see the Mulliken charges for each atom in Fig. 4a, the charge sharing between Cu-Au has significantly increased from high-T to SRO$_2$. Similar trends were found Löwdin charges in Fig. 4b, where charge distribution has widened with increasing SRO. The increased charge sharing is commensurate with improved bonding strength with increasing SRO in Fig. 3. Despite some differences, we found one thing in common for both Mulliken and Löwdin charge distribution that Au-gain more charge with increasing SRO, which can also be attributed both to increased SRO and higher Au electronegativity (1.92 (Au) > 1.85 (Cu) on Allen scale). Although charge spread is larger for Mulliken over Löwdin but the scatter plot in Fig. 4c shows similar trends, i.e., basic conclusions are not expected to change.

Figure 4. (a) Mullikan, and (b) Lowden charge analysis of highT, SRO$_1$, and SRO$_2$ cases of f.c.c. Cu$_3$Au. (c) Comparative charge analysis of Lowden vs Mullikan.

Effect of SRO on electronic structure and bonding and antibonding contributions to the band-structure energy: We provide a detailed discussion on electronic structure for f.c.c. Cu$_3$Au with and without SRO. The partial DOSs of Cu and Au s/d states are shown in Fig. 5a-f and Fig. 6a-f. We found that electronic pDOS gets smoother due to increased ordering strength, i.e., SRO.
The major electronic changes due to SRO were found on Cu-t_2g (d_{xy}, d_{xz}, d_{yz}) and Au-e_g (d_{3z^2}, d_{xy,yz}) states below Fermi-level as shown in **Fig. 5b,c,e** and **Fig. 6d,f**. If we carefully look at Cu and Au pDOS, clearly, the hybridization of Cu-t_2g(d_{yz}) in Fig. 5c with Au-s and Au-t_2g(d_{yz}) have increased significantly with increasing SRO, which in clear from the appearance of local electronic pDOS near -5 eV in **Fig. 5c** and **Fig. 6a-f**. It was found that Cu/Au-d electronic pDOS at lower energies shows band-splitting and moved away from the Fermi level with increasing ordering strength. The SRO significantly increases the smoothness of Au-5d in **Fig. 6**, however, smoothness of Cu-3d pDOS shows no major changes in **Fig. 5**. This change in d-band smearing of Cu-3d /Au-5d states can be attributed to change in nearest neighbor configuration of atoms in presence of SRO. Furthermore, no major changes were observed in Cu-s and Au-s states in **Fig. 5a** and **Fig. 6a**, except minor increase in pDOS at Fermi level, which has been found to correlate with coefficient of electronic specific heat and phase stability of such alloys [50,51].

**Figure 5.** (a-f) Cu 4s and 3d partial DOS relative to the Fermi energy (vertical dashed line) for High-T, SRO_1 (450°C), and SRO_2 (405°C) of f.c.c. Cu_3Au.

In disordered phase, Cu/Au in f.c.c. Cu_3Au are mixed in 3:1 ratio, where f.c.c. has 12 nearest neighbors (nnb), i.e, Au and Cu will have 3 and 9 nnb, respectively. But the increased SRO or ordering modifies the disordered configuration so the structural and thermodynamic are expected to change, which has been discussed in detail in previous sections. Moreover, in **Figure 5 & 6**, we note a significant narrowing of the Cu-3d bands in pDOS near -4 eV below Fermi level due to introduction of SRO, which shows suppression of electronic features. In the high-T phase, disorder scattering introduces chemical-disorder broadening of states, as shown by DOS (grey). The increased SRO sharpens the deeper states near/at -5.25 eV at the expense of low-lying (higher-energy) states near -3.75eV, which has also improved Cu-3d and Au-5d hybridization. The major change in pDOS was found at/near -4 eV below Fermi level, where Cu-3d shows
increased electronic hybridization with Au-5d that contributes to enhanced phase stability in presence of SRO. In contrast, the relative change in electronic structure of SRO\(_1\) and SRO\(_2\) cases is not as significant as compared to disorder vs SRO cases. This corroborates well with small \(\Delta E_{\text{form}}\) change in SRO, as shown in Table 1, where \(\Delta E_{\text{form}} = 4.5\) meV-per-atom. This suggests that SRO can be tuned to manipulate local electronic behavior as well that will give strong control on thermodynamic, electronic, and structural properties.

![Figure 6](image)

**Figure 6.** (a-f) Au 6s and 5d partial DOS relative to the Fermi energy (vertical dashed line) for High-T, SRO\(_1\) (450\(^\circ\)C), and SRO\(_2\) (405\(^\circ\)C) cases of f.c.c. Cu\(_3\)Au.

Furthermore, we tried to understand the bonding behavior by projected crystal orbital Hamilton population (pCOHP) and projected crystal orbital bond indices (pCOBI) analysis of in f.c.c. Cu\(_3\)Au. The pCOHP is indicative of bond strength in alloys. Since, metal-metal bonds are delocalized, we are expecting smaller charge-transfer (fewer electrons per bond) compared to covalently bonded systems (e.g., intermetallic compounds), which also depends on type of elements participating in metal-metal bonding. Here, Cu and Au have significant size and electronegative difference, which warrants increased charge activity. We have shown in our charge analysis that in Fig. 4 that SRO has significantly increased the charge activity in f.c.c. Cu\(_3\)Au. In Fig. 7, we plot pCOHP for f.c.c. Cu\(_3\)Au, where positive and negative values indicate antibonding and bonding contributions of local electronic states in the given energy range. As discussed in Fig. 5-6, the increased number of bonding states at -5 eV in Fig. 7. We also observed significant increase in anti-bonding states near Fermi-level, which suggests that main electronic contribution to bonding arises from deep lying t2g states of Cu/Au. This further affirms our electronic-structure predictions of increased hybridization with increasing SRO in f.c.c. Cu\(_3\)Au.
Figure 7. (a,b) Projected crystal orbital Hamilton populations (pCOHP), and (c,d) projected crystal orbital bond indices (pCOBI) of highT, SRO\textsubscript{1}, and SRO\textsubscript{2} cases of f.c.c. Cu\textsubscript{3}Au.

**Phonon tunability:** The phonon properties are very sensitive to the force on atom and cell lattices. Therefore, we carefully relaxed each SRO-optimized SCRAPs such that net force on each atom is zero. The SRO dependent phonons for f.c.c. Cu\textsubscript{3}Au (Fig. 8a) in fully disordered (black), SRO\textsubscript{1} (red), and SRO\textsubscript{2} (blue) cases were done at DFT-calculated equilibrium lattice constant, as shown in Table 1. In Fig. 8a, we show an explicit effect of change in chemical correlation on shape and position of phonon modes. The phonon frequencies in Fig. 8a suggests that bonding behavior in homogeneously disordered and SRO cases are not analogues, as is clearly visible in Fig. 2a.

Figure 8. The effect of increasing degree of SRO on (a) phonon dispersion (THz), (b) phonon density of states (states/atom), (c) free-energy (eV), and (b) vibration entropy (k\textsubscript{B}) of f.c.c. Cu\textsubscript{3}Au.
Notably, the slopes of the phonon bands on energy scale are used to find a general connection between the phonon bands and chemical SRO. The phonon band-structure in **Fig. 8a,b** shows imaginary acoustic phonons along Z-Y high-symmetry point of the Brillouin zone in disordered phase (black) and density of states, indicative of structural (weak) instability in the crystal structure. The introduction of SRO washes the imaginary modes away. The phonon frequency becomes more and more positive with increasing degree of ordering. The inclusion of zone boundaries shows a high density of bands in phonon band-structure coming from flat part (optical modes) of dispersion curve in **Fig. 8a**. These changes in phonon bands (or lattice vibrations) and DOS in **Fig. 8a,b** can be attributed to slow propagation of phonon wave packets and local atomic displacement ($\Delta u$) due to inclusion of SRO. We found a significant impact of SRO on $\Delta u$ (**Fig. 2b**) and bond-length stiffness (**Fig. 2a**) on phonon stability and dispersion in **Fig. 8a**. A constant shift of optical modes was also observed in the frequency range 0.75-1.0 THz to 0.8-0.9 THz 1.1-1.2 THz with increasing SRO in **Fig. 8a**, however, major changes in shape of phonon bands were seen in acoustic modes that shows transition from imaginary to positive definite. In **Fig. 9**, we provide full dispersion plot for clarity.

**Figure 9.** Full phonon dispersion (THz) for f.c.c. Cu$_3$Au with increasing degree of SRO, i.e., (a) highT, (b) SRO$_1$, and (c) SRO$_2$.

**Effect of SRO on free-energy, and vibrational entropy:** In **Fig. 10**, for comparison, we plot change in free energy and vibrational entropy for f.c.c. Cu$_3$Au, where we found significant change in free-energy and vibrational entropy with increasing degree of SRO. The free energy change ($\Delta F$) for SRO states (SRO$_1$ and SRO$_2$) in **Fig. 10a** was found to increase (i.e., more positive, see **Fig. 11**) with increase due to reduced entropic contribution ($\Delta S_{vib}$) in **Fig. 10b** for the high-T limit with respect to disordered phase. At lower temperature, we found a sharp increase in $\Delta S_{vib}$ that saturates nearing RT. This shows the importance of low temperature contribution of $S_{vib}$ to phase stability. Moreover, in high-T limit, vibrational contribution saturates to a constant value between two SRO states (i.e., -1.6$k_B$ in **Fig. 10b**). This suggests that basic conclusion such phase stability and structural changes remain invariant with respect to change in $\Delta S_{vib}$. This change in phonon entropy of mixing is also reflected through small variation in phonon DOS as a function of SRO in **Fig. 8b**.
Figure 10. The effect of SRO on (a) free-energy (eV) and (b) vibration entropy (k_B) of f.c.c. Cu$_3$Au.

The dependence of phonon entropy of mixing on the local arrangement of atoms delivers a deeper insight into the understanding of thermodynamic stability of complex alloys. In different chemical environment, we found a large variation in free energy from 50 meV at RT to 150 meV at 1000K due to increased degree of SRO as shown in Fig. 10a. Similarly, a max change of $-1.6k_B$ in phonon entropy $\Delta S_{\text{vib}}$ relative to disordered phase was seen in Fig. 10b, which could be attributed to change in local atomic environment due to SRO. The phonon entropy provides a key detail about change in structural stability of any alloy. We have also shown full free energy (Fig. 11a) and vibration entropy (Fig. 11b) plots to provide right context to Fig. 10. Furthermore, knowing the temperature dependence and magnitude of phonon entropy between different states of chemical complex alloys remains a key problem in determining phase stability.

Figure 11. (a) Free-energy (kJ/mol) and (b) vibration entropy (J/K/mol) up to room temperature for f.c.c. Cu$_3$Au with increasing degree of SRO, i.e., (a) highT, (b) SRO$_1$, and (c) SRO$_2$. 
Elastic Properties: Mechanical properties are key for selection of materials for any technological applications. Yin et al. argued that SRO should have no systematic measurable effect on mechanical response [52], while Zhang et al. claimed increase in mechanical response [2]. The discrepancy in these studies might originate from complex thermomechanical processes. Notably, SRO distinctly affecting mechanical properties still remains controversial; therefore, we used a classic example of f.c.c. Cu₃Au to understand the elastic properties.

The mechanical stability criteria were categorized by Born for cubic (isotropic) systems as (i) tensile (isotropic) deformation \( (C_{11} + 2C_{12} > 0) \), (ii) axial tensile (two-fold) deformation \( (C_{11} - C_{12} > 0) \), and (iii) shear (threefold degenerate) deformation \( (C_{44} > 0) \). The \( C_{11}, C_{12}, \) and \( C_{44} \) calculated from DFT in high-T (zero SRO), SRO₁ and SRO₂ phase in cubic systems. The elastic \( C_{ij} \) parameters for High-T, SRO₁ and SRO₂ satisfy the mechanical stability criterion in Eq. (4). The elastic moduli for each case are tabulated in Table 3.

From DFT, we can see that SRO also influences elastic properties, such as bulk moduli, a measure of the resistance to compressibility of a material. The bulk moduli show systematic increase, but Young’s and shear moduli show decrease with increasing degree of SRO. The high (low) B/G ratio proposed by Pugh’s [53] was associated to ductility (brittleness) where the critical value of 1.75 separates the ductile materials from brittle. The calculated Pugh’s ratio in Table 3 shows increase with increasing SRO, which suggests the SRO could also help improve the ductility of chemically complex alloys.

Crystals anisotropy in solid can be understood in terms of stiffness associated with a <110> shear on a plane, which was defined by Zener as \( A_Z = C_{44}/C' \), here \( C' = (C_{11} - C_{12})/2 \). The Zener’s anisotropy is a useful criterion to identify elastically anisotropic materials. Moreover, \( A_Z \) could also be useful when we are probing martensitic transformations in crystal as in certain cases where \( A_Z \) approaching zero means structural instability. For f.c.c. Cu₃Au in Table 3, we can see that disordered crystal at high-T is anisotropic, which decreases with increasing SRO. This also suggests that anisotropy in crystals can be tuned by tuning chemical inhomogeneity, i.e., SRO.

Table 3. SRO dependent elastic parameters, moduli, anisotropy and Pugh’s ratio (B/G) of f.c.c. Cu₃Au.

| Moduli      | High-T | SRO₁ | SRO₂ |
|-------------|--------|------|------|
| C₁₁         | GPa    |      |      |
| C₁₂         |        |      |      |
| C₄₄         |        |      |      |
| Bulk        |        |      |      |
| Young’s     |        |      |      |
| Shear       |        |      |      |
| Pugh ratio  |        |      |      |
| Poisson’s ratio |      |      |      |
| C’          | GPa    |      |      |
| A_Z         |        |      |      |

In Fig. 12a-d, we plot a three-dimensional (3D) curved surface of DFT-calculated Young’s and shear moduli to show its dependence on crystallographic directions, indicative of elastic anisotropy of given...
crystal phase. The 3D-curved surface is expected to be more spherical for an isotropic system. However, for SRO\textsubscript{2} (Fig. 12b,d), a strong deviation from isotropic behavior was found compared to the elastic moduli in the disordered phase (Fig. 12a,e), which shows an extent of increase in elastic anisotropy and tunability with increase of SRO in Cu\textsubscript{3}Au. We attributed this fact to the inhomogeneous atomic distribution along each cell dimension due to change in local environment on introducing SRO. Depending on local configuration along (x, y, z), the DFT relaxes each cell dimensions differently. This leads to anisotropy in both lattice constants and bond-length, which correlates well with our interpretation of directional dependence of Young’s/shear moduli.

Going back to electronic structure discussion in Fig. 5&6, while many physical quantities including thermodynamic and structural properties depend directly on change in pDOS. This makes sense as significant change in pDOS (in Fig. 5&6) strongly connects to change in lattice distortion (see Fig. 2), bonding behavior (see Fig. 3) and elastic properties (see Table 2 & Fig. 12).

![Figure 12](image)

**Figure 12.** Directional dependence of (a,b) Young’s moduli, and (c,d) shear moduli on SRO in f.c.c. Cu\textsubscript{3}Au.

**Conclusion**

We have demonstrated directly the effect of SRO on thermodynamic, structural, electronic, and mechanical properties of archetypal f.c.c. Cu\textsubscript{3}Au. The SRO shows strong effects on phase stability (formation energy at 0 K), phonon modes (dynamic stability), and directional dependence of mechanical response. And, we found an increase in intrinsic strength (i.e., bulk moduli) and ductility while a systematic (weak) reduction was seen in Young’s and shear moduli. The introduction of SRO in the disordered phase significantly improves the phase stability (E\textsubscript{form}) and soft phonon modes compared to disordered phase. The improved
electronic and structural properties of Cu₃Au arises from increased degree of short-range order that
enhances the Cu-Au chemical bonding strength due to increased Cu-3d/Au-5d hybridization as shown by
projected crystal orbital Hamilton population analysis. The increased bond-strength is reflected through
both electronic-structure, change in atomic charges, and change in phonon entropies. We emphasize that
SRO could be tuned to improve the local bonding, which helps to eliminate the unstable phonon modes
found in disordered phase, which shows the effect on electronic and structural properties by tuning the
SRO.

Finally, the magnitude of elastic parameters, elastic (bulk, Young’s and shear) and crystal
anisotropy in f.c.c. Cu₃Au shows finite change with increasing degree of SRO. We also found a strong
directional dependence of Young’s and shear moduli, which demonstrates the importance of including SRO
in alloy design. Therefore, the consideration of SRO on materials properties is recommend in the process
of alloy design, if not included, this may lead to a skewed view of the actual properties, e.g.,
thermodynamic, structural and elastic properties. Our results show potential for using chemical alloying as
a control parameter to tune SRO for desirable material properties in other more chemically complex alloys.

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