

First Principles Study of Finite Temperature Phase Stability in $(\text{Cu,Ag,Au})\text{In}_2$ and Al_2Cu Alloys

The common choice in computational approximations, from 0 K to room temperature, of solid materials is to assume the structure remains unchanged at low temperatures. Often such an approximation is a very reasonable assumption. However, this approximation is not absolute and can break down even for relatively simple materials such as the four metal alloys CuIn_2 , AgIn_2 , AuIn_2 and AlIn_2 . All the material's structures were explored at varying temperatures using the C1 and C16 structures. The contribution to the free energy from lattice vibrations in CuIn_2 , AgIn_2 and AlIn_2 causes the structures to change from C1 to C16 at high enough finite temperatures, while AuIn_2 , despite very similar bonding structure, remained in its initial state all the way until melting temperatures.

Introduction

In this study using first principle calculations at finite temperatures phase stability and relevance of entropy on free energy of metal alloys is explored. A phase change in structure at low temperatures, on the order of room temperature has been observed in CuIn_2 [?]. The cause of this phase change has been explored [?] but lacks more thorough theoretical confirmation. The following study details the process of computationally finding the minimum energy of $(\text{Cu}, \text{Ag}, \text{Au})\text{In}_2$ and Al_2Cu alloys at 0 K, and exploring the relationships to make prediction about the expected phase transitions.

To accomplish the goals of this study, Density Functional Theory (DFT) is applied to solve for the physical properties of the above materials. This study elaborates the physical principles utilized, to both understand and interpret the process used to find and evaluate the properties of these materials.

Background

One of the largest fields in physics today is the study of solid state materials. This field has created many methods to explore the properties of interesting materials but, while many materials have been explored experimentally, some are difficult enough that a more theoretical approach is necessary.

Al_2Cu is an example of a material that has predicted phase properties but is not experimentally observed to leave the C16 structure. The lack of phase transition shown experimentally but expected computationally is from the natural energy barrier needed to break the metal's bonds so that it can shift into its lower energy phase. Thus, while its lower energy state does not appear in nature it is predicted to exist. Despite this it is still interesting to explore the cause of the predicted phase change in Al_2Cu . However, a computation approach can be applied instead where experimental approaches cannot observe the desired behavior [?]. In the opposite case, AuIn_2 is observed to remain in the C1 structure even at high temperatures due to a significant energy gap between the two structures minimum energies[?].

The two remaining materials CuIn_2 and AgIn_2 both have predicted and observed phase transitions. However, even these materials are difficult to explore experimentally. CuIn_2 has been created and by heating the separate elements along an interface and then flash frozen to observe the thermal phase transitions. However, such a trick does not work on AgIn_2 , making experimental approaches even more difficult for observing this behavior[?]. Because of this common difficulty in metals that share the outlined behavior a computational approach is applied in this study to observe the expected phase transition behavior. The information presented can be used to explore properties of similar phase transitions materials.

Description

Using a first principle computational approach based on Density Functional Theory (DFT) I explore the common assumption of low temperature metal alloys atomic lattice structures. The approximation states that the influence to the total energy of the system is not significantly affected by the changing entropy as a function of temperature[?]. While this is true

with most metal alloys, the four materials explored here in have two states very close in energy where the entropy term will become very significant in deciding the final state of the metals.

Solving for the alloys minimum energy states using computational first principles DFT approaches returns the minimum energy of the respective metals. Along with the minimum energy, the structure parameters for these minimized energy states are presented. These structure parameters can be used as comparison and to aid in better recreation of results.

This study can be used as an example to elaborate on the small but relevant effects of lattice vibrations upon an atomic structure. Using these calculations, experiments involving these materials and within the found temperature ranges can predict and control the properties of such alloys and thin films.

Physical Principles

The explored C1 and C16 structures are three dimensional repeated lattices which can be represented as set of three vectors. This information can be represented as a matrix of lattice vectors with chosen positions for a set of initial atoms known as the basis, from which the rest of the structure can be generated. A simple example is the cubic lattice of a single atom. The basis vectors are written:

$$a \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

a is the chosen length of the lattice basis vectors (constant). The only additional information required is the position of the initial atom which can be written as a simple matrix relative to the origin where instead the position is defined from the lattice vectors in the above matrix.

$$\begin{pmatrix} 0 & 0 & 0 \end{pmatrix}$$

In this case the origin is generally chosen for the initial atom to make the choice of position for additional atoms easier. Since there is only 1 atom in this example, the origin is chosen. However, in more complicated systems with special symmetry it is reasonable to choose the initial atoms to be elsewhere.

Because the C1 structure can be represented with a face centered cubic (fcc) lattice as can be observed in figure 1(a), the following matrix is generated.

$$\text{C1}_{\text{basis}} = a \begin{pmatrix} 0 & \frac{1}{2} & \frac{1}{2} \\ \frac{1}{2} & 0 & \frac{1}{2} \\ \frac{1}{2} & \frac{1}{2} & 0 \end{pmatrix}$$

However the basis of all the explored C1 metal alloys contains three atoms, instead of one. Thus for symmetry we chose the following positions of copper and two indium respectively top to bottom.

$$\text{C1}_{\text{positions}} = \begin{pmatrix} 0 & 0 & 0 \\ \frac{1}{4} & \frac{1}{4} & \frac{1}{4} \\ -\frac{1}{4} & -\frac{1}{4} & -\frac{1}{4} \end{pmatrix}$$

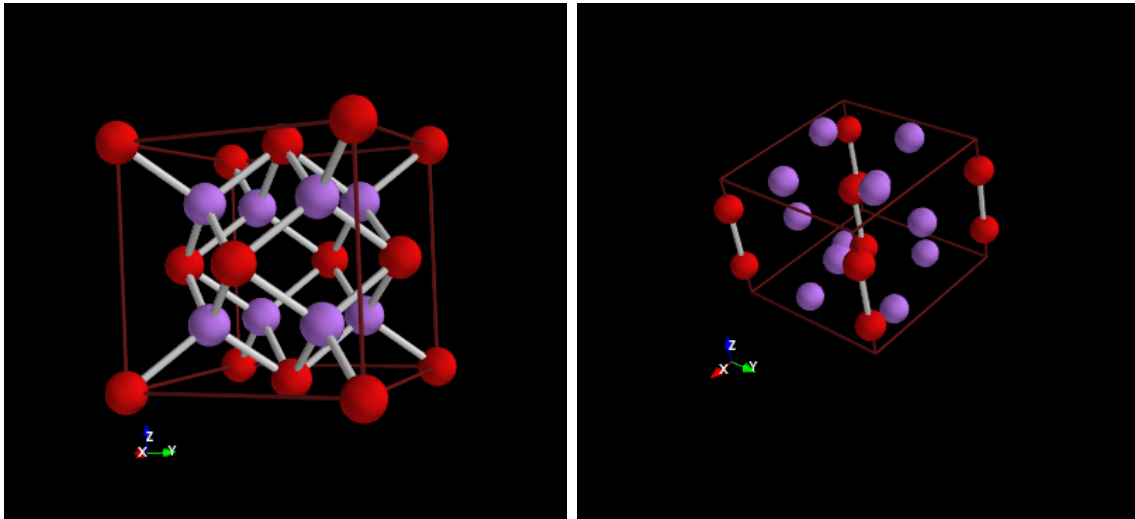
Finally the C16 structure, depicted in figure 1(b) does not share the cubic nature of the previous example and instead follows a tetragonal form of the space group $I4/mcm$. Thus a second lattice constant c is defined to find the basis distance in the z direction. This structure can be written as follows:

$$\text{C16}_{\text{basis}} = \begin{pmatrix} a & 0 & 0 \\ 0 & a & 0 \\ \frac{1}{2}a & \frac{1}{2}a & \frac{1}{2}c \end{pmatrix}$$

In addition due to the non-cubic lattice, twice the normal numbers of atoms are needed to create the initial lattice structure. The following positions are chosen for the two copper and four indium atoms of C16 CuIn_2 :

$$\text{C16}_{\text{positions}} = \begin{pmatrix} -\frac{1}{4} & -\frac{1}{4} & \frac{1}{2} \\ \frac{1}{4} & \frac{1}{4} & -\frac{1}{2} \\ X & \frac{1}{2} + X & 0 \\ -X & \frac{1}{2} - X & 0 \\ \frac{1}{2} - X & X & 0 \\ \frac{1}{2} + X & -X & 0 \end{pmatrix}$$

Identical structures are generated for the other alloys with their respective atoms. X is a chosen parameter dependent on the material being analyzed. It is usually found experimentally, but it can be found computationally by allowing VASP to adjust the position of the atoms to relax the system into a minimum energy state. For this project a reasonable guess for X is chosen for all four alloys, and relaxation is used to determine the optimal X for each structure.



(a) C1 fcc Structure

(b) C16 Tetragonal Structure

Figure 1: Red: Cu, Ag and Au; Pink: Al or In.

The stable phase for a system is determined by the minimum Gibbs free energy defined as

$$G(P, T) = E_{\text{coh}} + PV - TS$$

where E_{coh} is the cohesive energy or energy needed to separate the atoms. In order to compare two materials a difference in Gibb's energy is necessary

$$\Delta G(P, T) = \Delta \overline{E}_{\text{coh}} + P\Delta V - T\Delta S$$

As mentioned earlier the common and reasonable assumption for solids is that the temperature and entropy term is very small compared to the others terms and is thus ignored. However in the case of the explored metal alloys it no longer becomes irrelevant. Because of this it becomes advantageous to develop a deep understanding of the behavior of the third term.

The entropy as a function of temperature in these systems is caused by the phononic behavior of the solid. The contribution to the entropy term due to disorder of the lattice is usually small in metals and will be ignored. Phonon's (waves representing lattice vibrations) generate an entropy term that changes as a function of temperature. We know the total entropy due to vibration of a solid with N atoms is

$$S(T) = N \int_0^{\omega_{\text{max}}} S(\omega) F(\omega) d\omega \quad [?]$$

where ω is the phonon frequency of the solid and $F(\omega)$ is a function that models the behavior of the system. This equation for entropy as a function of temperature can be further explored to gain better understanding of the relevance of temperature on entropy. A common choice is the Debye model which takes the form

$$S_D(T) = \frac{12Nk_B}{\omega_D^3} \int_0^{\omega_D} \frac{\frac{\hbar\omega^3}{k_B T} d}{\exp\left(\frac{\hbar\omega}{k_B T}\right) - 1} d\omega - 3Nk_B \ln \left[1 - e^{-\frac{\hbar\omega_D}{k_B T}} \right]$$

To analyze the systems required for this experiment, density functional theory (DFT) was utilized. DFT allows the properties of many electron systems to be calculated using functionals of electron density that require only three spatial coordinates. This theory takes the many-body problem of interacting electrons in an effective potential and reduces it to a simpler system of non-interacting electrons.

To calculate the effective potential of the system the sum of both the exchange and correlation interactions is required. However, DFT alone cannot calculate these, as they are unknown using only the chosen assumption of non-interactivity. New approximations are made, instead to make solutions calculable. Primarily, this is done using local-density approximations (LDA). LDA is a functional that assumes the effective potential is only dependent on the electron density at the coordinates where the functional is evaluated.

Methods

The following section is devoted to explaining the computational process used. It details the basic setup of VASP calculations, use and interpretation of VASP's results. Specific inputs are given to allow recreation of the observed results.

VASP

This project made use of the computational tool, VASP[?][?][?], to calculate the minimum energy states of metal alloys CuAl_2 and $(\text{Cu}, \text{Ag}, \text{Au})\text{In}_2$ in the C1 structure and the C16 structure. VASP is a program that when given a lattice structure of atoms, handles the large amount of integral computation needed to calculate properties of such structures. The properties include volume, minimum energy, relaxation of structure into lower energy structures and atomic bonding information useful in calculating forces between atoms. VASP is also capable of performing the same computations with varied approximations and computational approaches. These alternate approaches produce results that can be compared to the standard results. Thus, using only VASP, one can test multiple different methods to find and confirm results.

VASP requires four basic files: INCAR, KPOINTS, POSCAR and a POTCAR. The INCAR file contains a list of parameters which are defined to inform VASP how to perform a specific calculation, what approximations to make, maximum electron energy states to handle (cut off energy) and what information about the calculation is requested. The KPOINTS file lists how many differential points in k-space are required along each lattice vector. POSCAR is a file much like the matrices depicted in the physical principles section. It contains the chosen shape of the structure of a material and its corresponding atom locations. Finally POTCAR is a large file of material electron potentials and energy states. This file is generally not created and instead pulled from a database provided by VASP libraries.

To prepare a minimum energy unit cell or base structure, the computational parameters were increased in accuracy and adjusted until consistent results were found. The parameters commonly changed were the number of differential distances each k-space lattice vector was broken into for integration, or K-points, and the effective temp value σ for Fermi smearing. The primary measure of accuracy for parameter adjustment was the variance in the minimal energy at some reasonable volume of the structure. As accuracy improved the results fluctuated above and below the expected computational result, narrowing to the correct result with increased accuracy. To increase computational efficiency, the number of K-points was adjusted to make differential distances along all lattice vectors approximately the same.

The energy of the structures was then calculated for a range of lattice sizes to create a set of data from which the predicted minimum energy of the alloys was found. These DFT calculations were done using local-density approximations (LDA). Energies calculated at incorrect volume sizes would be larger than the minimum energy state. The range of volumes would contain within it the minimum energy point creating a curve of energy as a function of volume that can be computationally solved to find the volume where the structures total energy is minimal. The process of determining the correct range of volumes requires some level of guess work and a potentially wide range of volume sizes to narrow in on the minimum point. Once found, the computationally solved minimum energy is confirmed by VASP and used as the minimum energy state at temperature = 0 K in future calculations.

K-points chosen for the materials varied based on required accuracy desired. C1 structure calculations used 16^3 k-point grids for all except CuIn_2 which used a 24^3 k-point grid. C16 structure calculations were more varied with both CuIn_2 and AgIn_2 using a $13 \times 13 \times 20$ k-point grid while AuIn_2 used a $16 \times 16 \times 24$ grid and Al_2Cu only required a $10 \times 10 \times 16$ grid.

Before the chosen minimum energy could be used for future calculations, it needed to

be confirmed using additional approximation parameters which VASP handles. The first is to enhance the accuracy of the system by increasing the maximum energy or cutoff energy. Initially the cutoff energy was chosen to be 400 eV (with the exception of 295.521 for Al_2Cu), for higher cutoff energies, 1.3, 1.7 and 2 times the standard cutoff energy of the system was chosen to verify results. Increasing energy cutoff increases the number of electron states accepted in the calculation which can provide a better result of the minimum energy, by adding in more terms to the approximation. Often the cut off energy is chosen from a suggested cut-off energy found in the POTCAR files used by VASP. In addition, the standard approximation used Fermi-smearing and checked with Blöch corrections for Brillouin zone. Another test consisted of changing the number of ionic steps from 80 to 0. To remove error from VASP's relaxation calculations, results were confirmed by removing VASP's ability to relax the given structure (the input structure was already relaxed at such a point) and only return the structures unrelaxed energy, which should be the same as when relaxation of the lattice was allowed. Finally, the energy results were also confirmed using another similar calculation tool, Flair.

Data: Zero Temperature

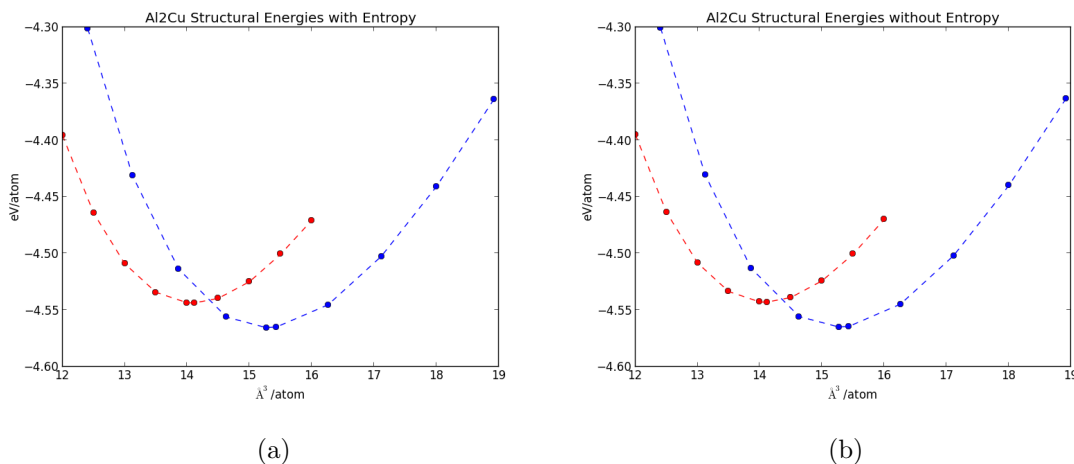


Figure 2: Al_2Cu in C1 structure (Blue) and C16 (Red).

As can be observed in figure 2 for Al_2Cu the C1 structure is to have a predicted lower energy at 0K when compared to ideal C16 structure. In addition the difference in the two minimum energies is reasonably small, which is expected from the necessity of the entropy term being also being a reasonably small term. The only primary difference between figures 2 (a) and (b) is which energy VASP returned, was used. In theory there can be a significant entropy term due to the structure at 0K from the disorder in the lattice. However, as stated in the physical principles, metals disorder entropy term is shown to be extremely small, which is well confirmed from the difference in energy between (a) and (b). Since the disorder entropy results uniformly do not influence, neither the curve nor significant difference in the magnitudes of the points, other materials are not presented with their no entropy curves.

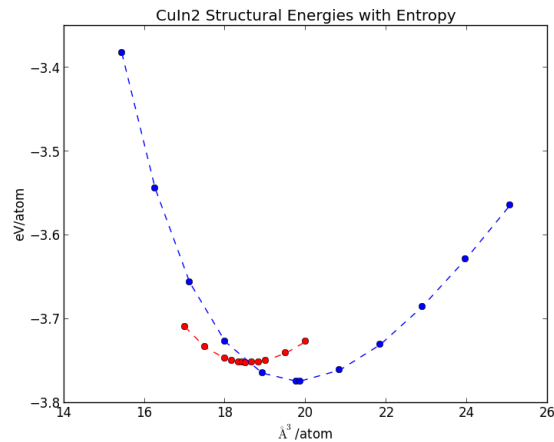


Figure 3

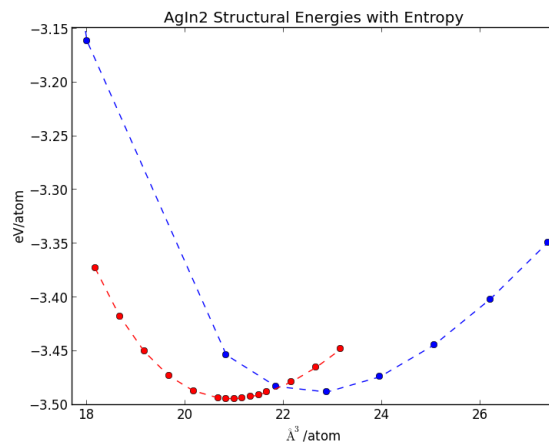


Figure 4

Again in figure 3 an even smaller difference in energies can be seen encouraging even more expected phase transition behavior. However in figure 4 a different behavior is observed. Instead of the expected phase preference of C1 being the lower energy state, an observed lower energy state for C16 exists. This discrepancy may be caused by a lack of proper relaxation in one of the two structures. It could have also been caused due to a less than ideal guess for the structure. Often DFT calculations that are not given reasonably close guesses can return inaccurate results. This is because, in the attempt to relax the system, the program realizes it is far from the ideal relaxed state and makes a large step towards the relaxed state. This large step can be well past the relaxed state. When this happens it finds itself instead of moving down in energy and thus moving closer to the actual relaxed state but up and farther from. In some cases this causes the algorithms to miscalculate the minimum energy structure and return inaccurate results. The second is the more likely possibility and is further upheld because of the extremely small difference in minimum energy states. Further accuracy, relaxation and a superior initial guess for the structure may have likely resulted in better agreement with expectations.

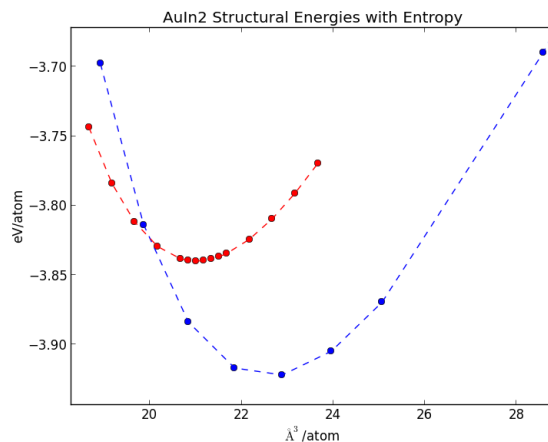


Figure 5

A much larger difference in the energies can be observed from figure 5. This larger energy difference is why even at higher than room temperature AuIn_2 , despite its similar structural behavior, does not exhibit the same phase transitions as other metals and has only been observed in the C1 structure. This material can thus be used as an example of what minimum energy differences are likely to result in phase transitions for like materials.

Analysis

The following parameters were calculated from the above results. The following results list the minimum energy states of all the materials, as well as the lattice parameters a and c . The lattice correction term X is also presented.

LDA (CX)	E_{\min} (eV)	Vol (\AA^3)	a (\AA)	c (\AA)	X
Al_2Cu (C1)	-13.697	45.770	5.678	—	—
Al_2Cu (C16)	-27.263	84.516	5.956	4.776	0.159
CuIn_2 (C1)	-11.323	59.340	6.192	—	—
CuIn_2 (C16)	-22.513	111.377	6.506	5.262	0.163
AgIn_2 (C1)	-10.464	68.588	6.498	—	—
AgIn_2 (C16)	-20.965	125.601	6.772	5.532	0.155
AuIn_2 (C1)	-11.766	66.842	6.442	—	—
AuIn_2 (C16)	-23.040	126.076	6.780	5.602	0.153

It is important to gain a stronger understanding of the difference in the materials. As such a comparison of their energies is necessary as well as a comparison of the relative volumes. For both the energy and volume calculations they are scaled to have the same number of atoms influencing the final results. This is done because of the atoms needed to calculate the C16 structure information.

LDA	$E_{\min_{C1}} - E_{\min_{C16}}$ (eV)	$\text{Vol}_{C16}/\text{Vol}_{C1}$	ΔE (eV)/atom
Al_2Cu	-0.131	0.923	-0.022
CuIn_2	-0.132	0.984	-0.022
AgIn_2	0.036	0.916	0.007
AuIn_2	-0.493	0.943	-0.082

For most of the materials the expected result of lower energy in the C1 structure at 0 K is observed. AgIn_2 however did not return the expected results. As discussed above, incorrect relaxation may have been the result, however, it is also possible that this material does not exhibit the expected behavior and that instead it remains in the C16 structure from the observed higher energies all the way down to nearly 0 K.

Again the expected phase transition behavior can be predicted from the small energy difference in structures. However in the case of AuIn_2 the difference is almost four times greater than that of Al_2Cu and CuIn_2 . This further hints at AuIn_2 's lack of phase transition behavior. Of additional note is, that the C16 structure has a smaller volume for all the materials, which is to be expected, but the ratio for all the metals, while similar does not hint into the possible phase transition behaviors.

For further analysis the data is also presented with a difference in energy term per total atoms of each structure. This is a common way to express the energy and aid comparisons to other works that found very similar results to the above. It is often chosen so that the number of atoms is not a relevant part of the structures average energy.

Conclusion

A strong indication of the phase transition properties of both Al_2Cu and CuIn_2 has been observed. In addition the similar metal alloy AuIn_2 is shown to have a much larger difference in minimum energy between the C1 and C16 structures indicative of a lack of phase transition at high enough temperatures. However, AgIn_2 which has been observed as having the same behavior, is calculated to have reversed minimum energy states instead preferring to be in the C16 structure at 0 K. While it is possible that an error in calculations has resulted in this discrepancy it is also possible that the material goes through a minor phase transition and then returns to the C16 structure at the very low temperature range. In addition the lattice parameters of each material have been presented with reasonable ranges of accuracy.

While the initial conditions and lattice parameters are a solid step towards observing calculable results for the phase transition, an additional area for exploration would include exploration thermal properties and phononic behavior as a function of temperature. This would allow all the metal structures material properties at higher temperature to be explored and used as model to find the transitions temperatures. In addition the same phononic thermal properties could be used to model the entropy and confirm the expected entropy influence to the phase transition. Future explorations of these materials may very well lead to a complete exploration of this phase behavior both in experimental observation and in theoretical prediction.

Appendix I: Thermal Behavior and Dispersion Relations

Calculations for exploring the minimum energy states of the chosen metal alloys have been successfully explored at absolute zero. It was the intention to further use density functional theory (DFT) computational approaches to explore all four metals at finite temperature. However, due to complications in both initialization of setup to perform computation evaluations and unexpected results which could not be resolved in the time frame allowed, the results found are not presented. Once these issues can be resolved the thermal properties of the phase change in the materials can be easily modeled and evaluated.

In this appendix the basic process used to compute the thermal and phononic properties is detailed, and unexpected results presented. This is done with the intention of showing that such work has been performed and elaboration on the value of the potential of the results, should the complications be resolved.

Methods

With each alloy's minimum energy state confirmed, the structures were used to extrapolate expected lattice vibration distributions caused by finite temperatures, to compute when each alloy's minimum energy state switches from the C1 structure to the C16 structure. This was done computationally with a program called Phonopy. Phonopy can be used to create a set of larger, nearly identical structures which contain specific changes to represent spatial perturbations in the lattice. These perturbations reflect slightly energized materials. In effect, Phonopy creates a set of new, larger structures with atoms dislocated due to ambient kinetic energy or finite temperature. The effects of a chosen perturbation were observed and calculated using VASP to extrapolate the eigenstates of lattice vibration. Once these new energies are calculated, Phonopy can utilize them to calculate the eigenstate forces caused by such perturbations on the system. This information allows Phonopy to further calculate the dispersion relation of the examined alloys as well as model their thermal properties such as entropy, free energy and heat capacity.

The density of states for the alloys in C1 structure would then be compared to that of the C16 structure. At finite temperatures a shift in the states minimum energy can be calculated for CuIn_2 and AgIn_2 , while the unchanging phase behavior of Al_2Cu and AuIn_2 would also be confirmed.

Data:

Some states can be seen as having imaginary frequencies which are represented as negative in figure 6. This is particularly alarming as this material is not documented or physically expected to have such phonon frequencies.

Looking more closely at the dispersion relationship in figure 7 a relevant band of phonon states is observed at negative frequencies. This unphysical result can occur because this system of bands is generated from a frequency squared equation. However it is not an expected result for this material. Initially the expectation for why this occurs is the material is not sufficiently relaxed by VASP before its properties are calculated by Phonopy. However, that does not seem particularly likely due to the strong symmetries of the C1 structure, which

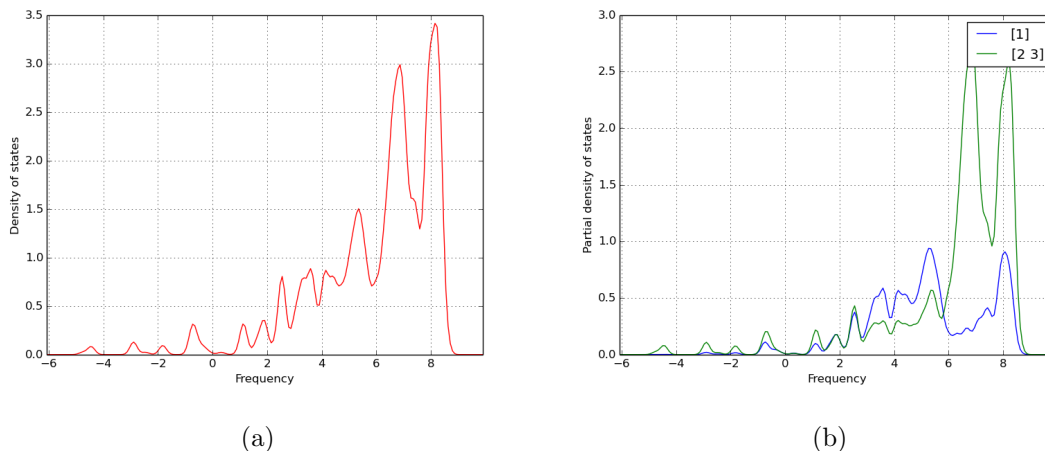


Figure 6: C1 Al_2Cu structures phonon density of states with frequency in the THz regime. (a) Total density of phononic states. (b) Partial density of phononic states with copper (Blue) and Aluminum (Red).

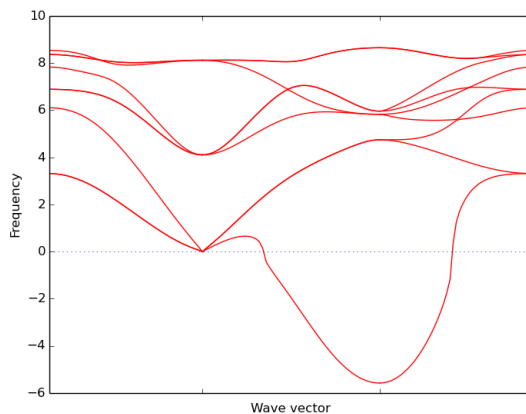


Figure 7: Dispersion Relation of Al_2Cu from points $0.5\ 0.5\ 0.5$ to Γ to $0.5\ 0.5\ 0.0$ to $0.0\ 0.0\ 0.5$ on the THz frequency range.

only requires a single eigenstate to compute forces due to vibration. It is especially alarming to further consider relaxation as the cause, because for a structure as simple as C1, the only parameter that can be used for relaxation is the lattice constant (or volume) which was adjusted as seen earlier to find the minimum energy state already. This was done with a high range of accuracy to avoid this type of unrelaxed error.

Looking at the thermal properties calculated by Phonopy, figure 8 provides insight into expectations for entropy, heat capacity and Gibb's free energy. Starting with entropy, it is as expected increasing and correlated is the decrease in the free energy. If data for the Al_2Cu C16 thermal properties was available a comparison of the free energy curves could be presented to find the point when they overlap. That point would be the thermal point of phase transition from C1 to C16. However given the unusual behavior observed in figures 6 and 7, these results may be significantly in error and cannot be trusted to be a correct model of Al_2Cu 's thermal behaviors.

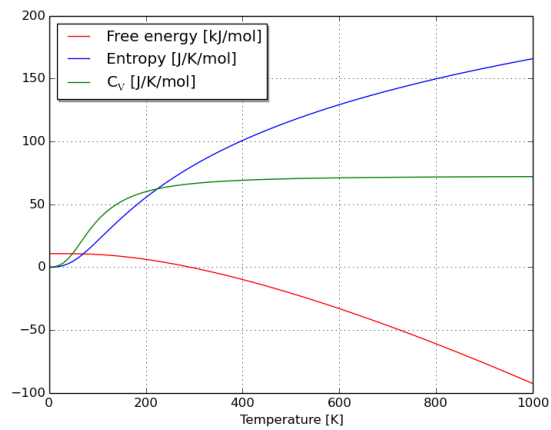


Figure 8: Thermal Properties of Al₂Cu

Final Thoughts

Because of the difficulties detailed above for getting Phonopy and its related computation results calculated successfully for the explored materials the final results for this experiment have been set aside. While work has been done further time and effort will be needed to yield the desired results for a complete exploration of the thermal phase transitions properties of Al₂Cu and (Cu, Ag, Au)In₂. Despite these setbacks already some of the expected behavior can be observed, even from the zero temperature calculations. Final Phonopy calculations would add as a support and confirmation of the expected results.