ABSTRACT

Many random substitutional solid solutions (alloys) will display a tendency to chemically order given the appropriate kinetic and thermodynamic conditions. Such order-disorder transitions will result in major crystallographic reconfigurations, where the atomic basis, symmetry, and periodicity of the alloy change dramatically. Consequently, phonon behavior in these alloys will vary greatly depending on the type and degree of ordering achieved. To investigate these phenomena, the role of the order-disorder transition on phononic transport properties of Lennard-Jones type binary alloys is explored via nonequilibrium molecular dynamics simulations. Particular attention is paid to regimes in which the alloy is only partially ordered. It is shown that, through exploitation of the long-range order parameter, thermal conductivity of binary alloys can be effectively tuned across half an order of magnitude at low-to-moderate temperatures.

INTRODUCTION

Substitutional solid solutions, or alloys, can exist in both chemically ordered and disordered states. These states, while identical in terms of composition, are distinguished from each other by their unique crystallographic configurations. In the disordered state (random alloy), atoms are arranged in a statistically random distribution among the atomic sites of the crystalline lattice, where the probability of finding a particular type of atom at any given atomic site is based on the stoichiometry of the solution itself [1]. In the ordered state (ordered alloy), atoms are arranged in a periodic distribution among the atomic sites of the crystalline lattice, and each type of atom is said to occupy its own sublattice [2]. It is important to note that, in this context, disorder does not imply a deviation from crystallinity (i.e., an amorphous solid) since both the ordered and random alloys described here are fully crystalline.

The particular crystallographic configuration in which a system will order depends on several factors, e.g., the number and types of constituent atoms comprising the solution, as well as the stoichiometric ratio of the solution itself. The L1_1 configuration is one in which atoms arrange themselves such that a 1 × 1 superlattice forms along the [111] crystallographic direction. As far as metallic systems, only CuPt and Cu_3Pt_5 are known to order in this configuration [2]. As such, this ordered configuration is commonly referred to as CuPt-type ordering. Ordering in this material system is achieved by annealing the disordered alloy with the appropriate composition at temperatures below the crit-
A disordered solid has a volume of \( l_{\text{A1}} \) (A1 Strukturbericht designation). The primitive cell of the ordering are still under debate [3–8]. Conditions, although the specific mechanisms responsible for this order is achieved through thin-film growth under very particular conditions, (e.g., as has been shown for SiGe alloys [9]). Instead, long range order will not achieve ordering, regardless of temperature or duration such ordering. However, in semiconductor systems, annealing and group III-V quaternary [8] semiconductor alloys can exhibit ical temperature [1, 2]. In addition to CuPt, it has been demonstrated that group IV binary [3–6], group III-V ternary [7, 8], and group III-V quaternary [8] semiconductor alloys can exhibit such ordering. However, in semiconductor systems, annealing will not achieve ordering, regardless of temperature or duration (e.g., as has been shown for SiGe alloys [9]). Instead, long range order is achieved through thin-film growth under very particular conditions, although the specific mechanisms responsible for this ordering are still under debate [3–8].

In disordered AB alloys, there is a 50/50 chance of finding either an A or B atom at each atomic site of a face-centered cubic lattice (A1 Strukturbericht designation). The primitive cell of the A1 disordered solid has a volume of \( \frac{1}{2}a^3 \) and is shown in Fig. 1a. Upon ordering in the L1₁ configuration, the atoms arrange themselves such that an A atom occupies the atomic site at (0, 0, 0) while a B atom occupies the site at (1, 1, 1), illustrating that the L1₁ configuration has a 2 point basis. The volume of the L1₁ primitive cell is \( \frac{1}{2}a^3 \), twice that of the A1 primitive cell. Despite the fact that both the A1 and L1₁ primitive cells are rhombohedral, the L1₁ primitive cell can only be formed along a single body diagonal of the conventional cell, demonstrating the single axis of three-fold (trigonal) symmetry of the L1₁ configuration, as opposed to four of the A1 configuration. The L1₁ primitive cell is shown in Fig. 1b.

As a result of this crystallographic reconfiguration, the properties of the ordered and random alloys can differ greatly. Several studies have examined how the disorder \( \rightarrow \) order transition affects the electrical conductivity [10, 11], electronic band-gap [12, 13], optical properties [14, 15], magnetic anisotropy [16], Raman-shift [6, 17, 18], and vibrational properties [19, 20] in both metallic and semiconductor alloys. Despite these investigations, the role of the disorder \( \rightarrow \) order transition on phononic thermal conductivity has been left largely unexplored.

In the present study, we have investigated the behavior of phononic thermal transport properties of AB Lennard-Jones type binary alloys in both the A1 (random) and L1₁ (ordered) configurations via non-equilibrium molecular dynamics (NEMD) simulations. We pay particular attention to the thermal conductivity of alloys exhibiting partial ordering, i.e., a Bragg-Williams long-range order parameter between 0 and 1 [2]. It is shown that the thermal conductivity of a binary alloy of fixed composition can be effectively tuned across half an order of magnitude at low-to-moderate temperatures by varying the degree to which the alloy is ordered.

**Molecular Dynamics Simulations**

We have employed non-equilibrium molecular dynamics (NEMD) simulations to study the thermal conductivity of ordered, partially-ordered, and disordered Lennard-Jones (LJ) binary alloys. Non-equilibrium molecular dynamics is a technique in which a heat flux is applied across a computational domain and a steady-state, one-dimensional temperature gradient is established. With the thermal flux and temperature gradient known, thermal conductivity can be calculated via Fourier’s law. This technique has been used extensively to investigate transport properties in nanoscopic systems, e.g., thermal conductivity [21–26] and thermal boundary conductance [27–30]. Although non-equilibrium and equilibrium, or Green-Kubo (GK), procedures for determining thermal conductivity will demonstrate good agreement assuming properly sized computational domains [31, 32], the NEMD procedure was chosen over the GK approach due to the inherent difficulty of specifying the converged value of the heat current auto-correlation function when investigating thermal conductivity of superlattices [32]. While the LJ interatomic potential implemented in this study cannot exactly reproduce the properties of many materials beyond inert gases, such simulations are still able to produce physically meaningful results [22, 24–29].

**Computational Details**

We have calculated the predicted thermal conductivity of AB alloys in the [100] crystallographic direction relative to the conventional cell vectors. The A- and B-type atoms were distinguished by their atomic masses, which were 40 and 120 amu, respectively. The LJ parameters for both the A and B atoms were fixed (\( \varepsilon = 0.0503 \text{ eV} \) and \( \sigma = 3.307 \text{ Å} \)). This approach, where atoms differ only by atomic mass, has been routinely implemented in the literature [22, 28–31, 33]. All results are presented in non-dimensional (reduced LJ) units,

\[
E^* = \frac{E}{\varepsilon}, \quad T^* = \frac{T}{k_B}, \quad \omega^* = \frac{\omega \sigma m^{0.5}}{\varepsilon}, \quad \kappa^* = \frac{\kappa m^{0.5} \sigma^2}{\varepsilon^{0.5} k_B}, \quad (1)
\]

where \( m \) is the mass of an A atom (40 amu), and \( E, T, \omega, \) and \( \kappa \) are energy, temperature, angular frequency, and thermal conductivity, respectively. From this point forward the asterisks will be dropped and all results and discussion will make use of non-dimensional units.
(a) complete order, $\eta = 1$
\[
\begin{array}{cccccccccc}
R & R & R & R & R & R & R & R & R & R \\
\end{array}
\]

(b) incomplete order, $\eta < 1$
\[
\begin{array}{cccccccccc}
R & R & R & W & W & R & R & R & R & W & W & R \\
\end{array}
\]

**FIGURE 2. DEFINITION OF THE ORDER PARAMETER.**

All eight computational domains implemented in this study were $31.6 \times 31.6 \times 232$ Å$^3$ and contained 6,336 atoms. The four outermost layers of atoms in all domains formed a rigid wall to prevent sublimation from the free surface of the domain during non-equilibrium heating. The eight layers of atoms immediately inside these rigid walls were “bath” atoms, to which energy was added or removed during non-equilibrium heating. The domains differed from each other by way of their respective Bragg-Williams long-range order parameter, $\eta$, given as

$$
\eta = \frac{R - W}{R + W}.
$$

Here, $R$ and $W$ refer to the number of atoms that are in the “right” and “wrong” positions in the context of the perfectly ordered crystal. The distinction between right and wrong atoms is further illustrated in Fig. 2. Order-parameters of the domains implemented in this study were 1, 0.99, 0.95, 0.90, 0.85, 0.75, 0.50, and 0. Schematics of selected computational cells ($\eta = 1, 0.75$, and 0) are shown in Fig. 3.

During the simulation, the equations of motion for the system were integrated using the Nordsieck fifth-order predictor corrector algorithm [34]. Periodic boundary conditions were initially applied in all directions and the system was equilibrated at a predefined temperature via a velocity scaling routine (0.046 $\leq T \leq 0.470$, depending on the simulation) and zero pressure. Zero pressure was maintained by the Berendsen barostat algorithm [35]. Once equilibration was complete, the periodic boundary conditions in the $z$-direction were switched to free boundary conditions and the non-equilibrium heating procedure was implemented. The addition of energy to/removal from the baths was performed through a constant energy approach, allowing for thermal flux across the computational cell to be controlled explicitly. This routine slightly changes the forces acting on a particular atom depending on the amount of energy to be added or removed. The total force acting on atom $i$ is given by

$$
F_{i,\text{total}} = F_i + \xi m_i v_i^T,
$$

where $m_i$ is the mass of the atom, $v_i^T$ is the thermal velocity of the atom, and $\xi$ is a scaling factor. This scaling factor is expressed as

$$
\xi = q \frac{1}{2K} = \frac{\Delta E}{2\Delta T},
$$

where $q$ is the flux across the domain, $\Delta t$ is the time step used in the MD integration of the equations of motion, $\Delta E$ is the amount of energy to be added to or removed from the bath per time step, and $K$ is the total thermal kinetic energy of the bath [36]. To ensure the baths were not being perturbed far from equilibrium they were sized such that the amount of energy added to or removed from the bath was less than 1% of the bath kinetic energy. This constant-energy approach was preferred over maintaining the baths at a specific temperature because applied flux was known explicitly and not subject to statistical fluctuations, as is the case when baths are maintained at constant temperatures through a thermostat routine.

During non-equilibrium heating, the system was divided into 40 equally sized slices such that a spatial temperature profile could be calculated along the $z$-axis. The temperature of each of these slices was determined through the relationship,

$$
\frac{3}{2}N_S k_B T_S = \sum_{i=1}^{N_S} \frac{1}{2} m_i (v_i^T)^2,
$$

where $N_S$ is the number of atoms in a particular slice $S$, and $k_B$ is the Boltzmann constant. Each slice was comprised of approximately 100 atoms, but varied slightly due to thermal vibrations causing atoms near slice boundaries to move between neighboring slices. Linear fits of slice temperature, $T_S$, versus time data were made for discrete time intervals during the simulation and the slopes of these lines were used to determine the onset of the steady-state regime. Once in the steady-state regime, time-averaged spatial temperature profiles were created. To determine the temperature gradient, a linear least squares fit was performed.
for each temperature profile. The slices (roughly two atomic layers) nearest to the baths were not included in the fits. From the spatial-temperature profiles, and with the applied flux known, thermal conductivities of the alloys were calculated via Fourier’s law. The applied fluxes were chosen such that the temperature drop across the domain did not exceed 15% of the average domain temperature. However, this limit was only realized for the lower-temperature simulations. In reality, the temperature drop was closer to 5% of the average domain temperature for the majority of the simulations presented in this study.

Density of States Calculations

Phonon density of states (DOS) curves of the eight computational domains were first calculated. The DOS is defined as the Fourier transform of the velocity correlation function [28,37] but in practice is calculated using standard estimation procedures for power spectral density. For each atom, the velocity is obtained at each integration time step to give a velocity fluctuation time series of 36,384 points. The Welch method of power spectral density estimation is then applied by creating eight 50% overlapping segments of 8,192 points to give an angular frequency resolution of 0.0029 (reduced units). Each segment is then multiplied by a Hamming window and the fast Fourier transform (FFT) is computed. The power spectral density, i.e., DOS, is then obtained by ensemble averaging the Fourier transform magnitudes of each segment.

The DOS curves of three selected alloys are shown in Fig. 4. All domains have the same effective cutoff frequencies, which can be explained by the fact that the highest frequency vibrational modes will be those between two A atoms. That is, the effective spring constant between all atoms is the same (LJ potential). Still, it is clear from these plots that the distribution of vibrational modes changes dramatically between the random and ordered states. In particular, attention is drawn to the development of vibrational peaks at ω = 3.5 and 9.5 and the subsequent trough between them. This behavior can be explained as follows. As the order-parameter increases, the domain approaches the limit in which a 1 × 1 superlattice appears along the [111] crystallographic direction. It has been shown that in short-period superlattices, phonon interference leads to the formation of “optical” type phonon branches, band flattening, and in turn, the formation of phononic band gaps or stop bands [22]. This behavior manifests itself in the DOS curves through the formation of the respective peaks and troughs described above and is consistent with the two-atom atomic basis of the L11 system. However, a full band gap is not realized, as the DOS curve represents the vibrational summary of the entire Brillouin zone, not just that in the direction perpendicular to the superlattice.

FIGURE 4. PHONON DENSITY OF STATES CURVES.

Thermal Conductivity Predictions

Thermal conductivity predictions for the eight order parameters considered are shown as functions of temperature in Fig. 5. Each individual point represents the mean result of five independent simulations, and error bars represent the standard deviation of thermal conductivity predictions. In order to make the trends of Fig. 5 more discernible, a least squares fit of each series of data (i.e., for each different η) is performed such that the resulting trend line is of the form αTβ + γ. For the sake of clarity, these trend lines are subsequently plotted by themselves in Fig. 6. We will now discuss the several features of these plots that deserve explicit attention.

First, the dependence of thermal conductivity on temperature in the limits of η = 1 and 0 is indicative of the specific phonon scattering mechanisms that dominate thermal conductivity in these domains. In the limit of absolute order (η = 1), the exponent of the trend line β ≈ −1, suggesting that the dominant phonon scattering mechanism is the Umklapp three-phonon scattering event [38]. In the limit of complete disorder (η = 0), thermal conductivity is only very weakly a function of temperature, and is ultimately limited due to scattering of phonons by mass fluctuations and inelastic processes [39].

Second, the thermal conductivities of all domains begin to converge at elevated temperatures. In reality, the absolute convergence point is not directly observed as the crystals melt before this temperature is achieved (the melting temperature of LJ solids, T_melt, is approximately 0.5 [28]). Thermal conductivity,
Reduced thermal conductivity is often expressed as

\[ \kappa = \frac{1}{3} c_v v^2 \tau, \]

where \( c_v \) is the volumetric heat capacity, \( v \) is the phonon group velocity, and \( \tau \) is the scattering time of all individual phonon scattering processes combined. Heat capacity of all domains will be the same \( (c_v = 3Nk_B \rho) \), suggesting differences in thermal conductivity are the result of differences in the \( v^2 \tau \) product. Thus, at high temperatures, the combination of reduced phonon group velocity (due to band flattening) and increased Umklapp scattering \( (\tau_U \propto T^{-1}) \) in the more ordered alloys “catches up” to the rate of impurity scattering in the random alloys.

Lastly, it is clear that at low to moderate temperatures \( (0 > T > 0.25, \text{ or up to } \approx 0.5T_{\text{melt}}) \) thermal conductivity is very strongly dependent on \( \eta \). In addition, it appears the strongest sensitivity to \( \eta \) is in the regime where \( \eta \) approaches unity. For example, at \( T = 0.133 \), thermal conductivity decreases by 48% when \( \eta \) goes from 1 to 0.9, whereas it only decreases 31% when \( \eta \) goes from 0.9 to 0.75. This behavior is consistent with that observed in dilute Si\(_{1-x}\)Ge\(_x\) alloys, where the effect of the inclusion of more Ge “impurities” on thermal conductivity becomes less pronounced with increasing Ge concentration [40]. The concentration of impurities is, in this case, analogous to the number of “wrong” atoms in the crystal, \( W \), described above in the context of the ordering parameter.

Finite Size Considerations

In order to ensure the above results were not affected by the limited size of the computational domain, a second computational domain at \( \eta = 1 \) was created 50% larger than that reported above. Thermal conductivity predictions of this larger domain were within the standard deviation of the predicted values of the smaller domain, suggesting the eight domains described above were large enough to capture the largest bulk phonon mean-free-paths that contribute to thermal conductivity. Finite size effects were considered with regard to the \( \eta = 1 \) domain alone, as in all other cases, the mean-free-path of phonons will be inherently limited by the impurities or imperfections within the crystal. Thus, if this perfectly ordered domain passes finite size checks, all others will as well.

CONCLUSION

We have examined the role of the A1 \( \rightarrow \) L1\(_1\) transition on thermal conductivity of binary alloys via non-equilibrium molecular dynamics simulations. It has been shown that at low to moderate temperatures \( (0 > T > 0.25, \text{ or up to } \approx 0.5T_{\text{melt}}) \) thermal conductivity of binary alloys can be effectively tuned across half an order of magnitude. Additionally, thermal conductivity of a perfectly ordered alloy \( (\eta = 1) \) is equal to that of its random counterpart at elevated temperatures. This behavior is attributed to the convergence of the respective \( v^2 \tau \) product (group velocity squared times phonon scattering time) in the ordered and disordered states.
REFERENCES


