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# Lattice thermal conductivity of multi-component alloys

M. Caro [a, *], L.K. Béland [b], G.D. Samolyuk [b], R.E. Stoller [b], A. Caro [a]

[a] Materials Science and Technology Division, Los Alamos National Laboratory, Los Alamos, NM 87545, USA
[b] Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN 54321, USA

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ABSTRACT

High entropy alloys (HEA) have unique properties including the potential to be radiation tolerant. These materials with extreme disorder could resist damage because disorder, stabilized by entropy, is the equilibrium thermodynamic state. Disorder also reduces electron and phonon conductivity keeping the damage energy longer at the deposition locations, eventually favoring defect recombination. In the short time-scales related to thermal spikes induced by collision cascades, phonons become the relevant energy carrier. In this work, we perform a systematic study of phonon thermal conductivity in multiple component solid solutions represented by Lennard-Jones (LJ) potentials. We explore the conditions that minimize phonon mean free path via extreme alloy complexity, by varying the composition and the elements (differing in mass, atomic radii, and cohesive energy). We show that alloy complexity can be tailored to modify the scattering mechanisms that control energy transport in the phonon subsystem. Our analysis provides a qualitative guidance for the selection criteria used in the design of HEA alloys with low phonon thermal conductivity.



In the search for new materials with outstanding properties for novel applications, a new direction involving high entropy alloys (HEA) is proving promising. These materials composed of more than five elements, have shown improved strength, and remarkable fracture toughness such as in the case of CrMnFeCoNi alloy [1] with toughness levels comparable to Ni-based super alloys and several stainless steel such as 316 SS. By a mixture method of synthesis, design, and element selection, high entropy alloys have been developed for advanced applications, e.g. $Co_{1.5}$ $CrFeNi_{1.5}$ $Ti_{0.5}$ with high temperature strength and oxidation resistance, which is proposed for high temperature tensile testing machines up to 1000 °C, or $Al_{0.3}$ $CrFe_{1.5}$ $MnNi_{0.5}$ with high hardness and wear resistance which could replace shot peening or other methods currently used for surface hardening [2]. Also, single-phase solid solution HEAs have been investigated such as FCC CoCrFeNi [3] and CoCrFeMnNi [4] and BCC alloys such as WNbMoTa, WNbMoTaV, and TaNbHfZrTi [5].

High entropy of mixing is the main characteristics of HEA alloys, i.e. high configurational entropy due to the large number of elements at, or close to, equiatomic composition. The combination of different elements in HEA alloys, including elements with large atomic radius difference, may induce lattice distortion [6], which in turn influences the alloy structure and properties.

HEA could have potential applications in radiation environments if extreme disorder improves their damage response. A possible element is their ability to recover damage by increasing defect recombination soon after the damage energy is deposited in the lattice. This effect could be due to a longer duration of the thermal spike produced by a reduced thermal conductivity. Clearly, supporting experimental evidence is still missing. To our knowledge, very few experimental studies have been performed on radiation effects in high entropy alloys [7]. A scoping study by Kumar et al. [8] showed poor phase stability for the examined single-phase polycrystalline FCC FeNiMnCr alloy. Significant (Cr and Mn) radiation induced segregation at grain boundaries was observed in the alloy specimens after 3 MeV Ni ion irradiation at 500 °C to 1 and 10 dpa. In contrast, Nagase et al. [9] reported phase stability for CoCrCuFeNi HEA after fast (2 MeV) electron irradiation to over 40 dpa at room temperature (298 K) and 500 °C (773 K). HEA behavior under irradiation still remains vastly unexplored.

At the center of this topic is the hypothesis that HEA inherent high configuration entropy will promote the stability of the solid solution phase and that reduced thermal conductivity will promote defect recombination, enhancing radiation resistance. Defect recombination could be enhanced by increasing the time at which thermal energy remains close to the high-energy collision cascades

* Corresponding author.
*E-mail address:* magda@lanl.gov (M. Caro).

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sites. This thermal energy is transported away by phonons, electrons, and magnons. In kinetic theory of gasses, thermal conductivity depends on the product of the group velocity and carrier mean free path. Mean free path of carriers decreases as a consequence of extreme disorder. Thermal conductivity of metals is primarily due to electrons. Phonons become relevant only in the short time scale related to thermal spikes in collision cascades, where energy is deposited first into the ions, and only after a time scale given by the strength of the electron–phonon interaction, the electrons start capturing and conducting this energy away from the deposition region. Therefore, phonons, although not the main heat carriers in metals under normal conditions, become relevant during the time scale of few picoseconds of the heat spike regime.

HEA thermal conductivity could be tuned by varying the alloy elemental composition and concentration. Computer simulations can efficiently help in the search for optimized HEA with desired properties, as we show in this work. Using *ab initio* molecular dynamics simulations and CALPHAD methodology, Gao et al. identified several possible FCC and HCP multicomponent solid solution compositions in several HEA alloys [3]. Using molecular dynamics with a tight-binding potential, Kao et al. investigated the rapidly solidified structure of equimolar HEAs with eight elements Ni–Al–Cu–Co–Ti–V–Zn–Zr and explored the effect of the variation in atomic structure and size [10]. An atomistic modeling approach was applied to study W–Nb–Ta–Mo and W–Nb–Ta–Mo–V HEA with refractory elements [11]. First-principle studies within density-functional theory (DFT) have been performed to determine the composition effect on lattice constant and formation enthalpy of the five-element FeNiCrCuCo HEA alloy [12].

In this work, Non-Equilibrium Molecular Dynamics (NEMD) and equilibrium Green-Kubo (GK) approaches are applied to study phonon thermal conductivity of multicomponent alloys, aiming at understanding the role of alloy complexity on thermal transport properties. Our study focuses on the effect that the choice of elements and composition has on reducing HEA thermal conductivity. We perform a systematic study of phonon thermal conductivity, $\kappa$, in multiple component solid solutions represented by LJ potentials, looking for conditions minimizing phonon mean free path via extreme alloy complexity. We find that by varying alloy constituents, i.e. by combining elements in the alloy with different size, mass, and cohesive energy, different phonon thermal conductivities are obtained. We show that alloy complexity can be tailored to modify the scattering mechanisms that control energy transport in the phonon subsystem. Our analysis provides guidance for the design of HEA alloys with low phonon thermal conductivity, which entails maximum phonon scattering.

## 1. Simulation methods

While strictly speaking HEA are those composed of five or more components, we restrict our study to binaries, ternaries, and quaternaries, where the parameter space is large but manageable, and we call them HEAs. To study the interactions between elements of multicomponent alloys, we use a model system described by the Lennard-Jones (LJ) potential given in Eq. (1):

$$V_{ij}(r_{ij}) = 4\varepsilon\left[(\sigma/r_{ij})^{12} - (\sigma/r_{ij})^{6}\right], \quad (1)$$

$V_{ij}$ in Eq. (1) is the potential energy of a pair of particles ($i$ and $j$) separated by a distance $r_{ij}$, parameter $\epsilon$ is the potential well depth, and $\sigma$ is the distance at which $V_{ij}(\sigma) = 0$. The equilibrium pair separation is $2^{1/6}\,\sigma$. A switching function with a cut-off distance $r_c = 2.5$ is used to have a smooth truncation in the simulations. The ground state is an FCC crystal.

In this study, we vary the HEA constituent properties, i.e. elements size, and cohesive energy, by varying $\sigma$ and $\epsilon$ parameters in Eq. (1). The range in $\sigma$ and $\epsilon$ is selected to adequately represent several typical elements in HEA, such as those listed in Table 1, which allows a one-to-one relation between the model LJ system and some real crystal.

To analyze the effect of element mass, atomic size, and cohesive energy on the thermal conductivity, $\kappa$, of the LJ solid, NEMD and GK simulations were performed. The NEMD technique is known to reproduce well phononic transport properties [13,14]. In the direct thermostatting method [15], a heat flux is applied across the z axis of a rectangular box and a steady state, one-dimensional temperature gradient is established. The flux of energy, $\Delta Q$, needed to maintain the temperature gradient, $\Delta T$, is monitored during the simulation run. In this case, the thermal conductivity, $\kappa$, is given in Eq. (2):

$$\kappa = \Delta Q \Delta z/(2A\Delta t \Delta T), \quad (2)$$

where $\Delta z$ is the box height, $A$ is the cross-sectional area of the box, and $\Delta$ t is the time step in the simulation.

A second approach to compute thermal conductivity of a solid makes use of the equilibrium method based on Green-Kubo (GK) formalism [16]. In this case, the transport coefficient $\kappa$ is given in terms of the integral over time $t$, of the ensemble average of the auto-correlation of the heat flux, $\mathbf{J}$, given in Eq. (3):

$$\kappa = V\Big/\left(3k_B T^2\right)\int_0^\infty <\mathbf{J}(0)\mathbf{J}(t)>dt \quad (3)$$

where $V$ is the box volume, $T$ is the solid temperature, and $k_B$ is the Boltzmann constant. The local heat flux, $\mathbf{J}$, given by Eq. (4), is calculated by computing the per-atom energy (kinetic and potential), $e_i$, the atomic velocity, $\mathbf{v}_i$, and per-atom stress, $\mathbf{S}_i$.

$$\mathbf{J} = \frac{1}{V}\left[\sum_i e_i \mathbf{v}_i - \sum_i \mathbf{S}_i \mathbf{v}_i\right] \quad (4)$$

## 2. Radiation damage simulations

To place our research in context, we study first the effects of thermal conductivity on the duration of thermal spikes induced by collision cascades. We aim at proving that by varying thermal conductivity we can affect the duration of the spike. The actual proof that by varying thermal conductivity we can alter the defects production, is beyond the scope of this work and will be reported in a forthcoming publication.

To study collision cascades and defect formation, reliable interatomic potentials are desirable, as those commonly called many-body potentials, which are well beyond the simplicity of the

**Table 1**
Lennard-Jones $\epsilon$, and $\sigma$ parameters for elements typically present in HEA alloys.

| Element | $\epsilon$ (eV) | $\sigma$(Å) |
|---|---|---|
| Al | 0.392 eV | 2.620 |
| Co | 0.516 eV | 2.284 |
| Cr | 0.502 eV | 2.336 |
| Cu | 0.409 eV | 2.338 |
| Fe | 0.527 eV | 2.321 |
| Ni | 0.520 eV | 2.282 |
| Si | 0.0175 eV | 3.826 |
| Zr | 0.739 eV | 2.932 |