Electron–phonon coupling and related transport properties of metals and intermetallic alloys from first principles

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The fundamental scattering mechanisms between electrons and phonons in metals and metallic alloys dictate a wide range of phenomena in their materials’ physics. Using first-principles calculations carried out on dense electron and phonon wavevector grids, we determine the mode-level descriptions of electron–phonon interactions for nine characteristic metals, shedding light on their electrical and thermal transport properties at a range of electron and phonon temperatures. Our results reveal that even though there are similarities between the phonon density of states of various simple metals, the electronic structure can significantly affect the modal contributions to electron–phonon coupling in metals. More specifically, we find that in the free-electron-like aluminum, the longitudinal high-frequency phonons contribute significantly to the mass enhancement parameter, whereas transverse phonons dominate the electron–phonon coupling in the noble metals with high density of d-band electrons near the Fermi level. In contrast, for intermetallic copper–gold alloys and superconducting metals such as Nb and Ta, the spectral contributions are mostly determined by the phonon density of states. The temperature-dependent volumetric electron–phonon coupling factor depends strongly on the electronic structures of the metals as it increases for the noble metals and their intermetallic alloys, decreases for Nb and Ta, and demonstrates a non-monotonic change for Al. For copper–gold alloys, the electron–phonon coupling strength and the volumetric electron–phonon coupling factor cannot be taken as the geometric mean of the two metals and are relatively much larger than that of their elemental constituents. We also find that the electron thermal conductivity of the 50/50 CuAu alloy is relatively higher than that of Cu3Au and CuAu3, and the electron thermal conductivities of the 25/75 and 75/25 alloys are similar to experimental measurements of disordered copper–gold alloys with the same compositions.

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1. Introduction

Energy relaxation mechanisms between electronic and vibrational excitations dictate a wide range of physical phenomena such as superconductivity [1–5], spin caloritronics [6,7], laser induced phase transitions [8–10], phonon-assisted absorption [11], thermoelectric effects [12,13], and electrical and thermal resistivities in materials [14,15]. Therefore, for a thorough quantitative and in-depth understanding of these phenomena, the proper description of the fundamental scattering processes and interactions dictating electron–phonon coupling needs to be established. In this regard, first-principles calculations based on linear response theory have studied the spectral nature of electron–phonon coupling in several elemental metals with good agreement shown between the Eliashberg function predicted by theory and tunneling experiments [15–17]. However, these calculations were performed on coarse meshes of phonon (q) and electron (k) wavevectors in the Brillouin zone and therefore, intrinsically lack the detailed mode-level descriptions of electron–phonon interactions and linewidths quantifying energy carrier lifetimes with sufficient resolution to
accurately predict contributions from individual phonon modes \[3,18,19\]. Moreover, fine meshes of \( \mathbf{q} \) and \( \mathbf{k} \) wavevectors in the Brillouin zone are also necessary for properly accounting for interactions between all phonon modes and electronic eigenstates that dictate the electron–phonon mass enhancement parameter, \( \lambda \), which can affect physical properties such as electronic heat capacity, electrical resistivities, and transition temperatures of superconductors \[3,20\].

The early works by Kaganov et al. \[21\], Anisimov et al. \[22\], and Allen et al. \[23,24\] describe the energy exchange between the electronic and the vibrational states with a two-temperature approach. This formulation has been extensively used for interpreting experimental results at low electron and phonon temperature perturbations \[25–29\]. For elevated temperature excursions, first-principles-based calculations have shown that the volumetric energy transfer rate between the two subsystems is significantly enhanced at these highly non-equilibrium conditions for free-electron-like and noble metals \[30–32\]. More recently, through solving the Boltzmann Transport Equation (BTE) in conjunction with first-principles calculations that take into account contributions from both phonon–phonon and electron–phonon scattering processes, the lattice contribution to thermal conductivity in metals has been predicted for various types of metals at intermediate temperatures \[33,34\]. Moreover, the importance of electron–phonon coupling factors are also calculated for the metals and the results demonstrate that \( G \) can either increase (as in the case of Au, Ag, Cu, copper–gold alloys) or decrease (as in the case of Nb and Ta), or it can also demonstrate a non-monotonic change (as in the case of Al) as a function of electron temperature, depending on the electronic structures of the metals. For the alloys, the electron–phonon coupling strength, \( \lambda \), and the volumetric electron–phonon coupling parameter, \( G \), cannot be taken as the geometric mean of the two metals and are relatively much larger than that of their elemental constituents. We also find that the electron thermal conductivity of the 50/50 CuAu alloy is relatively higher than that of Cu3Au and CuAu3, and the electron thermal conductivities of the 25/75 and 75/25 alloys are similar to experimental measurements of disordered copper–gold alloys with the same compositions.

2. Methodology

In this section, we briefly describe the basic physical quantities studied in this work. Our calculations of the electron–phonon coupling coefficients are performed under the density functional perturbation theory implemented in the Quantum Espresso package \[17,36\]. The imaginary part of the electron and phonon self-energies are calculated as \[20,37\].

\[
\Sigma_{nk}(\omega, T) = \sum_{mn} \left[ \frac{d\mathbf{q}}{\Omega_{\text{BZ}}} \langle \mathbf{g}_{mn,\mathbf{q}}(\mathbf{k}, \mathbf{q}) \rangle^2 \times \left[ \frac{N_{q,n}(T) + f_{mk,q}(T)}{\omega - (\epsilon_{mk,q} - \epsilon_F) + i\hbar} + \frac{N_{q,n}(T) + 1 - f_{mk,q}(T)}{\omega - (\epsilon_{mk,q} + \epsilon_F) - i\hbar} \right] \right],
\]

(1)

\[
\Pi_{qf}(\omega, T) = 2 \sum_{mn} \left[ \frac{d\mathbf{k}}{\Omega_{\text{BZ}}} \langle \mathbf{g}_{mn,\mathbf{k}}(\mathbf{q}, \mathbf{k}) \rangle^2 \times \frac{f_{nk}(T) - f_{mk,q}(T)}{\epsilon_{mk,q} - \epsilon_{nk} - \omega - i\hbar} \right],
\]

(2)

where the factor of 2 in the electron self-energy accounts for spin degeneracy, \( g_{mn,q}(\mathbf{k}, \mathbf{q}) \) is the electron–phonon matrix element computed using density functional perturbation theory over all phonon and electron wavevectors, \( \mathbf{q} \), and \( \mathbf{k} \), respectively, and quantifies the scattering process between the Kohn–Sham states \( mk' \) and \( nk \). \( \epsilon_F \) is the Fermi energy, \( N_{q,n} \), is the Bose–Einstein distribution, \( f_{nk}(T) \) is the Fermi–Dirac distribution at band \( n \), \( \delta \) is a small positive real parameter to avoid numerical instabilities and thus guarantees the correct analytical structure of the self-energies, and the integrals are extended over the Brillouin Zone (BZ) of volume \( \Omega_{\text{BZ}} \) \[20,37\]. Note, the commonly used approximation known as the “double-delta function” approximation, which neglects the phonon frequencies \( \omega_{q} \), and takes the limit of small broadening \( \delta \), is not required in the electron–phonon Wannier (EPW) package used for the calculations of the self-energies in this work \[37,38\].

We calculate the electron–phonon spectral function or the Eliashberg coupling function, \( \alpha^2F(\omega) \), which measures the probability of specific phonon modes (with energy \( \hbar\omega \)) to decay into an electron–hole pair (from an electron eigenstate in the Fermi surface to another). The sum or average of the electron–phonon coupling over all phonon wavevectors, \( \mathbf{q} \) with branch index \( v \), throughout the entire Brillouin Zone is required, which is given as \[14,17\].
where $g_{\mathbf{k}, \mathbf{q}, \mathbf{k}_0}^{\mathbf{q}}$ is the electron–phonon matrix element that quantifies the scattering of an electron eigenstate $|\mathbf{k}_0\rangle$ at Fermi surface to the state $|\mathbf{k} + \mathbf{q}, \mathbf{k}\rangle$, and $N(\varepsilon_f)$ is the density of states of electrons per spin at the Fermi level. The efficiency factor

$$\eta_{\mathbf{k}, \mathbf{q}, \mathbf{k}_0} = 1 - \frac{\mathbf{v}_{\mathbf{k}_0} \cdot \mathbf{v}_{\mathbf{k}, \mathbf{q}, \mathbf{k}_0}}{|\mathbf{v}_{\mathbf{k}_0}|^2},$$

(4)

which depends on the electron velocity $\mathbf{v}_{\mathbf{k}_0}$ and accounts for the anisotropy by considering different scattering directions, is the difference between the transport spectral function defined in Eq. (3) and the spectral function $\alpha_\omega^2 F(\omega)$. [20,39]. From the spectral functions, we calculate the electron–phonon mass enhancement parameter ($\lambda$) and the transport constant ($\lambda_{\mathbf{k}_0}$), which quantifies the strength of electron–phonon coupling is given as,

$$\lambda_{\mathbf{k_0}} = 2 \int_0^\infty \alpha_\omega^2 F(\omega) d\omega.$$

(5)

Along with the total mass enhancement parameter, the mode-resolved mass enhancement parameter ($\lambda_{\mathbf{k}_0}$) for each phonon wavevector $\mathbf{q}$ and branch index $\nu$ can also be calculated to determine the relative contributions from different phonon polarizations in our calculations.

As mentioned earlier, fine $\mathbf{q}$, and $\mathbf{k}$ wavevector grids in the BZ are a prerequisite to accurately predict Eq. (3). To this end, we calculate the electron–phonon coupling matrix within the framework of the EPW code [20]. The recently formulated maximally localized Wannier functions basis [40], the e-p matrix elements, band energies, and phonon modes are interpolated from an initial coarse grid of $18 \times 18 \times 18$ and $6 \times 6 \times 6$ electron ($\mathbf{k}$) and phonon wavevector grids ($\mathbf{q}$), respectively, to uniform grids of $40 \times 40 \times 40$ and $30 \times 30 \times 30$, for $\mathbf{k}$ and $\mathbf{q}$, respectively, to conduct integration via the tetrahedron method. For our calculations, we use a plane wave energy cutoff of 816.3 eV (60 Ry) and a Gaussian smearing of 0.34 eV (0.025 Ry).

To ensure that the interpolated wavevector grids are dense enough to produce numerically converged values of $\lambda$, we performed calculations of Eq. (5) with different combinations of $\mathbf{q}$ and $\mathbf{k}$ wavevector grids as shown in Fig. 1 for Al. The triangle symbols represent calculations carried out on the coarse $18 \times 18 \times 18$ electronic wavevector grids, whereas the square symbols represent those carried out on the dense interpolated grids (of sizes $30 \times 30 \times 30$ and $40 \times 40 \times 40$ represented by filled and hollow squares, respectively). The coarse electron and phonon wavevector grids clearly underpredict the mass enhancement parameter for Al, whereas increasing the phonon grid size above $20 \times 20 \times 20$ results in less than ~1% variation in the calculated $\lambda$. Furthermore, the agreement between the calculated $\lambda$ and the two electronic grid sizes also shows that convergence has been reached in terms of the dense electron wavevector grid sizes utilized in this work. Additionally, we also perform calculations on different electron grid sizes with a fixed phonon grid size of $30 \times 30 \times 30$ as shown in the inset of Fig. 1 to make sure that convergence has been achieved with regard to both electron and phonon wavevector grids.

From the calculated $\alpha_\omega^2 F(\omega)$, $\lambda$, and the second moment of the phonon spectrum, ($\omega^2$), we predict various transport coefficients for the metals considered in this work. We calculate the electron–phonon coupling factor derived by Allen [1], which is applicable to metals with arbitrary density of states and not limited to metals with relatively constant or slowly varying electronic densities of states around the Fermi energy, that is given by,

$$G(T_e) = -\frac{\pi \hbar k_B \lambda(\omega^2)}{N(\varepsilon_F)} \int \varepsilon N^2(\varepsilon) \frac{d\varepsilon}{d\varepsilon} d\varepsilon.$$

(6)

where $\hbar$ is the reduced Plank’s constant, $k_B$ is the Boltzmann constant, $T_e$ is the electron temperature, $N(\varepsilon)$ is the density of states of the electronic system. Although this general form of the electron–phonon coupling factor in a metal is applicable for high temperatures where electronic states away from the Fermi surface are considered for calculations, it should be noted that this expression inherently assumes a fully thermalized electron and phonon subsystems, and it is also assumed that electron–electron interactions do not influence electron–phonon scattering processes.

Next, we calculate the electron thermal conductivity, $\kappa_e$, based on the Eliashberg spectral functions, which we determine from the integral over the entire Brillouin Zone. As we are mostly concerned with moderate temperatures for the prediction of $\kappa_e$ in this work, electron–phonon scattering is the dominant contribution to the thermal resistivity, and we can safely ignore the contributions from electron–electron scattering and electron–impurity scatterings at these temperatures. We use the lowest order variational approximation of the Boltzmann transport equation to determine $\kappa_e$, given as [41].
Fig. 2. Calculated phonon dispersion curves of (a) Al, (b) Cu, (c) Ag, (d) Au, (e) Nb, and (f) Ta along several high symmetry directions. The color intensity indicates the linewidth values (the inverse of phonon lifetimes calculated from electron–phonon coupling in the momentum space) from the self-energies of the phonons. Also plotted are the corresponding phonon density of states on the right for the metals.
greater linewidths, although the contributions to the total metal's longitudinal and higher frequency phonon modes have stants calculated for all metals considered in this work). For all Table 1 for a comparison of the electron scattering rate (\(\tau_{\text{phonon}}\)) of the phonon coupling strength in nine different metals. For comparison, electron–phonon coupling strength measured via tunneling experiments is also included where available. Also listed are the calculated and experimental superconducting transition temperatures, \(T_{\text{c,Exp}}\), and the Columbic psuedopotential, \(\mu_c\), used to predict the \(T_{\text{c,Exp}}\). (7) provides an upper bound to the thermal conductivity of metals. Overall, the values for the linewidths (in meV) are much greater in Al as compared to those in the noble metals since Al has a stronger electron–phonon coupling constant. It is even higher for the case of Nb and Ta (see Table 1 for a comparison of the electron–phonon coupling constants calculated for all metals considered in this work). For all metals, the longitudinal and higher frequency phonon modes have greater linewidths, although the contributions to the total

\[
\frac{1}{\kappa_e} = \frac{1}{L_0 T} = \frac{4\pi n e^2 \hbar}{6\pi^2 k_B T} \int_0^\infty \left( \frac{\hbar \omega}{k_B T} \right) \left( 1 - \exp \left[ - \frac{\hbar \omega}{k_B T} \right] \right) \left( 1 - \frac{3}{2\pi} \frac{\hbar \omega}{k_B T} \right) d\omega
\]

where \(k_B\) is the Boltzmann constant, \(n\) is the number of electrons per unit volume, \(e\) is the charge of an electron, \(m_e\) is the mass of an electron, and \(L_0\) is the Lorenz number, \((\pi^2 / 3) (k_B/e^2)^2\). This expression assumes that the lattice vibrations are in thermal equilibrium within itself, the so-called Bloch’s Annahme. It should be noted that this is an excellent approximation for intermediate and high temperatures where phonon drag has negligible contributions to the resistivity [14]. In deriving Eq. (7), it is also assumed that the electron scattering rate (\(\tau_{\text{phonon}}\)) is isotropic and energy independent. As such, Eq. (7) provides an upper bound to the thermal conductivity of metals.

3. Results and discussions

The calculated phonon dispersions along high symmetry directions and their corresponding density of states for Al, Cu, Ag, Au, Nb, and Ta are shown in Fig. 2a–f. For Al, Au, Ag, and Cu, although the maximum frequency of the longitudinal and transverse branches is different among the various metals, the phonon dispersion relations and the density of states are very similar. Note the similarities in the phonon dispersion and density of states between the noble metals and the free-electron-like Al due to their characteristic FCC lattices, despite the fact that they have drastically different electronic structures, as will be discussed later. In contrast to these metals, the presence of anomalies such as the dip of the longitudinal mode and the softening of the long wavelength transverse modes along the \(\Gamma \rightarrow X\) direction for Nb and Ta that belong to group V of the Periodic Table with BCC lattices are clearly shown in Fig. 2e and f, respectively.

The intensities of the line colors in the phonon dispersions in Fig. 2 correspond to the phonon linewidths, \(\gamma = \hbar / \tau\), that is, the imaginary part of the phonon self-energy, which is related to the finite lifetimes, \(\tau\), of the phonon modes due to emission of electron–hole pair [42]; as previously mentioned, we only consider electron–phonon interactions, and thus these line widths do not account for phonon–phonon interactions. Overall, the values for the linewidths (in meV) are much greater in Al as compared to those in the noble metals since Al has a stronger electron–phonon coupling constant. It is even higher for the case of Nb and Ta (see Table 1 for a comparison of the electron–phonon coupling constants calculated for all metals considered in this work). For all metals, the longitudinal and higher frequency phonon modes have greater linewidths, although the contributions to the total

Fig. 3. Calculated Eliashberg spectral functions, \(\alpha^2 F(\omega)\), for (a) Al, (b) Cu, (c) Ag, (d) Au, (e) Nb, and (f) Ta. For comparison, the phonon densities of states are shown in the background. The integrated electron–phonon coupling strength, \(\lambda\), is also shown (solid red line).
The electron–phonon coupling strength due to the longitudinal and transverse branches vary significantly in the free-electron-like Al as compared to the noble metals; in Al, the longitudinal acoustic phonons contribute ~ 60%, whereas in Ag, Au, and Cu, these modes contribute ~ 41%, ~ 30%, and ~ 31%, respectively. Similar to Cu and Au, the transverse phonons contribute more toward electron–phonon coupling in Nb and Ta.

The relatively larger contribution of longitudinal phonons in Al is clearly seen in the Eliashberg spectral functions, $\alpha^2 F(\omega)$, plotted for the elemental metals in Fig. 3. Contrary to the similarity in their phonon density of states, the electron–phonon spectral functions show remarkable differences between Al and the noble metals where the peak in the spectral function arises at relatively higher frequencies for Al while the main features in the spectral functions for the noble metals are mainly dictated by the corresponding density of states (shown in the background of Fig. 3). The converged values of the electron–phonon mass enhancement parameter, $\lambda$, and its accumulation (red solid line) for the metals are also shown in the Fig. 3. The accumulation of $\lambda$ also clearly shows the significant high-frequency contribution to $\lambda$ for Al, whereas the low-energy transverse modes in Au contribute the most among the four metals. Compared to the other metals, the spectral function for Nb and Ta exactly follows the phonon density of states with larger contributions from higher frequency phonons. Note, our calculated values of $\lambda$ for these elemental metals agree very well with prior studies as compared in Table 1.

Next, we consider the case of copper–gold alloys with varying atomic compositions. Fig. 4 shows the phonon dispersion along high-symmetry directions for Cu$_3$Au, CuAu, and CuAu$_3$ along with the corresponding phonon density of states shown on the right. The introduction of an alloy species with a different atomic mass gives rise to optical phonons in the dispersion relation, which have relatively higher phonon linewidths, and therefore shorter phonon lifetimes as depicted by the line color intensities in Fig. 4. This is more pronounced for the case of Cu$_3$Au (see Fig. 4a) with relatively higher phonon frequencies as compared to CuAu and CuAu$_3$ since Cu, which has a lighter mass than Au, constitutes 75% of the atomic concentration. This manifests in a broader phonon spectrum with a relatively larger cutoff frequency as compared to that of CuAu and CuAu$_3$. Note CuAu has a tetragonal L1$_0$ crystal structure, whereas, Cu$_3$Au and CuAu$_3$ are cubic structures. Moreover, the contributions to electron–phonon coupling from the optical phonons are ~74%, 46%, and 76% for Cu$_3$Au, CuAu, and CuAu$_3$, respectively. These high contributions from the optical phonon modes lead to relatively larger values of $\lambda$ for the alloys as compared to their elemental counterparts (see Table 1). Moreover, the approximation for $\lambda$ in an alloy of composition $A_{1-x}B_x$ of $\lambda_{\text{alloy}}=(1-x)\lambda_A+x\lambda_B$, which agrees with the trends in $T_c$, is grossly inaccurate for the case of alloys in general [14,43,44]. This is most probably due to the strong contributions from the optical modes in these alloys.

Fig. 5 shows the calculated Eliashberg spectral functions, the corresponding phonon density of states, and the accumulation for $\lambda$ for the copper–gold alloys. As in the case of Nb and Ta (see Fig. 3e and f), the peaks in the spectral functions are already determined by their corresponding density of states with significant contributions from the optical modes as mentioned earlier.

The predicted $\lambda$ from the Eliashberg spectral functions can be used to solve the Eliashberg gap equation and the superconducting transition temperature, $T_c$, using McMillan’s formula given by [2,45].
function of atomic percentage of gold. (f) Ta(e) Nb(d) Au(c) Ag(b) Al(a) as calculated from electronic structure performed with Quantum Espresso package. Volumetric electron–phonon coupling factor, G, for (c) the elemental metals along with experimental data for Al (Ref. [50]), Cu (Ref. [51]), and Au (Ref. [52]), and (d) copper–gold alloys as a function of atomic percentage of gold. (f) G as a function of atomic percentage of gold for the copper–gold alloys.

\[ \tau_{e}^{\text{McM}} = \frac{\omega_{\text{log}}}{1.2} \exp \left( -\frac{1.04(1 + \lambda)}{\lambda - \mu_{c}^{e}(1 + 0.62\lambda)} \right) \]  

(8)

where \( \omega_{\text{log}} \) is a logarithmic average of the phonon frequency and \( \mu_{c}^{e} \) is the Columbic pseudo-potential. The values of \( \mu_{c}^{e} \) define the electron–electron repulsive interaction in metals and are typically taken as \(-0.1–0.13\) as these values are usually not known [14,16]. We note that in our calculations, we do not directly compute \( \mu_{c}^{e} \) from first principles, which is beyond the scope of this study as it requires the proper implementation of both electron–electron and electron–phonon interactions. However, previous works have considered the Coulombic effects to directly compute \( \mu_{c}^{e} \) from first principles [46,47]. For Nb, we predict a \( T_{c} = 9.05 \) K with a \( \mu_{c}^{e} = 0.20 \) utilizing our iterative approach, which is very close to the experimentally measured values of \( T_{c} = 9.25 \) K [48]. A value of \( \mu_{c}^{e} = 0.13 \) predicts a \( T_{c} = 13.4 \) K, which clearly overestimates the critical temperature for Nb. Similarly, for Ta, we predict \( T_{c} = 4.83 \) K for \( \mu_{c}^{e} = 0.16 \), which is very close to the experimentally measured values of \( T_{c} = 4.47 \) K for Ta [48]. The larger values of \( \mu_{c}^{e} \) that correctly predict the critical temperatures for both these metals as compared to the typical values used for other metals suggest that electron–electron repulsive interactions could have a stronger influence in these metals as compared to the other metals studied in this work where \( \mu_{c}^{e} \approx 0.11 \) (see Table 1). However, to correctly validate this, one has to directly compute the Coulombic pseudo-potential by taking into account the electron–electron repulsive interactions along with the electron–phonon interactions as carried out in Refs. [46] and [47], which is beyond the scope of this work but clearly deserves further investigations.

Next, to better understand the physical processes occurring under highly non-equilibrium conditions that are characteristics of metals irradiated with short-pulse lasers or energetic ion bombardment of metal targets [10,53,54], we consider the effect of electron temperature on the volumetric electron–phonon coupling factor. To this effect, we consider the electron–phonon coupling factor derived by Allen [1], as given in Eq. (6). Fig. 6a–d show our calculations of the electronic density of states and G(\( T_{c} \)) for the elemental metals and the copper–gold alloys. In Fig. 6c, we also
include the room-temperature measurements of $G$ for Al, Au, and Cu from pump-probe thermoreflectance measurements for comparison with our calculations [25,50,52]. Overall, the calculations of Eq. (6) agree very well with the pump-probe experimental results at room temperature for three metals. Note, experimental results at relatively high electron temperatures are non-existent in literature, which is mostly due to the lack of analytical formulations (that can be applied beyond the Drude approximations) to correctly interpret the results from pump–probe thermoreflectance experiments [55,56]. For Al, $G$ is independent of electron temperature, which is characteristic of the free-electron-like density of states of Al (see inset of Fig. 6a). For the rest of the metals with $d$-band electrons, at relatively weak thermal excitations ($\sim k_B T_e$), where the density of states is similar to the free-electron gas model with negligible $d$-band excitation, $G$ is independent of temperature. However, at relatively large thermal excitations, significant $d$-band electrons can be excited resulting in a sharp increase in $G$. The $d$-band electrons in Au, Cu, and their alloys (as shown in Fig. 6d and inset of Fig. 6d, respectively) lie $\sim 2$ eV below the Fermi energy, therefore $G$ starts to increase at $T_e \sim 3000$ K. However, for Ag, $G$ remains relatively constant below $T_e < 5000$ K since the $d$-bands are located $\sim 3$ eV below the Fermi energy as shown in Fig. 6a. In contrast to the aforementioned metals, $G(T_e)$ decreases monotonically with electron temperature for the transition metals. This can be attributed to the fact that both Nb and Ta have a wider electron energy spectrum (with $\sim 10$ eV window around Fermi level) and a local dip in the density of states around the Fermi level as shown in Fig. 6b.

Next, we report on the electron thermal conductivities calculated based on the lowest order variational approximation of the Boltzmann transport equation to determine $\kappa_e$, as given in Eq. (7). Fig. 7 shows the thermal conductivity of Al, Ag, Cu, Au, Nb, and Ta for the intermediate temperatures considered in this work. Overall, our predictions of thermal conductivity agree well with the experimentally measured thermal conductivities for these elemental metals. However, for all metals, the theory underestimates the electron-driven thermal conductivity at relatively low temperatures since in our calculations the lattice contributions have been neglected; because of the weak anharmonicity at low temperatures, the lattice contribution to the total thermal conductivity cannot be ignored at relatively low temperatures [58]. The largest discrepancy with experiments is observed for Cu at intermediate temperatures. This could be attributed to the apparently weak contribution from electron–phonon scattering mechanisms to the thermal resistivity in Cu due to the weak electron–phonon coupling ($\lambda = 0.14$). In experimental measurements, the thermal conductivity could also depend on sample purity and the lattice contributions to thermal resistivity, which could substantially lower the measured thermal conductivity.

For our copper–gold alloys, although the electron–phonon mass enhancement parameter increases proportionally with atomic percent of gold as shown in Fig. 6e, the electrical resistivities ($\rho$) do not follow a similar trend as shown in Fig. 8a (solid red squares). Our results of $\rho$ for the copper–gold alloys agree very well with the experimentally measured resistivities for ordered alloys. For comparison, we also include the resistivities measured for disordered alloys in Fig. 8a (hollow black squares). Along with the electron–phonon coupling, the thermal and electrical resistivities also depend on the crystal structure and unit cell volume as is clear from Fig. 8a.

Fig. 8b shows the calculated $\kappa_e$ as a function of atomic percentage of gold for our copper–gold alloys. For comparison, we have included experimental results for ordered (hollow blue circles) and disordered (hollow black squares). In the 50/50 ordered alloy, Cu and Au occupy successive lattice sites, which results in coherent scattering of electron waves and the reduction in resistivity compared to the disordered copper–gold alloys where incoherent scattering of electron waves leads to larger electrical resistivities that increase proportionally with the number of the alloy species as shown in Fig. 8a and also result in lower thermal conductivities. For the 50/50 alloy, our predicted thermal conductivity is higher than that of the disordered alloy measured experimentally. However, our predicted value agrees very well with that of a 50/50 ordered alloy. Surprisingly, our predictions of thermal conductivities for the Cu$_3$Au and CuAu$_3$ alloys agree well with the experimental values for their disordered counterparts. This suggests that coherent scattering of electron waves in ordered systems with large volume fraction mismatch between the two constituents has the same influence on the electronic thermal resistivity as in the case of incoherent scattering of electron waves in the disordered systems for these binary alloys.

### 4. Conclusions

We have calculated the electron–phonon coupling matrix elements considering a dense electronic and phononic wavevector grids under density functional perturbation theory for nine characteristic metals. From the calculated Eliashberg spectral functions, we determine the electron–phonon mass enhancement parameter,
volumetric electron–phonon coupling factor, electrical and thermal resistivities, and superconducting transition temperatures, which agree very well with available experimental data. Our results reveal that even though there are similarities between the phonon density of states of various simple metals, the electronic structure can significantly affect the modal contributions to electron–phonon coupling in metals. While the longitudinal high-frequency phonons contribute significantly to the electron–phonon coupling strength for the free-electron-like aluminum, the transverse phonons dominate the electron–phonon coupling in the noble metals that have high densities of d-band electrons near the Fermi level. In contrast, for intermetallic copper–gold alloys and superconducting metals such as Nb and Ta, the spectral contributions are mostly determined by the phonon density of states–phonon coupling factor. We also find that the temperature-dependent volumetric electron–phonon coupling factor depends strongly on the electronic structures of the metals as it increases for the noble metals and their intermetallic alloys, decreases for the superconducting Nb and Ta, and demonstrates a non-monotonic change for Al. For the copper–gold alloys, the electron–phonon coupling strength and the volumetric electron–phonon coupling factor cannot be taken as the geometric mean and are relatively much larger than that of their elemental constituents. We also find that the electron thermal conductivity of the 50/50 CuAu alloy is relatively higher than that of CuAu and Cu3Au, and the thermal electronic conductivities of the 25/75 and 75/25 alloys are similar to experimental measurements of disordered copper–gold alloys with the same compositions.

Author Contributions
A.G conducted the first-principles calculations with the help of M.V.T. The conceptualization of the work was carried out by A.G, P.E.H., and O.V.P. A.G and P.E.H wrote the manuscript. M.V.T and P edited the manuscript. All authors discussed the data and commented on the manuscript.

Declaration of competing interest
The authors declare that they have no known financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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