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Ab Initio Electronic Relaxation Times and Transport in Noble Metals

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Relaxation times employed to study electron transport in metals are typically taken to be constants and obtained empirically. Here, we use fully ab initio calculations to compute the electron-phonon relaxation times of Cu, Ag, and Au, and find that they vary significantly on the Fermi surface, spanning ~ 15 – 45 fs values that are correlated with the Fermi surface topology. We compute room temperature resistivities in excellent agreement with experiment by combining GW quasiparticle bandstructures, Wannier-interpolated band velocities, and ab initio relaxation times. We introduce an importance sampling scheme to speed up the convergence of resistivity and transport calculations.

Copper, silver, and gold are noble metals with broad application in electronics, power generation, catalysis, and plasmonics. They have attracted interest since the early days of solid state theory as their electronic structure deviates from the free-electron model that applies to the alkali metals. The Fermi surface (FS) of noble metals is not spherical as in free-electron theory, but is deformed due to the proximity of the d bands to the free-electron-like sp band [1–4]. Electron scattering processes at the FS are of particular relevance for noble metal applications as they regulate charge and heat transport [5, 6]. At room temperature in relatively pure metals, scattering with phonons [7, 8] is dominant, while scattering with defects and impurities is important at low temperature and in alloys or samples with low purity.

Transport in metals can be understood heuristically with the Drude theory [9], which assumes free electrons with a constant (that is, band- and \mathbf{k} -independent) relaxation time (RT). Even in noble metals, where important deviations are expected from the Drude theory, resistive losses and optical experiments are routinely interpreted using constant relaxation times [9–11]. More advanced models, such as state-of-the-art ab initio calculations of resistivity and other transport properties [12, 13], typically employ density functional theory (DFT) bandstructures combined with constant RTs inferred from experiment or estimated heuristically.

However, the RT of an electron in a Bloch state depends, in general, on the band and crystal momentum \mathbf{k} , a point that has so far been often neglected. Accurate calculations of electron RTs are computationally costly as they require fine Brillouin zone (BZ) sampling [14–16], prompting adoption of simplified schemes that employ either a constant RT [17] or an average scattering strength [18]. An exception are recent transport calculations in Al [19] and two-dimensional materials [19–21] that included the band and \mathbf{k} dependence of the RTs.

As striking new experimental findings emerge in noble metals [22–24], predictive theories are needed to study electron scattering in these materials. For example, re-

cent experiments from Kim et al. [22] show a remarkable resistivity drop upon doping a single crystal of Ag with a small fraction of Cu, at odds with the intuition that the resistivity should increase upon alloying due to enhanced impurity scattering. While the constant RT approach may be too simplistic, at present it is not known whether more refined theories are necessary to improve quantitative understanding of the noble metals.

Here we compute electron-phonon (e -ph) RTs and GW band velocities of Cu, Ag, and Au on fine \mathbf{k} -point grids. We develop a linear interpolation approach to sample \mathbf{k} -points directly on the FS, and use it to study the correlation of the RTs and velocities to FS topology. We find that the e -ph RTs are far from constant on the FS. They vary by a factor of 2–3 between their minima and maxima, located at FS regions with different curvatures. The band velocity maps on the FS exhibit anti-correlation with the e -ph RT maps. We investigate approximations to compute the resistivity of Cu, Ag and Au at room temperature, and find excellent agreement (within $\sim 10\%$) with experiment only when ab initio RTs and GW velocities are used. Our FS sampling approach dramatically speeds up the convergence of resistivity calculations, and may be extended to study heat transport and thermoelectric effects in materials.

We carry out DFT calculations at experimental lattice constants (Cu: 3.61 Å, Ag: 4.09 Å, Au: 4.08 Å) using the local density approximation (LDA) [25] and a plane-wave basis with the QUANTUM ESPRESSO code [26]. Scalar-relativistic norm-conserving pseudopotentials [27] (including semicore s and p states) are employed, using kinetic energy cutoffs of 240 Ry for Cu and 180 Ry for Ag and Au and shifted 10^3 \mathbf{k} -point grids, to determine the ground state charge density. Spin-orbit effects are neglected. The quasiparticle energies are computed within the G_0W_0 and generalized plasmon pole approximations [28, 29] using the BERKELEYGW package [30]. Our GW calculations are well converged using a 50 Ry cutoff for the dielectric matrix, which was evaluated on a 8^3 \mathbf{k} -point grid for interband transitions (finite \mathbf{q}) and a

16^3 \mathbf{k} -point grid for intraband transitions ($\mathbf{q} \rightarrow 0$), and using ~ 1000 unoccupied bands, consistent with previous studies [31–33].

The e -ph matrix elements are computed on fine \mathbf{k} -point grids with a procedure detailed in Ref. [16]. Briefly, we use density functional perturbation theory [34] to determine the phonon dispersions and displacement patterns and e -ph coupling matrix elements on a coarse $4 \times 4 \times 4$ \mathbf{q} -point grid. The bandstructures, phonon dispersions, and e -ph matrix elements are interpolated using maximally localized Wannier functions [35–37] constructed

from Bloch states on a 12^3 \mathbf{k} -point grid. All quantities are interpolated using the EPW code [38, 39] with our recently developed approach [14–16]. The velocities are calculated in the Wannier representation [40] using GW eigenvalues. For e -ph and resistivity calculations, we use the tetrahedron method [41] to obtain the FS as a collection of triangular facets, whose centroids constitute an ultra-fine \mathbf{k} -point grid employed in the calculations to sample the FS. Following Mahan [8], the e -ph transport relaxation scattering rates $\Gamma_{n\mathbf{k}}$ (and their inverse, the RTs $\tau_{n\mathbf{k}} = \Gamma_{n\mathbf{k}}^{-1}$) are computed with perturbation theory, due to the interaction with phonons:

$$\Gamma_{n\mathbf{k}} = \frac{2\pi}{\hbar} \sum_{m\mathbf{q}\nu} |g_{nm,\nu}(\mathbf{k}, \mathbf{q})|^2 (1 - \cos \theta_{\mathbf{k}, \mathbf{k}+\mathbf{q}}) \cdot [(N_{\nu\mathbf{q}} + f_{m\mathbf{k}+\mathbf{q}}) \delta(\epsilon_{n\mathbf{k}} - \omega_{\nu\mathbf{q}} - \epsilon_{m\mathbf{k}+\mathbf{q}}) + (N_{\nu\mathbf{q}} + 1 - f_{m\mathbf{k}+\mathbf{q}}) \delta(\epsilon_{n\mathbf{k}} + \omega_{\nu\mathbf{q}} - \epsilon_{m\mathbf{k}+\mathbf{q}})] \quad (1)$$

where $g_{nm,\nu}(\mathbf{k}, \mathbf{q})$ are e -ph coupling matrix elements for an electron in Bloch state $|n\mathbf{k}\rangle$ (with quasiparticle energy $\epsilon_{n\mathbf{k}}$) that scatters into a Bloch state $|m\mathbf{k} + \mathbf{q}\rangle$ (with quasiparticle energy $\epsilon_{m\mathbf{k}+\mathbf{q}}$) due to a phonon with polarization ν , wavevector \mathbf{q} , and frequency $\omega_{\nu\mathbf{q}}$. Here, $\theta_{\mathbf{k}, \mathbf{k}+\mathbf{q}}$ is the scattering angle between \mathbf{k} and $\mathbf{k} + \mathbf{q}$. The two terms in square brackets correspond to phonon absorption and emission, respectively, and the temperature dependence stems from the occupation factors $f_{n\mathbf{k}}$ and $N_{\nu\mathbf{q}}$, for electrons and phonons respectively (in this work, both the electrons and the phonons are at 300 K). The conductivity tensor from Boltzmann transport theory within the relaxation-time approximation is expressed as the FS integral [5, 8]

$$\sigma_{\alpha\beta} = \frac{2}{(2\pi)^3} \frac{e^2}{\hbar} \sum_n \int dS_F \frac{v_{n\mathbf{k},\alpha} v_{n\mathbf{k},\beta}}{|\mathbf{v}_{n\mathbf{k}}|} \tau_{n\mathbf{k}} \quad (2)$$

where $v_{n\mathbf{k},\alpha}$ are Cartesian components ($\alpha = x, y, z$) of the velocities and $\tau_{n\mathbf{k}}$ e -ph RTs. The area elements dS_F correspond to the area of the triangular facets that make up the FS within our interpolation scheme. The resistivity ρ is obtained from the trace of the inverse of the conductivity tensor, i.e., $\rho = \text{Tr}[\sigma^{-1}]/3$ [42].

The computed Fermi surfaces (see Figure 1) exhibit well-known [1–4] topological features, including open-orbit regions with upward curvature (known as “necks”) near the L points of the BZ, spherical regions known as the “belly”, as well as flatter regions near the K points between the necks, and “bulges” where the FS approaches the BZ edge at the X points. The FS of Ag is noticeably different from those of Cu and Au, with much smaller necks and less pronounced bulges, and an overall more spherical shape due to the d bands being lower in energy compared to Cu and Au.

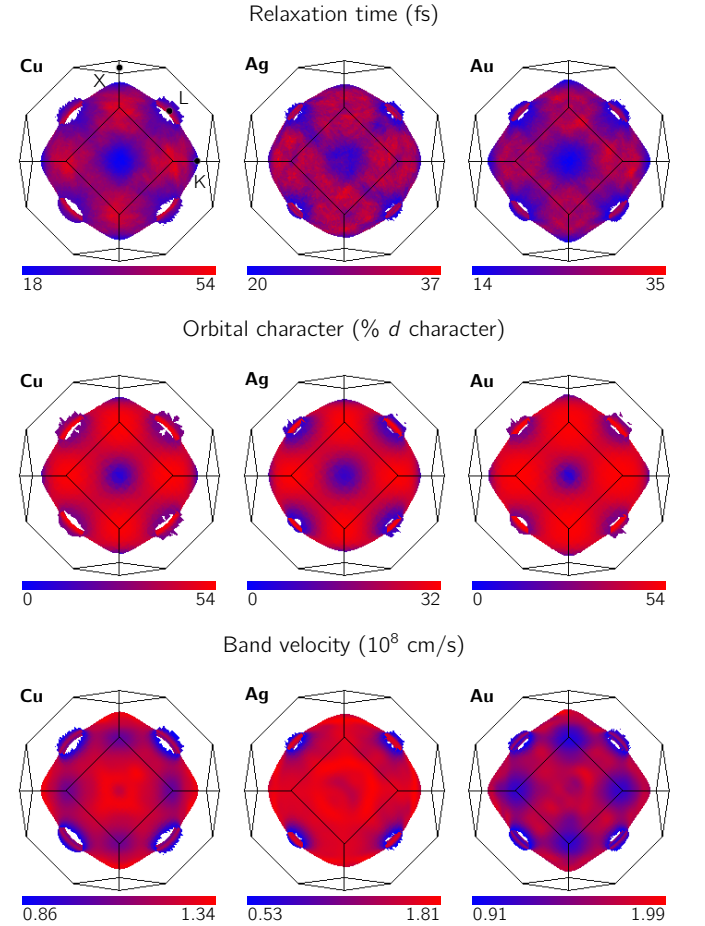


FIG. 1. Electron-phonon relaxation times (top panel), orbital character (middle panel), and band velocities (bottom panel) of states on the Fermi surface of Cu, Ag, and Au.

Figure 1 shows maps of the e -ph RTs and GW velocities calculated at \mathbf{k} -points on the FS. For all three materials, we find large variations in the RTs, with the necks

and bulges exhibiting shorter RTs than the belly and flat regions between the necks. The RTs vary the most in Cu and Au, with a factor of ~ 3 difference between the minima (located near the L and X points) and maxima (located near the K point), while the variation in Ag is smaller, only a factor of ~ 2 difference between minima and maxima. The velocities show an opposite trend, so that FS regions with longer (shorter) relaxation times are associated with smaller (larger) velocities. Cu and Au exhibit moderate variations in the velocities, while Ag shows a large difference. The difference between the minimal velocities at the necks and the maximal velocities at the belly is a factor of ~ 2 in Cu and Au and a factor of ~ 4 in Ag.

We investigate the physical origin of the variation of the RTs and velocities on the FS. By mapping the orbital character of the electronic states on the FS (see Figure 1), we find a correlation between the character of the state and its RT. Electronic states with a predominantly sp character, as found in the necks and bulges of the FS, are associated with shorter RTs, while states with large d character exhibit longer RTs.

In Figure 2, we explore quantitatively the origin of the anisotropic RTs for the case of Ag, by choosing initial states with sp and $sp+d$ character respectively, and computing the coupling matrix elements $|g|^2$ connecting these initial \mathbf{k} -points to all other final \mathbf{k} -points on the FS. These matrix elements are the ones entering the calculation of the RTs for each of the initial states within our approach [Eq. (2)], and we now seek to categorize them based on the character of the initial and final states in the e -ph scattering processes.

For an initial state near X with dominant sp character, the coupling, as measured by the sum over phonon polarizations of the matrix element between the initial and final states, $\sum_{\nu} |g_{\nu}|^2$, is strongest to final states with d admixture along the $[110]$ directions. We find that coupling to other final states with some d character is in general weaker and strongly anisotropic, so that different groups of final d -like states exhibit $|g|^2$ values distributed in multiple sets (see Figure 2). As the fraction of d character of the final state decreases, the coupling decreases monotonically.

For an initial state near the K point with large d character, coupling is strong to one set of d -like states (along $[110]$), and weak to most other d -like states. Two distinct sets of $|g|^2$ values are found for such d - d coupling (see Figure 2). As the d character of the final state decreases, different final states exhibit different trends: for some states the coupling becomes stronger, while for others it becomes weaker. Overall, the average $|g|^2$ is greater by a factor of 1.2 for the initial sp state near X , thus explaining the higher scattering rate (which is proportional to $|g|^2$) and shorter RT compared to states with large d character, as discussed above. While further in-

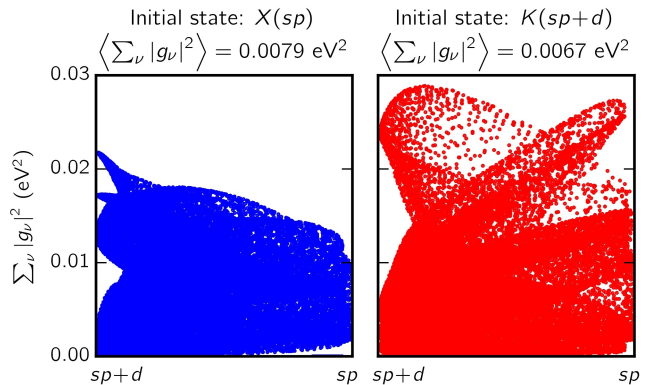


FIG. 2. Electron-phonon coupling matrix elements for an initial electronic state of predominantly sp character (left panel) and an initial state with large d character (right panel). Shown are the e -ph coupling matrix elements (summed over phonon polarizations) versus the character of the final electronic state involved in the e -ph scattering process. For each initial state, the average coupling matrix element is also given.

TABLE I. Comparison of relaxation times and velocities computed by averaging on the Fermi surface (values in brackets), versus the same quantities obtained within Drude theory (subscript D). The Fermi surface averaged relaxation times are computed using GW bandstructures, while the band velocities are given for both the DFT and GW bandstructures for comparison. The Drude values are obtained using Eq. (3) with resistivity experimental data [22, 43] from single-crystal samples.

	τ (fs)		v (10^8 cm/s)		
	$\langle \tau_{nk} \rangle$	τ_D	$\langle v_{nk}^{DFT} \rangle$	$\langle v_{nk}^{GW} \rangle$	v_D
Cu	37	27 ^a	1.13	1.19	1.57
Ag	30	41 ^b	1.45	1.55	1.39
Au	24	30 ^c	1.38	1.52	1.39

^a Ref. 43

^b Ref. 22

^c Using estimated SC resistivity

vestigation is needed to more completely understand the role of the character of the initial and final state and the perturbation potential, our results demonstrate that the e -ph matrix elements are highly anisotropic and depend strongly both on the character of the initial and final state and on the wavevector connecting the initial and final state through the perturbation potential induced by the phonons. The combination of these effects results in the anisotropic RTs found here. The variation in the velocities is easier to explain. It can be understood by considering the curvature of the FS: flatter regions have smaller velocities compared to more curved regions, given that the latter are associated to a higher gradient of the band at the Fermi energy.

To highlight the difference between the ab initio and empirical data, we compare in Table I Fermi-surface-

averaged RTs $\langle\tau_{n\mathbf{k}}\rangle$ and velocities $\langle v_{n\mathbf{k}}\rangle$, obtained by averaging the ab initio data in Fig. 1, with values derived from the free-electron Drude model:

$$\tau_D = \frac{m^*}{ne^2\rho}, \quad v_D = \frac{\hbar(3\pi^2n)^{1/3}}{m^*}. \quad (3)$$

where τ_D and v_D are the empirical Drude RT and free electron velocity, respectively. The ab initio average quantities $\langle X \rangle$ (with $X = \tau, v$) are computed over the triangular facets that compose the FS, using $\sim 10,000$ \mathbf{k} -points and weighing by the facet area:

$$\langle X \rangle = \frac{\sum_t A_t X_{\mathbf{k}_c}}{\sum_t A_t}, \quad (4)$$

with A_t the facet area for a triangle t and \mathbf{k}_c its centroid. The Drude RTs τ_D are calculated using the resistivity ρ measured on single-crystal samples [22, 43] (see Table II); we further obtain the charge density n using 1 free electron per unit cell and take the effective mass $m^* = m_e$, consistent with a simple Drude treatment of noble metals [9]. We find that $\langle\tau_{n\mathbf{k}}\rangle$ of Cu is 50% larger than the Drude value, while $\langle\tau_{n\mathbf{k}}\rangle$ of Ag and Au are 15–25% smaller than their respective Drude RTs. The magnitude of the velocities averaged over the FS show the opposite behavior, with $\langle v_{n\mathbf{k}}\rangle$ smaller in Cu and larger in Ag and Au than the Drude value. These results challenge the accuracy of the widely used empirical Drude model. In particular, since the tabulated Drude RTs are constants, they miss the complex trends and significant variation on the FS found here. The Drude RTs should thus be regarded as mere model parameters used to interpret transport and optical experiments in the absence of ab initio data.

Next, we use our results to compute the resistivity of Cu, Ag, and Au, comparing a range of approximations for the RTs and velocities. Table II shows the resistivities calculated with GW velocities in combination with i) full band- and \mathbf{k} -resolved RTs $\tau_{n\mathbf{k}}$, ii) Fermi-surface-averaged ab initio RTs $\langle\tau_{n\mathbf{k}}\rangle$, and iii) empirical Drude RTs τ_D . For comparison, we also compute the resistivities using the common hybrid approach which combines DFT (as opposed to GW) velocities with Drude RTs. We compare our calculated resistivities with experiments at 293 K for single-crystal (SC) samples. Polycrystalline (PC) experimental data [44] are also given. Since in pure SC samples at room temperature the source of resistivity is almost exclusively e -ph scattering, our approach using e -ph RTs is justified.

We first discuss the data in Table II obtained with our best approximation, namely ab initio $\tau_{n\mathbf{k}}$ and GW velocities. In the case of Cu, the agreement with SC experiment is excellent (within 1%). For Ag and Au we find resistivities that are larger by $\sim 10\%$ than experiment. We attribute this small discrepancy to a number of sources, including the ~ 0.1 eV accuracy of the quasiparticle energies obtained via the GW method, and a

TABLE II. Resistivity values (units of $\mu\Omega\text{ cm}$) at 300 K computed using GW band velocities and different approximations for the relaxation times. $\tau_{n\mathbf{k}}$ are band and \mathbf{k} -dependent from ab initio, $\langle\tau_{n\mathbf{k}}\rangle$ are Fermi surface averaged from $\tau_{n\mathbf{k}}$, and τ_D are empirical Drude relaxation times. Also shown are the computed values from DFT velocities and empirical Drude relaxation times. Experimental data for single crystal (SC) and polycrystalline (PC) samples are shown for comparison.

	Computed ρ				Experimental ρ	
	$\tau_{n\mathbf{k}}$	$\langle\tau_{n\mathbf{k}}\rangle$	τ_D	DFT+ τ_D	SC	PC
Cu	1.51	1.51	2.05	2.19	1.52 ^a	1.67 ^a
Ag	1.81	1.83	1.34	1.43	1.49 ^b	1.59 ^b
Au	2.24	2.24	1.82	2.01	2.0 ^c	2.26

^a Ref. 43

^b Ref. 22

^c Estimated from PC resistivity

$\sim 5\%$ uncertainty in the RTs depending on whether the cosine factor in Eq. (1) is employed or not [8]. Using the average RTs $\langle\tau_{n\mathbf{k}}\rangle$ with GW velocities gives nearly identical resistivities as the band- and \mathbf{k} -resolved RTs, thus suggesting that approximate schemes using a constant RT should employ Fermi-surface-averaged ab initio data rather than empirical data.

For all three materials, we find that the velocities obtained from the GW quasiparticle bandstructures are $\sim 10\%$ larger than those obtained via DFT (see Table I), consistent with previous studies in Au [33] showing large effect from GW on the d band energies and sp band width. For Ag and Au, the smaller DFT velocities, combined with Drude RTs that are larger than the ab initio values, yield resistivities in fortuitous agreement with experiment when using the DFT velocity plus τ_D approach, a result of compensation of errors. For Cu, on the other hand, the DFT velocity plus τ_D approach gives a resistivity almost 50% higher than experiment. Our results highlight the predictive character of calculations combining GW bandstructures and velocities with ab initio e -ph RTs.

The resistivity calculations in Table II are obtained with a novel approach that employs direct FS sampling instead of a homogeneous \mathbf{k} -grid in the BZ, affording orders of magnitude speed up the convergence of the resistivity with respect to the number of \mathbf{k} -points, as discussed in the Supplemental Material [45]. In addition, the convergence is monotonic with our FS integration approach, while the resistivity fluctuates significantly when a homogeneous \mathbf{k} -grid is employed [45]. This approach is highly promising to compute transport properties beyond the resistivity [45].

In conclusion, we show that the e -ph RTs and velocities vary considerably on the FS of Cu, Ag, and Au. The correlation between RTs, velocities and FS topology found here may extend to other classes of materials with

complex Fermi surfaces. Our work points out the shortcomings of employing empirical RTs, DFT bands, and uniform \mathbf{k} -grids to compute transport properties in materials. It further suggests that even energy-dependent (but not \mathbf{k} -dependent) RTs, also commonly employed in transport studies, would miss the complex interplay of bandstructure and scattering processes. These observations may extend to defect and impurity scattering, which will be the subject of future investigations. While complex non-equilibrium approaches are being explored for carrier dynamics, we argue that accurate ab initio state-dependent RTs may yield close agreement with experiment in many cases of practical interest, even within the semiclassical Boltzmann RT approach.

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- [45] See Supplemental Material at [URL] for Figure S1 showing the convergence with our FS integration vs. homogeneous \mathbf{k} -grid integration, and the related discussion.