Linear-Response Calculations of Electron-Phonon Interactions

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A new, generally applicable method is developed for *ab initio* calculation of the wave-vector dependent electron-phonon coupling. The screening of the one-electron potential is evaluated by linear-response theory using the local-density approximation and linear muffin-tin orbitals. We calculate electron-phonon coupling strengths and transport properties in Al and, for the first time, in Nb and Mo. Our results are consistent with the experimental results and are compared with previous theoretical results.

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The electron-phonon interaction is decisive for many properties of metals [1], such as the electrical and thermal resistivities, superconductivity, and the renormalization of the linear electronic specific heat. In the strong-coupling theory of superconductivity [2], a central quantity is the electron-phonon spectral distribution function $\alpha^2F(\omega)$ and its first reciprocal moment λ. The problem to calculate λ *ab initio* is important, in particular, for quantitative understanding of high-temperature superconductivity. The purpose of this Letter is to develop a new generally applicable method for calculating this quantity which essentially amounts to the self-consistent finding of the full low-energy excitation spectrum of the metal: the quasiparticle energies $E_{\mathbf{k}j}$ and the phonon frequencies $\omega_{\mathbf{q}\nu}$. The most popular estimate of $E_{\mathbf{k}j}$ is the one-electron band structure obtained from a density-functional calculation in the local-density approximation (LDA) [3].

Many previous attempts to compute λ, in particular for transition metals, focused on calculating merely the so-called electronic contribution [4], while the phonon frequencies and eigenvectors were usually taken from inelastic neutron-scattering data and the self-consistent adjustment of the one-electron potential to the phonon distortion was replaced by rigid-ion [5] or rigid-muffin-tin [6] approximations (RIA or RMTA). That these approximations are not justified in general was shown for the case of aluminium by Winter [7] using linear-response theory for the screening.

Accurate phonon frequencies and eigenvectors, as well as the self-consistent screening and, hence, the electron-phonon interaction, may however, be calculated with the frozen-phonon total-energy approach using supercells, but only for commensurate phonon wave vectors $\mathbf{q}$ [8–11]. With the crude sampling allowed by the limited size of the supercell, the accuracy of $\mathbf{q}$-integrated quantities like λ is usually not high enough for estimating for instance T_c.

An efficient linear-response technique based on the solid-state Sternheimer method [12] was recently developed and shown to produce accurate phonon dispersions and eigenvectors for arbitrary $\mathbf{q}$ in transition metals [13]. The important advantage of this method over that of Baroni *et al.* [12] that systems with narrow bands such as d bands are treated as easily as systems with only broad bands because it uses muffin-tin, rather than plane-wave, basis sets for the electron wave functions. In the present Letter, we generalize this method to the computation of the wave-vector dependent electron-phonon coupling. The screening potential for every $\mathbf{q}$ is found self-consistently without the use of any RMTA or RIA. $\alpha^2F(\omega)$ and λ are obtained by integration over the whole Brillouin zone. We demonstrate the applicability of this all-electron approach by computing $\alpha^2F(\omega)$ for a few elemental metals, the sp-band metal Al and for the d-band metals Nb and Mo. Moreover, we present the results for the transport properties: the dimensionless λ_{tr} as well as the phonon-limited electrical and thermal resistivities at 273 K. For the d-band metals, these are the first fully screened *ab initio* calculations.

Our method employs the expression [14]

$$\alpha^2F(\omega)=\frac{1}{2\pi N(0)}\sum_{\mathbf{q}\nu}\frac{\gamma_{\mathbf{q}\nu}}{\omega_{\mathbf{q}\nu}}\delta(\omega-\omega_{\mathbf{q}\nu}), \tag{1}$$

for $\alpha^2F(\omega)$ in terms of the phonon linewidths $\gamma_{\mathbf{q}\nu}$ arising from the electron-phonon interaction. Here, and in the following, we use atomic Rydberg units, $\sum_{\mathbf{q}}$ means the average over the Brillouin zone (BZ), ν numerates the phonon branches, and $N(0)$ is the electronic density of states per atom and per spin at the Fermi level. The linewidths are given by the Fermi "golden rule" which, when the energy bands around the Fermi level are linear in the range of the phonon energies, may be written as

$$\gamma_{\mathbf{q}\nu}=2\pi\omega_{\mathbf{q}\nu}\sum_{\mathbf{k}jj'}\delta(E_{\mathbf{k}j})\delta(E_{\mathbf{k}+\mathbf{q}j'})|g^{\mathbf{q}\nu}_{\mathbf{k}+\mathbf{q}j',\mathbf{k}j}|^2, \tag{2}$$

where j and j' are the band indices, $E_{\mathbf{k}j}$ are the energies with respect to the Fermi level, and $g^{\mathbf{q}\nu}_{\mathbf{k}+\mathbf{q}j',\mathbf{k}j}$ is the electron-phonon matrix element. The standard definition of g is simply the probability of scattering from the one-electron state $|\,\mathbf{k}j\rangle$ to the state $|\,\mathbf{k}+\mathbf{q}j'\rangle$ via the phonon $\mathbf{q}\nu$. In a case like ours, where the electronic states are approximated by superpositions of atom-centered orbitals, it is inconvenient to evaluate this expression because it involves the orbitals at the equilibrium atomic

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positions and the potential for the displaced lattice. The reason is that the states $|\ \mathbf{k}j\rangle$ in the band calculation are obtained not as *exact* solutions of the one-electron Scrödinger equation but as the best approximation for the equilibrium positions, using the Rayleigh-Ritz variational principle with a finite orbital basis $|\ \chi_\alpha^{\mathbf{k}}\rangle$. This introduces important incomplete-basis-set (IBS) corrections into the dynamical-matrix calculation [13]. The IBS terms must also be taken into account when evaluating the electron-phonon matrix elements. They can be easily found by repeating the standard quantum-mechanical derivation of the Fermi golden rule: The scattering rate for transitions from an initial, unperturbed state into a final, perturbed state is the overlap integral squared. Since the final state corresponds to the displaced lattice, the best variational estimate for it must include the orbitals centered at the new atomic positions and adjusted to the new one-electron potential. To linear order with respect to the displacements this leads to finding the change in the basis $|\ \chi_\alpha^{\mathbf{k}}\rangle$. The definition of g for use in (2) is thus

$$g^{\mathbf{q}\nu}_{\mathbf{k}+\mathbf{q}j',\mathbf{k}j} = \langle \mathbf{k}+\mathbf{q}j' \mid \delta^{\mathbf{q}\nu}V \mid \mathbf{k}j\rangle + \left\langle \sum_\alpha \delta^{\mathbf{q}\nu}\chi_\alpha^{\mathbf{k}-\mathbf{q}} A_\alpha^{\mathbf{k}+\mathbf{q}j'} \mid H - E_{\mathbf{k}j} \mid \mathbf{k}j \right\rangle + \left\langle \mathbf{k}+\mathbf{q}j' \mid H - E_{\mathbf{k}j} \mid \sum_\alpha \delta^{\mathbf{q}\nu}\chi_\alpha^{\mathbf{k}} A_\alpha^{\mathbf{k}j} \right\rangle, \quad (3)$$

where $A_\alpha^{\mathbf{k}j}$ are the coefficients of $|\ \chi_\alpha^{\mathbf{k}}\rangle$ in the expansion of $|\ \mathbf{k}j\rangle$, and where $\delta^{\mathbf{q}\nu}V$ and $\delta^{\mathbf{q}\nu}\chi_\alpha^{\mathbf{k}}$ are, respectively, the changes in the one-electron potential and the basis due to the phonon distortion [15]. Formula (3) is the linear-response analogy of evaluating $g^{\mathbf{q}\nu}_{\mathbf{k}+\mathbf{q}j',\mathbf{k}j}$ via the splitting of the bands in the frozen-phonon supercell method as done in Ref. [11]. It is less sensitive to the errors in the wave functions introduced by the variational principle, has a correct long wavelength behavior, and allows one to avoid the inclusion of $d-f$ transitions in d-electron systems. The IBS corrections are represented by the second and third contributions in (3). They disappear for plane-wave basis sets but should be taken into account when using linear muffin-tin-orbital (LMTO) and linear augmented-plane-wave (LAPW) bases [16], as we shall do.

The phonon linewidths $\gamma_{\mathbf{q}\nu}$ (2) often display violent variations through the BZ [17] for phase-space reasons, such as Fermi-surface nesting, and the $\mathbf{q}$ summation in expression (1) for $\alpha^2F(\omega)$ must therefore be performed on a rather dense mesh. The phonon frequencies $\omega_{\mathbf{q}\nu}$ are, however, relatively smooth functions of $\mathbf{q}$ and need therefore not be computed on such a dense mesh. The procedure we used is based on transformation of the dynamical matrix to real space: First, we performed self-consistent LDA-LMTO linear-response calculations [13] of $\omega_{\mathbf{q}\nu}$ for 10 special $\mathbf{q}$ points. Each electronic-structure calculation employed a large number of $\mathbf{k}$ points (256) and a double-κ *spd*-LMTO basis set [18] with the one-center spherical-harmonics expansions of the wave functions, as well as of the full potential, carried up to $l_{\max}$=8. Next, by summing over the 10 $\mathbf{q}$ points with the factor $e^{i\mathbf{q}\cdot\mathbf{T}}$, we constructed the dynamical matrix on the real-space lattice $\mathbf{T}$. Inverse Fourier summation and subsequent diagonalization finally yielded the phonon frequencies and eigenvectors for any $\mathbf{q}$. In order to calculate $\alpha^2F(\omega)$ and λ, the phonon linewidths were calculated for 47 $\mathbf{q}$ points. For each, the self-consistent screening potential $\delta^{\mathbf{q}\nu}V$ was found using a small setup (47 $\mathbf{k}$ points instead of 256 and a single-κ LMTO basis set) which introduces only a (1–2)% error of the final results. The $\mathbf{k}$-space integration in (2) involving the two δ functions was performed with a very large number of $\mathbf{k}$ points (752) and using the full-zone tetrahedron method [19]. The largest numerical error of $\alpha^2F(\omega)$ came from the $\mathbf{q}$-space integration in (1). Its magnitude, we estimated by performing the integration over merely the band-structure factor [which is $\gamma_{\mathbf{q}\nu}$ approximated by $\sum_{\mathbf{k}jj'}\delta(E_{\mathbf{k}j})\,\delta(E_{\mathbf{k}+\mathbf{q}j'})$] using respectively 47 and 752 $\mathbf{q}$ points and found it to be about 6% in both Nb and Mo. The total numerical error is thus about 10%. All the calculations were performed at the experimental lattice constants.

We now discuss our *ab initio* results obtained for Al. Figure 1 shows the calculated $\alpha^2F(\omega)$ (full line) in comparison with the tunneling measurements [20] (squares). The two curves are similar. Our $\alpha^2F(\omega)$ is found to be very close to the empirical pseudopotential result [21] based on the rigid-ion approximation. General agreement is also found between our and the *ab initio* frozen-phonon results of Dacorogna *et al.* [9] for the dispersion of $\gamma_{\mathbf{q}\nu}$ along the high-symmetry directions. The only exception is that, in the [110] direction, our longitudinal branch exceeds theirs by a factor of 2, which is presumably connected with replacing the δ functions in (2) by Gaussians used in Ref. [9]. However, the relative weight of our high γ values in the integrated quantity is found to be very small. Our λ value of 0.44 is very close to the value 0.42 extracted from the tunneling measurements [20] (see Ta-

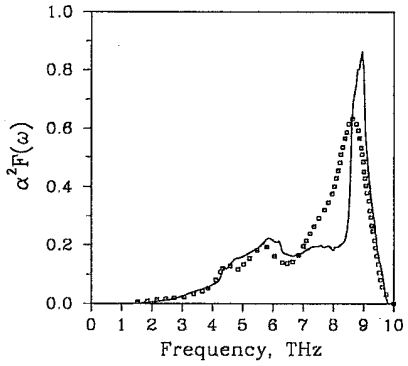

FIG. 1. Calculated spectral function $\alpha^2F(\omega)$ (solid line) for Al in comparison with the tunneling data (squares) [20].

TABLE I. Comparison between calculated and experimental values of electron-phonon coupling constant λ, electrical resistivity ρ [$\mu\Omega$ cm] and thermal resistivity w [K cm/W] at 273 K. Also shown are the calculated transport parameters λ_{tr}. Values in parentheses give decomposition of λ in Nb by the Fermi-surface sheets (octahedron, jungle gym, and ellipsoids).

	Al	Nb	Mo
λ^{calc}	0.44	1.26(1.44,1.37,1.08)	0.42
λ^{exp}	0.42[a]	1.33(1.71,1.43,1.10),[b] 1.04[c]	0.44[d]
λ_{tr}^{calc}	0.36	1.17	0.35
ρ^{calc}	2.35	13.67	4.31
ρ^{exp}	2.43[e]	13.30[e]	4.88[e]
w^{calc}	0.42	2.17	0.73
w^{exp}	0.42[e]	1.93[e]	0.72[e]

[a]Reference [20].
[b]Reference [26].
[c]Reference [20], see also Ref. [25].
[d]From T_c using μ^*=0.13.
[e]Reference [31].

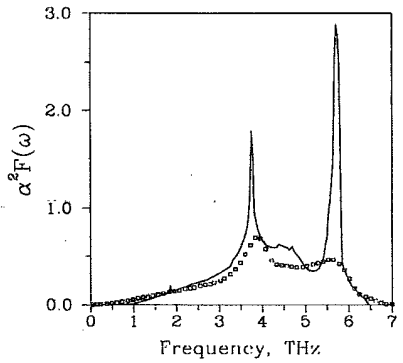

FIG. 2. Calculated spectral function $\alpha^2F(\omega)$ (solid line) for Nb in comparison with the tunneling data (squares) [20].

ble I). The frozen-phonon [9] and the linear-response calculation of Winter [7] gave, respectively, $\lambda = 0.45$ and 0.38. The λ value derived from specific-heat measurements with use of our calculated value for the density of states at the Fermi level, $N(0)$ =2.74 states/(Ry spin), is 0.42. In order to check previous conclusions [7,22] about the inapplicability of the RMTA for *sp* metals, we also performed such a calculation and indeed found λ =0.14. The further calculated quantities listed in Table I are the electronic transport parameter λ_{tr}, as well as electrical (ρ) and thermal (w) resistivities at 273 K. The computational method is analogous to that used in superconductivity theory and based on the low-order variational estimate of the solution of Boltzman's equation [23]. We have not found any qualitative differences in the calculated transport spectral function comparing to the usual one; our $\lambda_{tr} = 0.36$, which is close to the superconducting λ. The calculated values of ρ and w agree well with those measured.

Nb is the best studied elemental superconductor, mainly because of its relatively high $T_c = 9.25$ K. Many theoretical RMTA based calculations exist in the literature [17,22,24] and a large variety of λ (1.12–1.86) have been obtained. Also the results of tunneling measurements have been controversial [20]. In Fig. 2 we compare our calculated $\alpha^2F(\omega)$ (full lines) with the tunneling data of Ref. [20] (squares). Even though the theoretical $\alpha^2F(\omega)$ should be broadened because the δ function in Eq. (1) ought to be a Lorentzian of half-width $\gamma_{q\nu}$, this tunneling experiment yields a coupling (λ_{tun}=1.04 [20,25]) which is weaker than what we calculate (λ=1.26). We obtain similar results with the RMTA, in full agreement with earlier calculations [17,24], and thus conclude that the full inclusion of screening does not resolve this discrepancy. Comparison of our LDA band masses with those measured by the de Haas–van Alphen (dHvA) effect [26] yields an average mass enhancement of 1.33, which is close to the 1.26 found in our electron-phonon calculation. The ratio of the measured electronic specific heat coefficient to our calculated LDA density of states, $N(0)$ =10.21 states/(Ry spin), also yields an enhancement of 1.3. Another important result is that the measured *variation* of the mass enhancement for the various cyclotron orbits agrees well with what our linear-response calculation yields (Table I), but it strongly disagrees with what is found with the RMTA [26]. Now, since both the cyclotron masses and the electronic specific-heat coefficient are enhanced by electron-electron interactions, on top of the electron-phonon interactions, the tunneling data could still be correct and our calculation wrong. However, our calculated values of electrical and thermal resistivities are close to the measured values (see Table I). Moreover, the LDA value for the spin-lattice relaxation rate calculated without any spin enhancement (beyond about 10%) is in good agreement with the experimental value [27]. It therefore seems that the electron phonon λ is 1.2–1.3, and that the mass enhancement due to electron-electron interactions is less than 20% in Nb. Using such a large λ value together with the measured T_c value in the McMillan formula [28] requires a Coulomb pseudopotential of $\mu^* \sim 0.2$ rather than the smaller value $\sim$0.14 which is usually assumed [29].

We finally discuss our results for Mo. There are no tunneling data for this material because of its low $T_c = 0.92$ K and the weakness of phonon effects. Our linear-response calculations of $\alpha^2F(\omega)$ are found to be close to our RMTA calculations and to earlier ones [30]. Our total λ is 0.42, which is in a good agreement with the value 0.44 extracted from McMillan's T_c expression using μ^*=0.13. The calculated transport spectral function displays behavior very similar to that of the superconductor ($\lambda_{tr} = 0.35$); our electrical and thermal resistivities are close to those measured, as shown in Table I.

In summary, we have presented *ab initio* self-consistent linear-response calculations of the electron-phonon cou-

pling for Al, Nb, and Mo using the LDA and LMTO basis sets. Our results show generally good agreement between calculated and experimental electron-phonon-coupling strengths and transport properties. This indicates that *ab initio* calculations of electron-phonon interactions are now feasible for metals with broad, as well as with narrow bands. It seems that more experimental and/or theoretical work is necessary to account for the discrepancy between the existing tunneling and the other data for Nb.

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