

Nonlocal Screening, Electron-Phonon Coupling, and Phonon Renormalization in Metals

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A method for calculating the phonon self-energy in metals arising from the coupling between phonons and electrons near the Fermi surface is developed. The essence of this scheme is the separation of the inter- and intraband parts of the electron polarizability. The intraband contribution provides extra screenings and is closely related to the electron-phonon coupling and phonon softening in metals. Applications of this scheme to phonons in MgB₂ give excellent results when compared with experiments and previous theoretical work. In addition, both electron and hole dopings are found to reduce the renormalization effect of the E_{2g} phonon mode, which indicates a weakened electron-phonon coupling in the doped systems.

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Coupled electron-phonon (e -ph) systems are one of the most widely studied many-body problems. Interactions between electrons and phonons are responsible for a variety of interesting physical phenomena. For example, the effective (attractive) interaction between electrons near the Fermi surface arising from the exchange of virtual phonons is responsible for conventional superconductivity. The potential role such an interaction might play in the high transition temperature (T_c) cuprates is still under intensive investigation. In addition, electron-phonon interactions contribute to the finite lifetime of phonons and electrons and renormalize their energy. For phonon modes that are strongly coupled with electrons, the renormalization of the phonons could be significant, resulting in softened phonons in certain regions of the Brillouin zone (BZ). Allen and Cohen [1] studied this renormalization by comparing phonon spectra of TaC and HfC, two similar materials which differ greatly in T_c , and related the extra phonon softening in TaC to the e -ph coupling constant. This subject was discussed in more detail subsequently [2–4]. Recently, the discovery [5] of the unexpectedly high T_c in MgB₂ has ignited renewed interest in phonon-mediated superconductivity [6–11]. It is now generally accepted that the extremely strong coupling between E_{2g} phonons and $p\sigma$ electrons is responsible for the surprisingly high T_c . Therefore, it would be interesting to study the e -ph coupling induced phonon renormalization in this material and its derivatives.

In this Letter, we suggest a scheme for calculating the phonon renormalization in metals from first principles. This method is based on the observation that the electronic polarizability in metals consists of both inter- and intraband contributions. Accordingly, the phonon self-energy can be separated into these contributions. The intraband contribution accounts for an extra renormalization in metals. Furthermore, since this phonon self-energy is defined with respect to an “insulating” system, the magnitude of such renormalization relates directly to the strength of the e -ph coupling in the corresponding metallic system. Note that by “intraband” we mean contributions from all Fermi-

surface electrons. Another advantage of the present formulation is that the e -ph coupling matrix elements are not calculated explicitly and the computational cost is greatly reduced compared to usual perturbation approaches. In the study of coupled electron-phonon systems, it is often desirable to identify phonon modes that couple strongly with electrons. In this regard, the present formulation provides a convenient method for searching for such modes if they exist. Application of this technique to MgB₂ shows enormous but expected renormalization of the E_{2g} phonons due to the extremely strong e -ph coupling in this system. More interestingly, we find that both electron and hole doping reduce the e -ph coupling strength in this system, which explains the fact that, despite much effort, undoped MgB₂ still holds the record for highest T_c .

In a coupled electron-phonon system, the phonon dynamical matrix, or equivalently, the second derivative of the total energy, consists of three contributions: [12–15]

$$\begin{aligned} \frac{\partial^2 E}{\partial R_i^\alpha \partial R_j^\beta} &= \frac{\partial^2 E^{\text{ion}}}{\partial R_i^\alpha \partial R_j^\beta} + \int \frac{\partial^2 V^{\text{ion}}}{\partial R_i^\alpha \partial R_j^\beta} n(\mathbf{r}) d\mathbf{r} \\ &+ \int \frac{\partial V^{\text{ion}}}{\partial R_i^\alpha} \frac{\partial n(\mathbf{r})}{\partial R_j^\beta} d\mathbf{r}, \end{aligned} \quad (1)$$

where R_i^α denotes the α Cartesian coordinate of the i th ion. Here E^{ion} and V^{ion} are the ion-ion interaction energy and electron-ion potential, respectively, and $n(\mathbf{r})$ is the electronic charge density. The first and second terms of the right-hand side of Eq. (1) are of electrostatic origin which can be combined to define “bare” phonon energies. The last term is the electron-phonon contribution to the phonon energy and is the focus of our discussion. Within linear response theory, the electronic charge response to an external perturbation ΔV^{ext} can be expressed as:

$$\begin{aligned} \Delta n(\mathbf{r}) &= \int \chi(\mathbf{r}, \mathbf{r}') \Delta V^{\text{ext}}(\mathbf{r}') d\mathbf{r}' \\ &= \int \chi^0(\mathbf{r}, \mathbf{r}') \Delta V^{\text{scf}}(\mathbf{r}') d\mathbf{r}', \end{aligned} \quad (2)$$

where χ is the full response function and χ^0 the (irreducible) polarizability; V^{scf} is the self-consistent Kohn-Sham potential. For an insulating system, the charge response may be regarded as arising from changes in electronic wave functions as a result of lattice distortions: [16]

$$\Delta n(\mathbf{r}) = \sum_i f_i [\psi_i^*(\mathbf{r}) \Delta \psi_i(\mathbf{r}) + \text{c.c.}], \quad (3)$$

where f_i is the Fermi occupation factor. The connection between Eqs. (2) and (3) can easily be seen by noting that the change in wave functions responding to a phonon distortion is

$$\Delta \psi_i(\mathbf{r}) = \sum_{j \neq i} \psi_j(\mathbf{r}) \frac{\langle \psi_j | \Delta V^{\text{scf}} | \psi_i \rangle}{\epsilon_i - \epsilon_j}. \quad (4)$$

In metals, however, the existence of the Fermi surface provides additional screening: [15,17,18]

$$\Delta n(\mathbf{r}) = \sum_i f_i [\psi_i^*(\mathbf{r}) \Delta \psi_i(\mathbf{r}) + \text{c.c.}] + \sum_i \Delta f_i |\psi_i(\mathbf{r})|^2. \quad (5)$$

The second term in the above expression accounts for changes in electron occupation numbers in response to lattice perturbations. We shall call this metallic screening to be distinguished from the screening arising from the distortion of wave functions. This is equivalent to stating that the electronic polarizability in metals has both inter- and intraband contributions:

$$\begin{aligned} \chi^0(\mathbf{r}, \mathbf{r}') &= \sum_{i \neq j} \frac{f_i - f_j}{\epsilon_i - \epsilon_j} \psi_i^*(\mathbf{r}) \psi_j(\mathbf{r}) \psi_j^*(\mathbf{r}') \psi_i(\mathbf{r}') \\ &+ \sum_i \frac{\delta f_i}{\delta \epsilon_i} |\psi_i(\mathbf{r})|^2 |\psi_i(\mathbf{r}')|^2. \end{aligned} \quad (6)$$

It is therefore reasonable to separate the two contributions to the polarizability; the intraband contribution is due to the existence of the Fermi surface and is responsible for the extra phonon softening in metals. Another interesting observation is that, since this extra screening in metals is a result of the redistribution of electrons, it is fairly nonlocal, as will be discussed in more detail later. Combining Eqs. (1), (2), and (6), we define the phonon renormalization in metals:

$$\begin{aligned} \Delta(\omega^2) &= \omega^2 - \omega_0^2 \\ &= \frac{1}{M} \sum_i \delta(\epsilon_i) \langle \psi_i | \frac{\delta V^{\text{ion}}}{\delta Q} | \psi_i \rangle \langle \psi_i | \frac{\delta V^{\text{scf}}}{\delta Q} | \psi_i \rangle, \end{aligned} \quad (7)$$

where M and Q are the mass and the generalized coordinate associated with the phonon mode of interest, and ω is the true (renormalized) phonon energy in metals. The Dirac delta function $\delta(\epsilon_i)$ ensures that only electrons near the Fermi surface contribute to the phonon renormalization in the present definition. We introduce a reference phonon energy ω_0 for the corresponding insulating system, which can easily be evaluated with either frozen phonon or linear response approaches with band occupation numbers frozen. Note that ω_0 would have been the true phonon energy if there were no couplings to the electrons near the

Fermi surface, as in the case of insulators. Here we assume that the reference and renormalized phonons have the same polarization vector. Note that ω_0 includes all electronic effects except the coupling with the Fermi-surface electrons. Therefore, ω_0 may be regarded as the bare phonon energy with respect to the e -ph coupling in metals. The renormalization $\Delta(\omega^2)$ is then evaluated by taking the difference between the true phonon energy ω^2 and the reference one ω_0^2 . Denoting $\Delta V = \frac{1}{\sqrt{2M\omega}} \frac{\delta V}{\delta Q}$, we have

$$\Delta(\omega^2) = 2\omega \sum_i \delta(\epsilon_i) \langle \psi_i | \Delta V^{\text{ion}} | \psi_i \rangle \langle \psi_i | \Delta V^{\text{scf}} | \psi_i \rangle. \quad (8)$$

Equation (8) clearly shows the e -ph coupling effects on the phonon energy. The stronger the coupling, the greater the renormalization.

We now apply the above formulation to phonons in MgB_2 . Since the discovery [5] of the surprisingly high T_c in MgB_2 , much work has focused on searching for systems with higher T_c using MgB_2 as a template. It was observed that the T_c of MgB_2 decreases upon electron doping (by substituting Mg with Al or B with C) [19–26] due to the filling of the $p\sigma$ hole and possibly impurity scattering effects. Surprisingly, hole doping through substituting Mg with Li or B with Be was found to suppress the T_c , too, [27,28] leaving MgB_2 a naturally optimally doped superconductor. Therefore, it would be interesting to study the doping effects on the phonon renormalization as defined in Eq. (8). Figure 1 shows the phonon energies, ω and ω_0 , of the E_{2g} mode as functions of the doping level x (additional electrons/cell), assuming that doping does not lead to phase separations or phase transitions. For $x \leq 0.5$, the reference (unrenormalized) phonon energy ω_0 increases smoothly as doping level increases. As x increases beyond 0.5, the excess electrons start occupying weakly coupled $p\pi$ bands which have no noticeable effects on the E_{2g} phonon energy. The true (renormalized) phonon energy (ω), in contrast, increases sharply with increasing

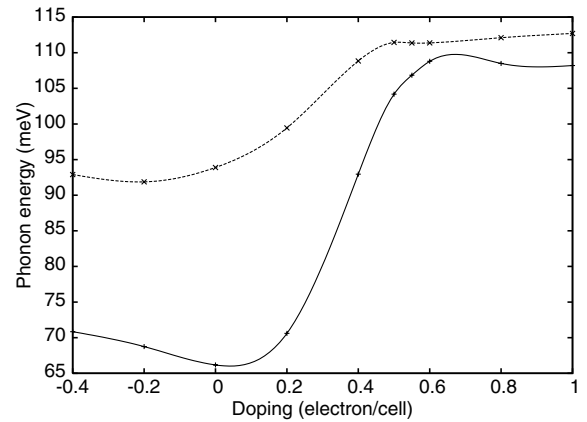


FIG. 1. Renormalized (solid line) and unrenormalized (dashed line) E_{2g} phonon energies in MgB_2 as a function of doping level. Symbols indicate calculated values and the curves are a guide for the eyes.

doping for $0.2 \leq x \leq 0.5$. This reveals a steep decrease of the renormalization effects. In order to focus on the e -ph coupling induced phonon renormalization, we neglect the structural changes due to doping and use the experimental lattice constant of undoped MgB_2 in all of our calculations. The E_{2g} phonon energy of $(\text{MgB}_2)^{1.0-}$ is about 121 meV if experimental lattice constants of AlB_2 are used, which agree well with the measured phonon energy in AlB_2 . However, this additional change in phonon energy arises from the change in lattice constants, not from the e -ph coupling.

A convenient indication of the renormalization effect is the parameter $\Delta(\omega^2)/\omega^2 = (\omega_0^2 - \omega^2)/\omega^2$, which is shown in Fig. 2. Indeed, this renormalization parameter drops from about 1.0 for the undoped system to 0.15 for $x = 0.5$. Further increase of the doping results in completely filled $p\sigma$ bands, and the e -ph renormalization effects become negligible. Our approach also reproduces well an abrupt decrease in phonon renormalization for $x \geq 0.2$, which was discussed previously [20,23,29]. Experimentally, it is well known that both T_c and the E_{2g} phonon energy depend strongly on the doping level, and T_c drops [20] to nearly zero in $\text{Mg}_{0.5}\text{Al}_{0.5}\text{B}_2$. Our results also agree well with a recent calculation of the E_{2g} phonon energy of $\text{Mg}_{1-x}\text{Al}_x\text{B}_2$ [30]. However, we calculate explicitly the phonon renormalization, not just the phonon energy, as a function of doping level, and our approach does not require explicit evaluations of the e -ph matrix elements. Table I shows the energy and renormalization for four phonon modes in MgB_2 . The E_{2g} modes, both at Γ and A , show enormous renormalization arising from the coupling with the Fermi-surface electrons. Phonons at the M point, in contrast, show negligible coupling effects. It is also interesting to point out that hole doping reduces the renormalization effects, too, which leaves little room for improving the e -ph coupling strength in MgB_2 through chemical doping. This might explain the fact that undoped MgB_2 still sets the record for highest T_c .

Following the idea of Allen and Cohen [1], we may relate the phonon renormalization $\Delta(\omega^2)$ to the phonon

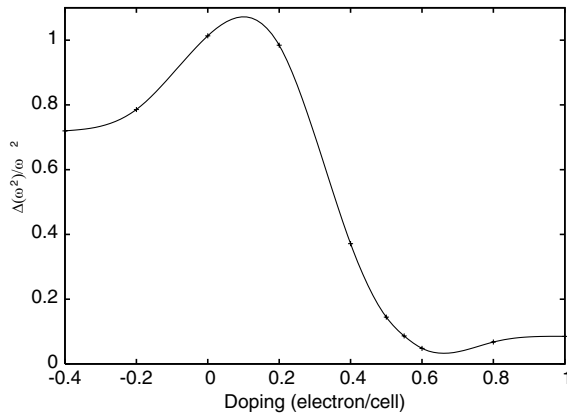


FIG. 2. The E_{2g} phonon renormalization in MgB_2 as a function of doping. The curve is a guide for the eyes.

linewidth (full width), defined as

$$\gamma = 2\pi\omega \sum_i \delta(\epsilon_i)\delta(\epsilon_i + \omega) |\langle \psi_i | \Delta V_{\text{scf}} | \psi_i \rangle|^2 \quad (9)$$

and to the e -ph coupling constant using the Allen formula [32]. Note that Eq. (8) contains the matrix elements of both screened and bare ionic potentials whereas Eq. (9) involves only those of the screened potential. Introducing an effective screening $\bar{\epsilon}$, Eq. (8) may be rewritten as

$$\Delta(\omega^2) = 2\bar{\epsilon}\omega \sum_i \delta(\epsilon_i) |\langle \psi_i | \Delta V^{\text{scf}} | \psi_i \rangle|^2. \quad (10)$$

If we replace δ functions in Eqs. (9) and (10) by Gaussians with a width of the phonon energy ω , we reach an approximation for γ , which is linear in $\Delta(\omega^2)$ as proposed by Allen and his collaborators: [1–3]

$$\gamma \approx \frac{\sqrt{2\pi}\Delta(\omega^2)}{\bar{\epsilon}\omega}. \quad (11)$$

The effective screening $\bar{\epsilon}$ from the interband transitions can be approximated by Ω^2/ω_0^2 , where Ω is the ionic contribution to the phonon energy. For the E_{2g} mode in MgB_2 , we obtain $\bar{\epsilon} \approx \Omega^2/\omega_0^2 = 4.9$. Phonon linewidths of four phonon modes calculated using Eq. (11) are listed in Table I, which agree surprisingly well with the results of Shukla *et al.* (shown in parenthesis) [31]. Note that the phonon linewidth at Γ is not available from the work of Shukla [31]; the value quoted is taken from $q = 0.2$ (Γ -A).

As we have mentioned earlier, the screening charge due to the change in the band occupation numbers [the second term of Eq. (5)] is fairly nonlocal. Electrons redistribute themselves in response to phonon distortions so that a constant Fermi level is maintained throughout the system. For the case of the E_{2g} phonon in MgB_2 , electrons move away from the elongated bonds and flow into the compressed ones, as shown schematically in Fig. 3(a). Therefore, we expect the screening to be fairly nonlocal. Figure 3(b) shows the Fourier transform of the screening charge due to the change in the band occupation numbers, which is calculated with a frozen phonon (E_{2g}) displacement of 0.1 a.u. The prominent peak at $|G|^2 \sim 6$ Ry is consistent with the observation that the charge redistribution occurs across a real-space distance $|\bar{a}|/2$.

Finally, we would like to point out that our formalism may also be applicable to the study of doping dependent

TABLE I. Phonon renormalization in MgB_2 . Numbers in parenthesis are results from the work of Shukla *et al.* [31].

Phonon mode	$E_{2g}(\Gamma)$	$E_{2g}(A)$	$E_{1u}(M)$	$A_{2u}(M)$
ω (meV)	66.17	59.72	56.90	51.46
ω_0 (meV)	93.89	78.73	56.91	52.25
$\Delta\omega$ (meV)	27.72	19.01	0.01	0.79
$\Delta(\omega^2)/\omega^2$	1.02	0.74	0.00	0.03
γ (meV)	34.1	22.5	0.01	0.81
	(~32)	(20.4)	(0.00)	(1.1)

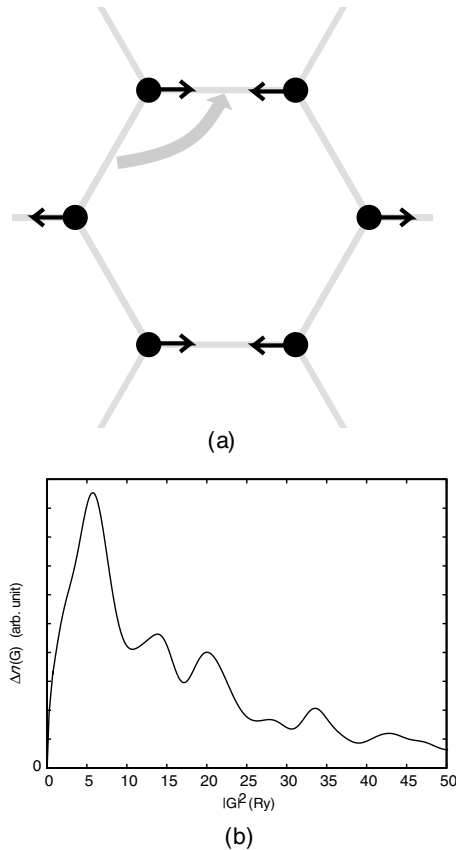


FIG. 3. Nonlocal nature of the metallic screening. (a) Schematics of the charge redistribution in the real-space as a result of phonon distortions. (b) Fourier transform of the metallic screening charge in MgB_2 , calculated with an E_{2g} phonon displacement of 0.1 a.u.

phonon softening in high T_c cuprates [33–36], provided that an accurate description of the Fermi surface is available. Despite nearly two decades of intensive research, electron-phonon coupling in high T_c cuprates is still a subject of controversy. An interesting and successful model for treating phonons in cuprates was proposed by Falter *et al.* [37–39]. The essence of this model, i.e., the separation of local and nonlocal charge responses, is in some sense similar to ours. However, we would like to emphasize the “first-principle” nature of our approach.

In summary, we propose a convenient scheme for calculating the phonon renormalization in metals due to the coupling between phonons and the Fermi-surface electrons. This scheme is based on the observation that the electronic polarizability in metals has both inter- and intraband contributions. The intraband contribution results in an additional (nonlocal) screening and accounts for the extra phonon softening in metals. Not surprisingly, we may relate this extra softening directly to the e -ph coupling strength in metals, as proposed by Allen and Cohen [1]. Since no explicit evaluation of the e -ph matrix elements is required, our method is also computationally advantageous compared with traditional approaches, and our results on

phonon renormalization in MgB_2 agree well with previous work. More importantly, we show that both electron and hole doping result in reduced e -ph coupling strength in MgB_2 ; this is a somewhat disappointing result for the search for high T_c but consistent with experiments.

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- [1] P.B. Allen and M.L. Cohen, Phys. Rev. Lett. **29**, 1593 (1972).
 - [2] P.B. Allen and R. C. Dynes, Phys. Rev. B **11**, 1895 (1975).
 - [3] W.E. Pickett and P.B. Allen, Phys. Rev. B **16**, 3127 (1977).
 - [4] F. Mauri *et al.*, Phys. Rev. Lett. **77**, 1151 (1996).
 - [5] J. Nagamatsu *et al.*, Nature (London) **410**, 63 (2001).
 - [6] J.M. An and W.E. Pickett, Phys. Rev. Lett. **86**, 4366 (2001).
 - [7] J. Kortus *et al.*, Phys. Rev. Lett. **86**, 4656 (2001).
 - [8] K.P. Bohnen *et al.*, Phys. Rev. Lett. **86**, 5771 (2001).
 - [9] A. Y. Liu *et al.*, Phys. Rev. Lett. **87**, 87005 (2001).
 - [10] Y. Kong *et al.*, Phys. Rev. B **64**, 20501 (2001).
 - [11] H.J. Choi *et al.*, Nature (London) **418**, 758 (2002).
 - [12] S. K. Sinha, Phys. Rev. **169**, 477 (1968).
 - [13] L.J. Sham, Phys. Rev. **188**, 1431 (1969).
 - [14] R.M. Pick, M.H. Cohen, and R.M. Martin, Phys. Rev. B **1**, 910 (1970).
 - [15] S. Baroni *et al.*, Rev. Mod. Phys. **73**, 515 (2001).
 - [16] We discuss Γ phonons only for simplicity. However, our approach is applicable to phonons with finite momentum.
 - [17] S. de Gironcoli, Phys. Rev. B **51**, 6773 (1995).
 - [18] S. Y. Savrasov, Phys. Rev. B **54**, 16470 (1996).
 - [19] T. Takenobu *et al.*, Phys. Rev. B **64**, 134513 (2001).
 - [20] P. Postorino *et al.*, Phys. Rev. B **65**, 20507 (2002).
 - [21] J.Q. Li *et al.*, Phys. Rev. B **65**, 132505 (2002).
 - [22] O. de la Peña, A. Aguayo, and R. de Coss, Phys. Rev. B **66**, 012511 (2002).
 - [23] A. Bianconi *et al.*, Phys. Rev. B **65**, 174515 (2002).
 - [24] W. Mickelson *et al.*, Phys. Rev. B **65**, 52505 (2002).
 - [25] M. Putti *et al.*, Phys. Rev. B **68**, 94514 (2003).
 - [26] R.H.T. Wilke *et al.*, Phys. Rev. Lett. **92**, 217003 (2004).
 - [27] Y.G. Zhao *et al.*, Physica C (Amsterdam) **361**, 91 (2001).
 - [28] J.S. Ahn *et al.*, Phys. Rev. B **65**, 172503 (2002).
 - [29] B. Renker *et al.*, Phys. Rev. Lett. **88**, 67001 (2002).
 - [30] G. Profeta *et al.*, Phys. Rev. B **68**, 144508 (2003).
 - [31] A. Shukla *et al.*, Phys. Rev. Lett. **90**, 95506 (2003).
 - [32] P.B. Allen, Phys. Rev. B **6**, 2577 (1972).
 - [33] L. Pintschovius and M. Braden, Phys. Rev. B **60**, R15039 (1999).
 - [34] R.J. McQueeney *et al.*, Phys. Rev. Lett. **87**, 077001 (2001).
 - [35] T. Fukuda *et al.*, Phys. Rev. B **71**, 060501 (2005).
 - [36] L. Pintschovius, Phys. Status Solidi B **242**, 30 (2005).
 - [37] C. Falter *et al.*, Phys. Rev. B **47**, 5390 (1993).
 - [38] C. Falter *et al.*, Phys. Rev. B **60**, 12051 (1999).
 - [39] C. Falter, Phys. Status Solidi B **242**, 78 (2005).