

Adiabatic and nonadiabatic phonon dispersion in a Wannier function approach

Matteo Calandra,¹ Gianni Profeta,² and Francesco Mauri¹

¹IMPMC, Université Paris 6, CNRS, 4 Pl. Jussieu, 75015 Paris, France

²Consiglio Nazionale delle Ricerche-Superconducting and Innovative Devices (CNR-SPIN), 67100 L'Aquila, Italy

(Received 13 July 2010; revised manuscript received 7 September 2010; published 8 October 2010)

We develop a first-principles scheme to calculate adiabatic and nonadiabatic phonon frequencies in the full Brillouin zone. The method relies on the stationary properties of a force-constant functional with respect to the first-order perturbation of the electronic charge density and on the localization of the deformation potential in the Wannier function basis. This allows for calculation of phonon-dispersion curves free from convergence issues related to Brillouin-zone sampling. In addition our approach justifies the use of the static screened potential in the calculation of the phonon linewidth due to decay in electron-hole pairs. We apply the method to the calculation of the phonon dispersion and electron-phonon coupling in MgB₂ and CaC₆. In both compounds we demonstrate the occurrence of several Kohn anomalies, absent in previous calculations, that are manifest only after careful electron- and phonon-momentum integration. In MgB₂, the presence of Kohn anomalies on the E_{2g} branches improves the agreement with measured phonon spectra and affects the position of the main peak in the Eliashberg function. In CaC₆ we show that the nonadiabatic effects on in-plane carbon vibrations are not localized at zone center but are sizable throughout the full Brillouin zone. Our method opens perspectives in large-scale first-principles calculations of dynamical properties and electron-phonon interaction.

DOI: 10.1103/PhysRevB.82.165111

PACS number(s): 63.20.dk, 71.15.-m, 63.20.kd

I. INTRODUCTION

Electron-phonon (EP) interaction is responsible of many important phenomena in solids. As an example, the temperature behavior of the electron relaxation time in metals is to a great extent due to the scattering between carriers and atomic vibrations¹ such that finite-temperature transport is largely ruled by the EP interaction. Similarly, the high-temperature heat capacity in metals is enhanced by the increased electronic mass due to the interaction with lattice vibrations.² In metals, at low temperatures, EP coupling can generate a superconducting state in which electrons move with no electrical resistance.³ It also can increase the effective mass of the carriers so much that the system is driven from a metallic to an insulating state, as it happens in case of polaronic or Peierls instabilities.⁴ Finally, the electron-phonon scattering is often the largest source of phonon damping in phonon-mediated superconductors.⁵

First-principles theoretical determination of the electron-phonon coupling strength in solids requires the calculation of the electronic structure, the vibrational properties, and the electron-phonon coupling matrix elements. In state-of-the-art electronic-structure calculations these quantities are obtained using the adiabatic Born-Oppenheimer approximation⁶ and density-functional theory (DFT) in the linear-response approach.⁷⁻⁹

More specifically, within the Born-Oppenheimer approximation, the determination of phonon frequencies, that are related to the real part of the phonon self-energy, requires the calculation, *in a self-consistent manner*, of the variation in the Kohn-Sham potential V_{SCF} with respect to a *static* ionic displacement $\mathbf{u}$,⁷ namely, $\frac{\delta V_{\text{SCF}}(\mathbf{r})}{\delta \mathbf{u}}$. As the displacement of the ions is static, the obtained $\frac{\delta V_{\text{SCF}}(\mathbf{r})}{\delta \mathbf{u}}$ is real. Conversely, the phonon linewidth, related to the imaginary part of the phonon self-energy, is obtained in a *nonself-consistent* procedure using the electron charge density and the previously deter-

mined $\frac{\delta V_{\text{SCF}}(\mathbf{r})}{\delta \mathbf{u}}$. The advantage of using a nonself-consistent procedure to study phonon linewidth is mainly related to the less expensive computational load with respect to a self-consistent one. In addition, as recently demonstrated, interpolation schemes^{10,11} of the electron-phonon matrix elements can be used to calculate the imaginary part of the phonon self-energy on ultradense k -point grid.

It is however unclear to what extent this procedure of calculating self-consistently the real part of the phonon self-energy and nonself-consistently the imaginary part is actually correct. Indeed, the proper way of treating phonons should be to consider a monochromatic time-dependent displacement (at the phonon frequency ω) and perform a time-dependent self-consistent linear-response scheme. The resulting variation in the self-consistent potential $\frac{\delta V_{\text{SCF}}(\mathbf{r}, \omega)}{\delta \mathbf{u}}$ would then be a complex quantity. The real part of the resulting phonon self-energy would then determine the phonon frequencies while its imaginary part would lead to the phonon linewidth. In this way, nonadiabatic (NA) (in the sense of Ref. 12) *dynamical* phonon frequencies could be accessed. Although feasible, in principle, this procedure would require a full rewriting of the linear-response code including time dependence and it would also be more expensive than a standard static linear-response calculation. Moreover, in the presence of Kohn anomalies and long-range force constants, where extremely accurate k -point sampling of the Fermi surface is needed to converge the phonon self-energy, the calculation would be unfeasible.

Thus, it would be desirable to have a nonself-consistent linear-response formulation to obtain both the real and imaginary phonon self-energy, both within the adiabatic/static and nonadiabatic/dynamic approximation. In this work we develop a scheme to calculate nonself-consistently both the real and the imaginary part of the phonon self-energy by using a functional¹³ that is stationary with respect to the variation in the self-consistent charge density. Our method

opens the way to calculate adiabatic/static and nonadiabatic/dynamic phonon frequencies using an ultradense sampling of the electron and phonon wave vector in a nonself-consistent way, starting from the static self-consistent variation in the time-independent Kohn-Sham potential $[\frac{\delta V_{\text{scf}}(\mathbf{r})}{\delta \mathbf{u}}]$, obtained with a coarse sampling. In this way, the main computational load related to phonon frequencies calculation is drastically reduced. The efficiency of the method is further enhanced by using the interpolation of the electron-phonon matrix elements¹⁴ based on Wannier functions.¹⁵

The method is applied to study the dynamical and superconducting properties of MgB_2 and CaC_6 , two of the most studied superconducting materials in the last few years. These applications are meaningful and computationally challenging. In fact, although many experimental and theoretical studies appeared, there are still important open issues and debated results.

For example, conflicting results for the calculate MgB_2 electron-phonon coupling (λ) are present in the literature mainly due to difficulties in Brillouin-zone sampling. This, apart its fundamental importance, prevents a full understanding of the normal and superconducting properties of this material.

In the case of CaC_6 , very large nonadiabatic effects were predicted¹² and measured¹⁶ at zone center. It is unclear to what extend nonadiabatic effects are sizable far from Γ point. In this last case, the adiabatic effects can be relevant for thermodynamic properties resulting from an average of the phonon frequencies over the Brillouin zone (BZ).

The paper is organized as follows. In Sec. II we derive a functional formulation¹³ of the force-constant matrix which is stationary with respect to the variation in the perturbed charge density. This will be done starting from the formal definition of force constants in the case of a monochromatic time-dependent ionic displacement (Sec. II A). In Sec. II B we discuss when nonadiabatic/dynamic effects should be expected in the phonon spectra. The linear-response equations for the dynamical matrix are introduced (Sec. II C) in the general case and then specialized in the density-functional formulation (Sec. II D).

In Sec. II E, we introduce the stationary functional of the force constants in the density-functional linear-response theory and outline the computational framework of phonon and electron-phonon coupling (Secs. II F and II G). In Sec. II H we show how our approach justify the use of the static screened potential in the calculation of the phonon linewidth due to decay in electron-hole pairs. Section III will be devoted to the description of the implementation of the theory using the Wannier-interpolation scheme.

In Sec. IV we reports results on dynamical and superconducting properties of MgB_2 (Sec. IV A) and CaC_6 (Sec. IV B). Section V summarizes our conclusions.

II. THEORY

A. Time-dependent dynamical matrix and phonon damping

We consider a crystal with N atoms in the unit cell submitted to a time-dependent perturbation, in which the position of an atom is identified by the vector

$$\mathbf{R}_I \equiv \mathbf{R}_L + \boldsymbol{\tau}_s + \mathbf{u}_I(t), \quad (1)$$

where $\mathbf{R}_L$ is the position of the L th unit cell in the Bravais lattice, $\boldsymbol{\tau}_s$ is the equilibrium position of the s th atom in the unit cell, $\mathbf{u}_I(t)$ indicates the deviation from equilibrium of the nuclear position, and $I=\{L,s\}$. The force at time t acting on the J th nucleus ($J=\{M,r\}$) due to the displacement $\mathbf{u}_I(t')$ of the atom I th at time t' is labeled $\mathbf{F}_J(t)$. The force-constant matrix is defined as

$$C_{IJ}(\mathbf{R}_L - \mathbf{R}_M; t - t') = - \frac{\delta \mathbf{F}_J(t)}{\delta \mathbf{u}_I(t')}, \quad (2)$$

where we used the translational invariance of the crystal and make evident the dependence of C_{IJ} on the lattice vector $\mathbf{R}_L - \mathbf{R}_M$ (to lighten the notation we omit it in the following equations where no confusion may arise). The ω transform of the force-constant matrix is thus

$$C_{IJ}(\omega) = \int dt e^{i\omega t} C_{IJ}(t) \quad (3)$$

while the force-constant matrix $C_{IJ}(t)$ is a real quantity, its ω -transform $C_{IJ}(\omega)$ is not real and has both a real and imaginary part. The Fourier transform of the force-constant matrix is

$$C_{sr}(\mathbf{q}, \omega) = \sum_L e^{-i\mathbf{q}\mathbf{R}_L} C_{Ls,Mr}(\omega), \quad (4)$$

where, without loss of generality, we have chosen $\mathbf{R}_M = \mathbf{0}$. The Hermitian and anti-Hermitian combination of the force-constant matrix in momentum space are

$$D_{sr}(\mathbf{q}, \omega) = \frac{1}{2\sqrt{M_s M_r}} [C_{sr}(\mathbf{q}, \omega) + C_{rs}(\mathbf{q}, \omega)^*], \quad (5)$$

$$A_{sr}(\mathbf{q}, \omega) = \frac{1}{2i\sqrt{M_s M_r}} [C_{sr}(\mathbf{q}, \omega) - C_{rs}(\mathbf{q}, \omega)^*], \quad (6)$$

where M_s is the mass of the s th atom in the unit cell. These quantities are associated to the real and imaginary part of the dynamical matrix in coordinate space. If the imaginary part of the dynamical matrix is small with respect to its real part, namely,

$$|A_{sr}(\mathbf{q}, \omega)| \ll |D_{sr}(\mathbf{q}, \omega)|, \quad (7)$$

then the self-consistent condition

$$\det[D_{sr}(\mathbf{q}, \omega_{\mathbf{q}\nu}) - \omega_{\mathbf{q}\nu}^2] = 0 \quad (8)$$

determines nonadiabatic/dynamic phonon frequencies $\omega_{\mathbf{q}\nu}$ and phonon eigenvectors $\{\mathbf{e}_{\mathbf{q}\nu}^s\}_{s=1,N}$ and $\nu=1, 3N$ indicates the phonon branches. The adiabatic/static phonon frequencies and eigenvectors are obtained considering a static perturbation, thus diagonalizing $D_{rs}(\mathbf{q}, \omega_{\mathbf{q}\nu}=0)$.

On the other hand, the imaginary part of the force-constant matrix determines the phonon damping,

$$\gamma_{\mathbf{q}\nu} = \frac{2}{\omega_{\mathbf{q}\nu}} \sum_{s,r} \mathbf{e}_{\mathbf{q}\nu}^s A_{sr}(\mathbf{q}, \omega_{\mathbf{q}\nu}) \mathbf{e}_{\mathbf{q}\nu}^r \quad (9)$$

and the phonon linewidth.

B. Adiabatic and nonadiabatic phonons

In the previous section we have defined the nonadiabatic/dynamic phonon frequencies as the eigenvalues of the Hermitian part of the time-dependent dynamical matrix and the adiabatic/static phonon frequencies as the eigenvalues of the static time-independent dynamical matrix. Solid-state textbooks^{1,17} and first-principles calculations of the phonon dispersion,^{7,9,18–20} usually treat only the adiabatic/static case, since it is commonly assumed that the adiabatic phonon frequencies coincide with the nonadiabatic ones.

In insulators, where the fundamental energy gap between the electronic ground state and the first available excited state is much larger than the phonon energy, the adiabatic/static approximation is well justified. In metals the situation is more complex.^{12,21,22}

The crucial parameter in metals is the electron relaxation time τ . In absence of electron-defect, electron-electron and electron-phonon scattering, τ is infinite. In a real metallic system, the presence of these scattering processes results in a finite relaxation time τ . We can define three cases: (i) a clean limit, when the electron relaxation time τ is much larger than the phonon period divided by 2π , (ii) a dirty limit, when the electron relaxation time τ is much smaller than the phonon period divided by 2π , and (iii) an intermediate regime, when the electron relaxation time τ is comparable to the phonon period divided by 2π .

It has been shown^{12,21,22} that in the dirty limit the nonadiabatic phonon frequencies coincide with the adiabatic ones also in metals. Instead, in the clean limit and in the intermediate regime, the adiabatic and nonadiabatic frequencies are, in general, different.

The nonadiabatic calculations based on time-dependent DFT (described in the following sections) are performed in the perfect clean limit. Indeed, in our time-dependent calculations, the electron relaxation time τ is infinite, since we use an instantaneous (real in the frequency space) exchange-correlation (XC) kernel, and we do not consider a broadening of the electronic levels due to defects and electron-phonon scattering.

Thus, our nonadiabatic/dynamic DFT frequencies should be used to reproduce the phonon frequencies measured in metal in the clean limit. Instead, the adiabatic/static DFT frequencies (those generally computed with DFT linear-response codes) should be used to reproduce the phonon frequencies measured in a metal in the dirty limit. Finally, to reproduce the phonon frequencies measured in a metal in the intermediate regime, one should explicitly include electron-lifetime effects in the linear-response calculation, as it has been done for zone center phonon in Refs. 12 and 23.

By considering a single band and by linearizing the electronic-band dispersion near the Fermi energy, it has been shown²¹ that the differences between the adiabatic and nonadiabatic phonons are largest at the center of the BZ and vanish for $q \gg \omega_{\text{ph}}/v_F$, where v_F is the Fermi velocity. Such differences, at the BZ center and in the clean limit, have been computed within DFT,¹² and can be very sizable (up to 30% of the phonon frequency). However a detailed DFT study of nonadiabatic effect away from the BZ center (beyond a linearized one-band approximation²¹) is still missing.

C. Time-dependent linear-response theory

The force-constant matrix can be evaluated in the linear-response theory, considering that the atomic displacement induces a perturbation in the external potential acting on the electrons.

The Hellmann-Feynmann theorem^{24–26} states that the force on atom J , $\mathbf{F}_J(t)$ can be evaluated in terms of the variation in the external potential,

$$\mathbf{F}_J(t) = - \int d\mathbf{r} n(\mathbf{r}, t) \frac{\delta V_{\text{ext}}(\mathbf{r})}{\delta \mathbf{R}_J}, \quad (10)$$

where $n(\mathbf{r}, t)$ is the electronic charge density and $V_{\text{ext}}(\mathbf{r})$ is the external potential, namely,

$$V_{\text{ext}}(\mathbf{r}) = - \sum_I \frac{Z}{|\mathbf{r} - \mathbf{R}_I|} + \frac{1}{2} \sum_{I \neq J} \frac{Z_I Z_J}{|\mathbf{R}_J - \mathbf{R}_I|}. \quad (11)$$

It is worthwhile to recall that $V_{\text{ext}}(\mathbf{r})$ does not depend explicitly on time but only through the dependence on time of the phonon displacement $\mathbf{u}_I(t)$. In linear response the force-constant matrix $C_{IJ}(\omega)$ is written as⁷

$$C_{IJ}(\omega) = \int \frac{\delta n(\mathbf{r}, \omega)}{\delta \mathbf{u}_I} \frac{\delta V_{\text{ext}}(\mathbf{r})}{\delta \mathbf{u}_J} d\mathbf{r} + \int n_0(\mathbf{r}) \frac{\delta^2 V_{\text{ext}}(\mathbf{r})}{\delta \mathbf{u}_J \delta \mathbf{u}_I} d\mathbf{r}, \quad (12)$$

where $n_0(\mathbf{r})$ is the unperturbed charge density, $n(\mathbf{r}, \omega)$ is the ω transform of the time-dependent charge density $n(\mathbf{r}, t)$, and $\frac{\delta V_{\text{ext}}(\mathbf{r})}{\delta \mathbf{u}_J}$ and $\frac{\delta^2 V_{\text{ext}}(\mathbf{r})}{\delta \mathbf{u}_J \delta \mathbf{u}_I}$ are real and time-independent quantities evaluated at the equilibrium position of the nuclei. On the contrary $\frac{\delta n(\mathbf{r}, \omega)}{\delta \mathbf{u}_I}$ is complex.

D. Time-dependent linear response in density-functional theory

In this section, we examine the linear-response calculation of the real-space force constants in the framework of density-functional theory. The derivations are kept in real space as we want to keep the presence of imaginary terms (damping) in the force-constant matrix as manifest.

In order to compute $n(\mathbf{r}, \omega)$, we assume a monochromatic perturbation of the form

$$\mathbf{u}_I(t) = \mathbf{u}_I(\omega)(e^{i\omega t} + e^{-i\omega t}), \quad (13)$$

where $\mathbf{u}_I(\omega)$ is real. In density-functional theory the resulting monochromatic perturbing potential is the external potential $V_{\text{ext}}(\mathbf{r})$ in Eq. (11). The derivative of the ω transform of the charge density with respect to an ionic displacement is written as⁷

$$\begin{aligned} n_I^1(\mathbf{r}, \omega, T) &= \frac{\delta n(\mathbf{r}, \omega)}{\delta \mathbf{u}_I} = 2 \sum_{\mathbf{k}i, \mathbf{k}'j}^{N_k(T)} [f_{\mathbf{k}i}(T) - f_{\mathbf{k}'j}(T)] \\ &\times \frac{\langle \psi_{\mathbf{k}'j} | \delta V_{\text{SCF}}(\mathbf{r}, \omega) / \delta \mathbf{u}_I | \psi_{\mathbf{k}i} \rangle}{\epsilon_{\mathbf{k}i} - \epsilon_{\mathbf{k}'j} + \omega + i\eta} \psi_{\mathbf{k}i}^*(\mathbf{r}) \psi_{\mathbf{k}'j}(\mathbf{r}), \end{aligned} \quad (14)$$

where $\mathbf{k}, \mathbf{k}'$ label the crystal momentum, i, j are band in-

dexes, the T is the electronic temperature (or broadening) in the Fermi function $f_{\mathbf{k}i}(T)$, η is an arbitrarily small positive real number, $N_k(T)$ is the number of k points needed to converge the sum in Eq. (14) at the electronic temperature T , and the factor 2 (here and in the following) accounts for the spin degeneracy. Finally, V_{SCF} is the Kohn-Sham self-consistent potential. The quantity $\delta V_{\text{SCF}}(\mathbf{r}, \omega) / \delta \mathbf{u}_I$ is complex and given by

$$\frac{\delta V_{\text{SCF}}(\mathbf{r}, \omega)}{\delta \mathbf{u}_I} = \frac{\delta V_{\text{ext}}(\mathbf{r})}{\delta \mathbf{u}_I} + \int K(\mathbf{r}, \mathbf{r}') n_I^1(\mathbf{r}, \omega, T) d\mathbf{r}', \quad (15)$$

where $K(\mathbf{r}, \mathbf{r}') = \frac{\delta E_{\text{HXC}}[n]}{\delta n(\mathbf{r}) \delta n(\mathbf{r}')}$ is the kernel of the Hartree and exchange and correlation functional, $E_{\text{HXC}}[n]$. As usual we have assumed the Hartree and exchange-correlation kernel to be instantaneous (real in ω space).

Substitution of Eq. (14) in Eq. (12) leads to

$$\begin{aligned} C_{IJ}(\omega, T) = & 2 \sum_{\mathbf{k}i, \mathbf{k}'j}^{N_k(T)} [f_{\mathbf{k}i}(T) - f_{\mathbf{k}'j}(T)] \\ & \times \frac{\langle \psi_{\mathbf{k}'j} | \delta V_{\text{SCF}}(\mathbf{r}, \omega) / \delta \mathbf{u}_I | \psi_{\mathbf{k}i} \rangle \langle \psi_{\mathbf{k}i} | \delta V_{\text{ext}}(\mathbf{r}) / \delta \mathbf{u}_I | \psi_{\mathbf{k}'j} \rangle}{\epsilon_{\mathbf{k}i} - \epsilon_{\mathbf{k}'j} + \omega + i\eta} \\ & + \int n_0(\mathbf{r}) \frac{\delta^2 V_{\text{ext}}(\mathbf{r})}{\delta \mathbf{u}_I \delta \mathbf{u}_I} d\mathbf{r}, \end{aligned} \quad (16)$$

where, from now on, we explicitly indicate the dependence on the electronic temperature T . This expression of the force-constant matrix is normally used in standard implementations of linear-response theory.⁷

Further substitution of Eq. (15) in Eq. (16) gives the following alternative but equivalent formulation for the force-constant matrix in linear-response theory:

$$\begin{aligned} C_{IJ}(\omega, T) = & 2 \sum_{\mathbf{k}i, \mathbf{k}'j}^{N_k(T)} \frac{f_{\mathbf{k}i}(T) - f_{\mathbf{k}'j}(T)}{\epsilon_{\mathbf{k}i} - \epsilon_{\mathbf{k}'j} + \omega + i\eta} \langle \psi_{\mathbf{k}'j} | \frac{\delta V_{\text{SCF}}(\mathbf{r}, \omega)}{\delta \mathbf{u}_I} | \psi_{\mathbf{k}i} \rangle \\ & \times \langle \psi_{\mathbf{k}i} | \frac{\delta V_{\text{SCF}}(\mathbf{r}, \omega)}{\delta \mathbf{u}_I} | \psi_{\mathbf{k}'j} \rangle + \int d\mathbf{r} n_0(\mathbf{r}) \frac{\delta^2 V_{\text{ext}}(\mathbf{r})}{\delta \mathbf{u}_I \delta \mathbf{u}_I} \\ & - \int \int n_I^1(\mathbf{r}, \omega, T) K(\mathbf{r}, \mathbf{r}') n_I^1(\mathbf{r}', \omega, T) d\mathbf{r} d\mathbf{r}'. \end{aligned} \quad (17)$$

In Eq. (17) the term including the second derivative of the external potential is real whereas all the other terms are complex.

Equations (16) and (17) are two different ways of calculating the force constants. At convergence of the self-consistent procedure the two expressions lead to the same result. It is tempting to define the phonon self-energy from Eq. (16) involving the product between the matrix element of the screened (V_{SCF}) potential and the matrix element of the bare (V_{ext}) potential [see the first term on the right-hand side (rhs) of Eq. (16)]. Indeed Eq. (16) does not contain a double-counting term of the electron-electron interaction which is on the contrary present in Eq. (17) (last term on the rhs). However such a procedure requires an accurate self-consistent determination of the screened potential at finite frequency ω . On the contrary the advantage of Eq. (17) is that it allows us

to introduce a stationary formulation of the force-constant matrix as it will be shown in the following. That formulation permits a definition of the phonon self-energy where nonself-consistent static screening is used with a negligible and controlled error.

E. Formulation of the stationary force-constant functional

We introduce the following force-constant functional F_{IJ} :

$$\begin{aligned} F_{IJ}[\rho(\mathbf{r}), \rho'(\mathbf{r}), \omega, T] = & 2 \sum_{\mathbf{k}i, \mathbf{k}'j}^{N_k(T)} \frac{f_{\mathbf{k}i}(T) - f_{\mathbf{k}'j}(T)}{\epsilon_{\mathbf{k}i} - \epsilon_{\mathbf{k}'j} - \omega + i\eta} \\ & \times \langle \psi_{\mathbf{k}'j} | \frac{\delta V_{\text{ext}}(\mathbf{r})}{\delta \mathbf{u}_I} + \int K(\mathbf{r}, \mathbf{r}') \rho(\mathbf{r}') d\mathbf{r}' | \psi_{\mathbf{k}i} \rangle \\ & \times \langle \psi_{\mathbf{k}i} | \frac{\delta V_{\text{ext}}(\mathbf{r})}{\delta \mathbf{u}_I} + \int K(\mathbf{r}, \mathbf{r}') \rho'(\mathbf{r}') d\mathbf{r}' | \psi_{\mathbf{k}'j} \rangle \\ & + \int d\mathbf{r} n_0(\mathbf{r}) \frac{\delta^2 V_{\text{ext}}(\mathbf{r})}{\delta \mathbf{u}_I \delta \mathbf{u}_I} \\ & - \int \int \rho(\mathbf{r}) K(\mathbf{r}, \mathbf{r}') \rho'(\mathbf{r}') d\mathbf{r} d\mathbf{r}'. \end{aligned} \quad (18)$$

With this definition the force-constant matrix reads as

$$C_{IJ}(\omega, T) = F_{IJ}[n_I^1(\mathbf{r}, \omega, T), n_I^1(\mathbf{r}, \omega, T), \omega, T]. \quad (19)$$

It is straightforward to note that the force-constant functional is quadratic with respect to ρ , namely,

$$\left. \frac{\delta F_{IJ}[\rho(\mathbf{r}), \rho'(\mathbf{r}), \omega, T]}{\delta \rho(\mathbf{r})} \right|_{\rho(\mathbf{r})=n_I^1(\mathbf{r}, \omega, T), \rho'(\mathbf{r})=n_I^1(\mathbf{r}, \omega, T)} = 0. \quad (20)$$

The same relation holds upon derivation with respect to ρ' .

The consequence of Eq. (20) is that $C_{IJ}(\omega, T)$ is an extremal point and that a given error on $n_I^1(\mathbf{r}, \omega, T)$ or on $n_I^1(\mathbf{r}, \omega, T)$ affects the functional and the phonon frequencies only at second order.

Our functional formulation is related to that used for dielectric tensors by Gonze *et al.* in Ref. 27. The main difference is that, while the functional formulation of Ref. 27 is variational with respect to the first-order perturbation of the wave function, our formulation is stationary with respect to the first-order perturbation of the electronic charge density.

F. Approximated force-constant functional

At this point we can exploit the results of the preceding section in order to develop a method to accurately calculate phonon and electron-phonon properties. Within density-functional theory the most precise force-constant matrix $C_{IJ}(\omega, T)$ is obtained when T coincides with the physical temperature T_0 (e.g., room temperature) of the system. However, in a metal, this temperature is prohibitively small and the self-consistent calculation of $C_{IJ}(\omega, T_0)$ would be computationally unfeasible as it requires a large number of k points

in order to properly converge the summation in Eq. (17). In addition, the self-consistent calculation of the imaginary part of $n_I^1(\mathbf{r}, \omega, T)$ and of $n_J^1(\mathbf{r}, \omega, T)$ at finite $\omega \neq 0$ requires to increase further the number of k points with respect to standard static linear-response calculations of $n_I^1(\mathbf{r}, 0, T)$.

A remedy to these problems is to define an approximated force constants matrix, $\tilde{C}_{IJ}$, as

$$\tilde{C}_{IJ}(\omega, T_0) = F_{IJ}[n_I^1(\mathbf{r}, 0, T_{\text{ph}}), n_J^1(\mathbf{r}, 0, T_{\text{ph}}), \omega, T_0], \quad (21)$$

that is, (i) the frequency dependence on $n_I^1(\mathbf{r}, \omega, T_{\text{ph}})$ is neglected and its static limit ($\omega=0$) is considered and (ii) n_I^1 and n_J^1 are calculated at the temperature T_{ph} instead of T_0 . The quantity T_{ph} is the electronic temperature commonly used in a self-consistent linear-response calculation. Usually T_{ph} is much larger than the physical temperature T_0 , (e.g., $T_{\text{ph}} \approx 4000$ K).²⁸ The main consequence of the stationary property of the functional F_{IJ} is that it allows us to compute phonon frequencies from an approximate force-constant matrix $\tilde{C}_{IJ}(\omega, T_0)$ in a *nonself-consistent* way and performing an error that is quadratic in $|n_I^1(\mathbf{r}, \omega, T_0) - n_I^1(\mathbf{r}, 0, T_{\text{ph}})|$.

Thus, a time-consuming self-consistent calculation of the nonadiabatic force constants $C_{IJ}(\omega, T_0)$ has been replaced by an approximate nonself-consistent one, $\tilde{C}_{IJ}(\omega, T_0)$, with an error that is negligible for the phonon frequencies, as it will be demonstrated in the applications considered in this work.

We now first add and subtract $C_{IJ}(0, T_{\text{ph}})$ (the standard linear-response adiabatic self-consistent force constants) in the left member of Eq. (21), and then perform a Fourier transform to obtain

$$\tilde{C}_{sr}(\mathbf{q}, \omega, T_0) = \Pi_{sr}(\mathbf{q}, \omega, T_0) + C_{sr}(\mathbf{q}, 0, T_{\text{ph}}), \quad (22)$$

where

$$\begin{aligned} \Pi_{sr}(\mathbf{q}, \omega, T_0) &= \frac{2}{N_k(T_0)} \sum_{kij}^{N_k(T_0)} \frac{f_{\mathbf{k}i}(T_0) - f_{\mathbf{k}+\mathbf{q}j}(T_0)}{\epsilon_{\mathbf{k}i} - \epsilon_{\mathbf{k}+\mathbf{q}j} + \omega + i\eta} \\ &\quad \times \mathbf{d}_{ij}^s(\mathbf{k}, \mathbf{k} + \mathbf{q}) \mathbf{d}_{ji}^r(\mathbf{k} + \mathbf{q}, \mathbf{k}) \\ &\quad - \frac{2}{N_k(T_{\text{ph}})} \sum_{kij}^{N_k(T_{\text{ph}})} \frac{f_{\mathbf{k}i}(T_{\text{ph}}) - f_{\mathbf{k}+\mathbf{q}j}(T_{\text{ph}})}{\epsilon_{\mathbf{k}i} - \epsilon_{\mathbf{k}+\mathbf{q}j}} \\ &\quad \times \mathbf{d}_{ij}^s(\mathbf{k}, \mathbf{k} + \mathbf{q}) \mathbf{d}_{ji}^r(\mathbf{k} + \mathbf{q}, \mathbf{k}) \end{aligned} \quad (23)$$

with the following definition of the deformation potential matrix element:

$$\mathbf{d}_{mn}^s(\mathbf{k} + \mathbf{q}, \mathbf{k}) = \langle \mathbf{k} + \mathbf{q}m | \frac{\partial v_{\text{SCF}}}{\partial \mathbf{u}_{\mathbf{q}s}} | \mathbf{k}n \rangle \quad (24)$$

and where $|\mathbf{k}n\rangle$ is the periodic part of the Bloch wave function, i.e., $|\psi_{\mathbf{k}n}\rangle = e^{i\mathbf{k}\cdot\mathbf{r}}|\mathbf{k}n\rangle / \sqrt{N_k}$ and $\mathbf{u}_{\mathbf{q}s}$ is the Fourier transform of the phonon displacement $\mathbf{u}_{Ls}$. The integration in Eq. (24) is understood to be on the unit cell. The quantity v_{SCF} is the periodic part of the static self-consistent potential, namely, $V_{\text{SCF}}(\mathbf{r}) = v_{\text{SCF}}(\mathbf{r})e^{i\mathbf{q}\cdot\mathbf{r}}$. This static self-consistent potential is calculated using standard linear response at temperature T_{ph} .

The calculation of $\Pi_{sr}(\mathbf{q}, \omega, T_0)$ requires the knowledge of band energies and eigenfunctions on a denser $N_k(T_0)$ k -point grid using an electronic temperature T_0 only in an energy window of width $\sim \max(T_{\text{ph}}, \omega)$ around the Fermi level. Moreover it does not require to recalculate the derivative of the self-consistent potential. As such it is much less time consuming than a linear-response self-consistent calculation to obtain $C_{rs}(\mathbf{q}, 0, T_0)$. The nonadiabatic phonon frequencies are calculated (in the clean limit) nonself-consistently from the Hermitian part of $\tilde{C}_{sr}(\mathbf{q}, \omega, T_0)$ [see Eq. (5)].

The expression of the adiabatic force constants at the physical temperature T_0 is obtained setting $\omega=0$ in the Eq. (22),

$$\tilde{C}_{sr}(\mathbf{q}, \omega=0, T_0) = \Pi_{sr}(\mathbf{q}, 0, T_0) + C_{sr}(\mathbf{q}, 0, T_{\text{ph}}). \quad (25)$$

In this case the force constants are Hermitian and the error in the approximated force constants is quadratic in $|n_I^1(\mathbf{r}, 0, T_0) - n_I^1(\mathbf{r}, 0, T_{\text{ph}})|$.

The advantage of the present procedure is that the linear-response self-consistent calculation is performed with a small number of k points $N_k(T_{\text{ph}})$ whereas the low-temperature force constants are obtained with a nonself-consistent calculation over much denser $N_k(T_0)$ k -points mesh. This approach requires, as in a conventional electron-phonon coupling calculation, the knowledge of the wave functions in a dense $N_k(T_0)$ k -points grid and in an energy window of the order of the maximum between T_{ph} and ω around the Fermi level, but does not require the self-consistent linear-response calculation of the derivative of the Kohn-Sham potential with respect to an atomic displacement. As such the procedure is substantially less time consuming.

Finally from Eq. (23) it is evident that the largest difference between the adiabatic and nonadiabatic phonon frequencies occurs at zone center ($\mathbf{q}=0$). Indeed the intraband contribution ($i=j$) leads to a zero denominator in the second term on the rhs and a nonzero one proportional to ω in the first term on the rhs (see also Refs. 12, 13, and 21).

G. Phonon frequencies interpolation over k points at fixed phonon momentum: Practical implementation

The practical implementation of the above theoretical formulation for the phonon frequencies proceeds as follows:

(1) Perform a standard linear-response calculation *for a given phonon momentum* $\mathbf{q}$ using a $N_k(T_{\text{ph}})$ k -points mesh and smearing T_{ph} for the electronic integration to obtain $C_{sr}(\mathbf{q}, 0, T_{\text{ph}})$.

(2) In order to perform the second summation in $\Pi_{sr}(\mathbf{q}, \omega, T_0)$ [Eq. (23)], calculate deformation-potential matrix element of Eq. (24) on the electron-momentum grid composed of $N_k(T_{\text{ph}})$ k points using a smearing T_{ph} .

(3) Generate wave functions $|\mathbf{k}n\rangle$ and energies $\epsilon_{\mathbf{k}n}$ on the denser $N_k(T_0)$ electron-momentum k -points grid.

(4) Perform a second nonself-consistent calculation of the deformation-potential matrix element on the more dense $N_k(T_0)$ k -points grid using smearing T_0 and v_{SCF} obtained on the $N_k(T_{\text{ph}})$ grid to obtain the first summation in $\Pi_{sr}(\mathbf{q}, \omega, T_0)$.

(5) Calculate $\tilde{C}_{sr}(\mathbf{q}, \omega, T_0)$ [or $\tilde{C}_{sr}(\mathbf{q}, \omega=0, T_0)$] using Eq. (22) [or Eq. (25)].

(6) Diagonalize the dynamical matrix to obtain phonon frequencies and phonon eigenvectors.

The procedure illustrated in this section is used to obtain at a fixed phonon momentum $\mathbf{q}$ well-converged phonon frequencies with respect to electronic k points and smearing. Then standard Fourier interpolation²⁹ can be performed to obtain dynamical matrices throughout the BZ. However, this procedure, has still two main computational shortcomings. First, the calculations of the wave functions and matrix elements (points 3 and 4) become cumbersome when very dense $N_k(T_0)$ k -points grid for the electron momentum are necessary to converge. Second, in presence of phonon anomalies and not-too-smooth phonon dispersion a dense k sampling of the phonon BZ is required.

An optimal solution to overcome these problems is represented by the use of maximally localized Wannier functions^{15,30} as an alternative electron basis function. The method and the implementation of the Wannier functions approach for the electron-phonon interpolation is presented in Sec. III.

H. Phonon linewidth and of the electron-phonon coupling

The imaginary part of the force-constant matrix is related to phonon damping, namely, the energy-conserving decay of a phonon into particle-hole pairs.

The imaginary part of Eq. (16) is

$$\begin{aligned} \text{Im}[C_{IJ}(\omega, T)] = & 2 \sum_{\mathbf{k}i, \mathbf{k}'j}^{N_k(T)} [f_{\mathbf{k}i}(T) - f_{\mathbf{k}'j}(T)] \\ & \times \left\{ \pi \langle \psi_{\mathbf{k}'j} | \text{Re} \left[\frac{\delta V_{\text{SCF}}(\mathbf{r}, \omega)}{\delta \mathbf{u}_I} \right] | \psi_{\mathbf{k}i} \rangle \right. \\ & \times \langle \psi_{\mathbf{k}i} | \frac{\delta V_{\text{ext}}(\mathbf{r})}{\delta \mathbf{u}_J} | \psi_{\mathbf{k}'j} \rangle \times \delta(\epsilon_{\mathbf{k}i} - \epsilon_{\mathbf{k}'j} + \omega) \\ & + \langle \psi_{\mathbf{k}'j} | \text{Im} \left[\frac{\delta V_{\text{SCF}}(\mathbf{r}, \omega)}{\delta \mathbf{u}_I} \right] | \psi_{\mathbf{k}i} \rangle \\ & \left. \times \langle \psi_{\mathbf{k}i} | \frac{\delta V_{\text{ext}}(\mathbf{r})}{\delta \mathbf{u}_J} | \psi_{\mathbf{k}'j} \rangle \times P \left[\frac{1}{\epsilon_{\mathbf{k}i} - \epsilon_{\mathbf{k}'j} + \omega} \right] \right\}, \end{aligned} \quad (26)$$

where P indicates the principal part. To obtain Eq. (26) we have assume that the unperturbed Hamiltonian is time-reversal symmetric so that a real set of eigenfunctions exists.

This expression is exact but it has two disadvantages. First it requires the expensive calculation of the derivative of the self-consistent potential at finite frequency both in its real and imaginary parts. Second the phonon decay in electron-hole pairs is not manifest in the term including the principal part. These problems persist if the imaginary part of Eq. (17) is considered, since, in this functional, both $\delta V_{\text{SCF}}(\mathbf{r}, \omega) / \delta \mathbf{u}_I$ and $n_I^1(\mathbf{r}, \omega, T)$ are complex quantities. These two shortcomings are absent if the approximated force-constant matrix in Eq. (21) is used. Indeed the imaginary part of Eq. (21) is

$$\begin{aligned} \text{Im}[\tilde{C}_{IJ}(\omega, T)] = & 2\pi \sum_{\mathbf{k}i, \mathbf{k}'j}^{N_k(T)} [f_{\mathbf{k}i}(T) - f_{\mathbf{k}'j}(T)] \\ & \times \langle \psi_{\mathbf{k}'j} | \frac{\delta V_{\text{SCF}}(\mathbf{r}, 0)}{\delta \mathbf{u}_I} | \psi_{\mathbf{k}i} \rangle \\ & \times \langle \psi_{\mathbf{k}i} | \frac{\delta V_{\text{SCF}}(\mathbf{r}, 0)}{\delta \mathbf{u}_J} | \psi_{\mathbf{k}'j} \rangle \delta(\epsilon_{\mathbf{k}i} - \epsilon_{\mathbf{k}'j} + \omega) \end{aligned} \quad (27)$$

with an error quadratic in $|n_I^1(\mathbf{r}, \omega) - n_I^1(\mathbf{r}, 0)|$. Fourier transforming and replacing Eq. (27) in Eq. (9) gives the well-known equation for the phonon linewidth $\gamma_{\mathbf{q}\nu}$ full width half maximum (FWHM), that is,

$$\begin{aligned} \gamma_{\mathbf{q}\nu}^{\text{Fermi}} = & \frac{4\pi}{N_k(T)} \sum_{\mathbf{k}, m, n}^{N_k(T)} |g_{nm}^{\nu}(\mathbf{k}, \mathbf{k} + \mathbf{q})|^2 \\ & \times (f_{\mathbf{k}n} - f_{\mathbf{k}+q, m}) \delta(\epsilon_{\mathbf{k}+q, m} - \epsilon_{\mathbf{k}n} - \omega_{\mathbf{q}\nu}), \end{aligned} \quad (28)$$

where $g_{nm}^{\nu}(\mathbf{k}, \mathbf{k} + \mathbf{q}) = \sum_s \mathbf{e}_{\mathbf{q}\nu}^s \cdot \mathbf{d}_{mn}^s(\mathbf{k} + \mathbf{q}, \mathbf{k}) / \sqrt{2M_s \omega_{\mathbf{q}\nu}}$.

In absence of the electron-electron interaction a similar expression involving only the derivative of the bare external potential is easily obtained using Fermi golden rule. In the presence of electron-electron interaction our formalism justify the replacement of the derivative of the bare external potential by the derivative of the static screened potential $V_{\text{SCF}}(\mathbf{r}, 0)$ in the Fermi golden rule with a well-controlled error.

Under certain conditions illustrated in Refs. 31 and 32, the phonon linewidth can be reduced to

$$\begin{aligned} \tilde{\gamma}_{\mathbf{q}\nu} = & \frac{4\pi\omega_{\mathbf{q}\nu}}{N_k(T)} \sum_{\mathbf{k}, m, n}^{N_k(T)} |g_{nm}^{\nu}(\mathbf{k}, \mathbf{k} + \mathbf{q})|^2 \\ & \times \delta(\epsilon_{\mathbf{k}n}) \delta(\epsilon_{\mathbf{k}+q, m} - \epsilon_{\mathbf{k}n} - \omega_{\mathbf{q}\nu}). \end{aligned} \quad (29)$$

Finally, neglecting $\omega_{\mathbf{q}\nu}$ in Eq. (29), we obtain Allen formula,³¹ namely,

$$\gamma_{\mathbf{q}\nu} = \frac{4\pi\omega_{\mathbf{q}\nu}}{N_k(T)} \sum_{\mathbf{k}, n, m}^{N_k(T)} |g_{nm}^{\nu}(\mathbf{k}, \mathbf{k} + \mathbf{q})|^2 \delta(\epsilon_{\mathbf{k}n}) \delta(\epsilon_{\mathbf{k}+q, m}). \quad (30)$$

The Allen formula^{2,31} is widely used, and represents a good estimation of the phonon linewidth due to electron-phonon effects, in the absence of anharmonic effects and other scattering processes. In addition, the Allen formula relates the phonon linewidth, as measured by inelastic neutron or x-ray measurements, to the electron-phonon coupling as

$$\lambda_{\mathbf{q}\nu} = \frac{\gamma_{\mathbf{q}\nu}}{2\pi\omega_{\mathbf{q}\nu}^2 \mathcal{N}_s}, \quad (31)$$

where $\mathcal{N}_s$ is the electronic density of states per spin at the Fermi energy.

With this definition, the isotropic Eliashberg function is

$$\alpha^2 F(\omega) = \frac{1}{2N_q} \sum_{\mathbf{q}\nu} \lambda_{\mathbf{q}\nu} \omega_{\mathbf{q}\nu} \delta(\omega - \omega_{\mathbf{q}\nu}), \quad (32)$$

where N_q is the number of phonon wave vectors. We also define the integrated electron-phonon coupling as

$$\lambda(\omega) = 2 \int_0^\omega \frac{\alpha^2 F(\omega')}{\omega'} d\omega'. \quad (33)$$

III. WANNIER FUNCTIONS

A. Wannier interpolation of the electron-phonon matrix element

In this section we explain how to interpolate the electron-phonon matrix element throughout the BZ using Wannier functions, summarizing what done in Ref. 10.

Using standard first-principles methods a set of Bloch functions $\psi_{\mathbf{k}n}$ are generated with $\mathbf{k}$ belonging to a uniform N_k^w k -points grid centered in Γ . A set of Wannier functions centered on site $\mathbf{R}$ are defined by the relation

$$|\mathbf{R}m\rangle = \frac{1}{\sqrt{N_k^w}} \sum_{\mathbf{k}n} e^{-i\mathbf{k}\cdot\mathbf{R}} U_{nm}(\mathbf{k}) |\psi_{\mathbf{k}n}\rangle. \quad (34)$$

A suitable transformation matrix, $U_{nm}(\mathbf{k})$, must be determined in the so-called Wannierization procedure. In this work we choose to work with maximally localized Wannier functions (MLWFs),^{15,30,33} although other Wannierization schemes are possible. In the MLWF case, the matrices $U_{nm}(\mathbf{k})$ are obtained following the prescription of Refs. 15 and 30, which guarantees the maximal space localization of the final Wannier functions. This last requirement will be essential in the spirit of interpolation of the electron-phonon matrix elements.

Specifically, if the band structure is formed by a composite group of bands and the number of Wannier functions is identical to the number of bands of the composite group of bands, then the matrix $U_{nm}(\mathbf{k})$ is a square matrix. On the contrary if the desired bands are entangled in a larger manifold, a preliminary disentanglement procedure from the manifold must be performed and then the square matrix $U_{nm}(\mathbf{k})$ is obtained.³⁰

The deformation-potential matrix elements $\mathbf{d}_{mn}^s(\mathbf{k}+\mathbf{q}, \mathbf{k})$ [see Eq. (24)] are calculated using linear-response scheme. In this calculation particular care is needed for the deformation potential at zone center, namely, $\mathbf{d}_{mn}^s(\mathbf{k}, \mathbf{k})$, as explained in Sec. III B.

It is crucial to note that the periodic parts $|\mathbf{k}n\rangle$ and $|\mathbf{k}+\mathbf{q}m\rangle$ entering in $\mathbf{d}_{mn}^s(\mathbf{k}+\mathbf{q}, \mathbf{k})$ have to be *exactly the same wave functions used for the Wannierization procedure*. If this is not the case, spurious (unphysical) phases appear in the $|\mathbf{k}n\rangle$'s (i.e., a phase added by the diagonalization routine or other computational reasons) and the localization properties of the Wannier functions in real space are completely lost. A way to enforce this condition is to use a uniform grid centered at Γ so that $\mathbf{k}+\mathbf{q}=\mathbf{k}'+\mathbf{G}$ with $\mathbf{k}'$ still belonging to the original grid. In this way $|\mathbf{k}+\mathbf{q}m\rangle$ can be obtained from $|\mathbf{k}'n\rangle$ simply multiplying by a phase determined by the $\mathbf{G}$ -vector translation and no additional phases occur.

Exploiting translational invariance, the deformation-potential matrix element in the Wannier function basis is obtained by Fourier transform as

$$\begin{aligned} \mathbf{d}_{mn}^s(\mathbf{R}, \mathbf{R}_L) &= \langle 0m | \frac{\delta V_{\text{SCF}}}{\delta \mathbf{u}_{s,L}} | \mathbf{R}n \rangle = \frac{1}{N_k^w} \sum_{\mathbf{k}, \mathbf{q}} \sum_{m', n'}^{N_k^w} e^{-i\mathbf{k}\cdot\mathbf{R}+i\mathbf{q}\cdot\mathbf{R}_L} \\ &\times U_{mm'}^*(\mathbf{k}+\mathbf{q}) \mathbf{d}_{m'n'}^s(\mathbf{k}+\mathbf{q}, \mathbf{k}) U_{n'n}(\mathbf{k}), \end{aligned} \quad (35)$$

where $\mathbf{R}$ and $\mathbf{R}_L$ belong to a N_k^w real-space supercell. At this point it is important to underline that *the grid of N_k^w k points on which the Wannierization process has been carried out has to be exactly the same grid for the phonon momentum on which the dynamical matrices have been computed*. One linear-response calculation for each k point in the phonon irreducible BZ of the N_k^w electron k -points grid has to be carried out. If this constrain is not respected, the localization properties of the electron-phonon matrix element in real space is not guaranteed.

The origin of this constrain can be understood considering the two one-dimensional examples illustrated in Fig. 1. In the first case the real-space periodicity of the Wannier functions is the same as that of the derivative of $\frac{\delta V_{\text{SCF}}}{\delta \mathbf{u}_{s,L}}$ and corresponds to a supercell composed of four real-space unit cells. In the second case the real-space periodicity of the Wannier functions is a unit cell while that of $\frac{\delta V_{\text{SCF}}}{\delta \mathbf{u}_{s,L}}$ is a supercell composed of four real-space unit cells. In the first case the real-space deformation potential becomes zero at the supercell border, the overlap between different supercells can be neglected and the Wannier interpolation of the electron-phonon matrix element can be carried out. In the second case the deformation potential at the supercell border is nonzero, the overlap between different supercells cannot be neglected and the Wannier interpolation method of the electron-phonon matrix element cannot be carried out. This examples demonstrates that in the general case it is necessary to have the same real-space periodicity for the electronic Wannier functions and $\frac{\delta V_{\text{SCF}}}{\delta \mathbf{u}_{s,L}}$. Of course, if the localization of $\frac{\delta V_{\text{SCF}}}{\delta \mathbf{u}_{s,L}}$ is actually much less than four unit cells, as, for example, the phonon linear-response calculation has been carried out on a denser phonon-momentum grid then the minimum one required to converge $\frac{\delta V_{\text{SCF}}}{\delta \mathbf{u}_{s,L}}$, then the constrain that the phonon-momentum grid has to be the same grid of N_k^w k points used for Wannierization can be released. Still it remains true that the minimal grid necessary to converge $\frac{\delta V_{\text{SCF}}}{\delta \mathbf{u}_{s,L}}$ has to be identical to that used for the Wannierization of the electronic band structure, as the example above demonstrates.

Inverting Eq. (34), we obtain

$$|\psi_{\mathbf{k}n}\rangle = \frac{1}{\sqrt{N_k^w}} \sum_{\mathbf{R}} \sum_m e^{i\mathbf{k}\cdot\mathbf{R}} U_{nm}^*(\mathbf{k}) |\mathbf{R}m\rangle. \quad (36)$$

Noting that $\mathbf{d}_{mn}^s(\mathbf{k}+\mathbf{q}, \mathbf{k}) = \frac{1}{N_k^w} \langle \psi_{\mathbf{k}+\mathbf{q}m} | \frac{\delta V_{\text{SCF}}}{\delta \mathbf{u}_{s,L}} | \psi_{\mathbf{k}n} \rangle$ and using Eq. (36) one obtains,

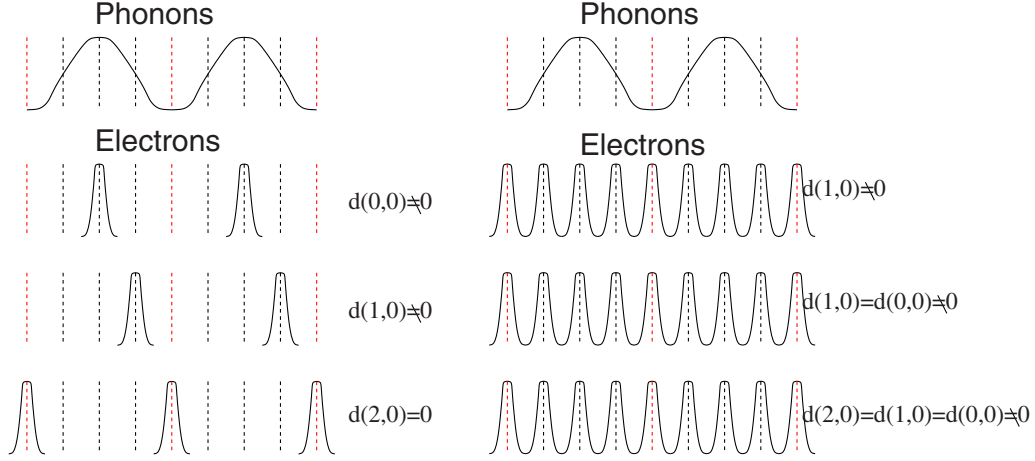


FIG. 1. (Color online) One-dimensional examples illustrating the need of having the same real-space periodicity for the Wannier functions and for the force constants. In the picture the vertical black dashed lines show the borders of the unit cell in real space. The vertical red dashed lines are the borders of the four unit cells real-space supercell. The quantity $\frac{\delta V_{\text{SCF}}}{\delta \mathbf{u}_{sL}}$ (labeled “phonons”) is considered to be localized in the supercell while the square modulus of the electronic Wannier functions, namely, $|\langle \mathbf{r} | \mathbf{R} m \rangle|^2$, (labeled “electrons”) are considered to be localized on a single unit cell. The quantity $d(\mathbf{R}, \mathbf{R}_L) = d_{mm}^s(\mathbf{R}, \mathbf{R}_L) = \int |\langle \mathbf{r} | \mathbf{R} m \rangle|^2 \frac{\delta V_{\text{SCF}}}{\delta \mathbf{u}_{sL}} d\mathbf{r}$ is the deformation potential as defined in Eq. (35). When the periodicity of the phonons and of the electrons is the same (left) then the deformation potential at the supercell boundary is zero [$d(2,0)=0$], $d(\mathbf{R}, \mathbf{0})$ is localized and Wannier interpolation can be carried out. On the contrary, if the periodicity in the right case where the periodicity is different, $d(\mathbf{R}, \mathbf{0})$ is always different from zero and the Wannier interpolation of the electron-phonon matrix element cannot be carried out.

$$\mathbf{d}_{mn}^s(\mathbf{k} + \mathbf{q}, \mathbf{k}) = \frac{1}{(N_k^w)^2} \sum_L \sum_{\mathbf{R}} \sum_{m'n'} e^{i\mathbf{k} \cdot \mathbf{R} + i\mathbf{q} \cdot \mathbf{R}_L} U_{m'm}(\mathbf{k} + \mathbf{q}) \mathbf{d}_{m'n'}^s(\mathbf{R}, \mathbf{R}_L) U_{nn'}^*(\mathbf{k}), \quad (37)$$

where $\mathbf{R}$ and $\mathbf{R}_L$ belong to a N_k^w real-space supercell. Now, if $\mathbf{d}_{mn}^s(\mathbf{R}, \mathbf{R}_L)$ is localized inside the N_k^w real-space supercell then the interaction between different N_k^w real-space supercells can be neglected and $\mathbf{d}_{mn}^s(\mathbf{k} + \mathbf{q}, \mathbf{k})$ can be obtained from Eq. (37) via a slow Fourier transform. In practice this means that in Eq. (37) now $\mathbf{k}$ and $\mathbf{q}$ are any k points in the BZ. As a result of the interpolation, $\mathbf{d}_{mn}^s(\mathbf{k} + \mathbf{q}, \mathbf{k})$ can be used to calculate any physical property as in a simple tight-binding scheme.

B. Deformation-potential matrix elements of optical zone-center phonons

In this section we discuss the peculiarities related to the calculation of the electron-phonon matrix elements for optical zone-center phonons ($\mathbf{q} = \mathbf{0}$). The periodic part of the self-consistent potential, induced by the phonon displacement at wavelength $\mathbf{q}$ of the atom s can be decomposed in the Coulomb (Cl) potential (the sum of the bare and Hartree potentials) and XC contributions,

$$\frac{\delta v_{\text{SCF}}(\mathbf{r})}{\delta \mathbf{u}_{qs}} = \frac{\delta v_{\text{XC}}(\mathbf{r})}{\delta \mathbf{u}_{qs}} + \frac{\delta v_{\text{Cl}}(\mathbf{r})}{\delta \mathbf{u}_{qs}}. \quad (38)$$

The integral of the Coulomb contribution over the unit-cell volume Ω is

$$\Delta_{qs} = \frac{1}{\Omega} \int d^3r \frac{\delta v_{\text{Cl}}(\mathbf{r})}{\delta \mathbf{u}_{qs}}. \quad (39)$$

In DFT linear-response codes, such as QUANTUM-ESPRESSO,³⁴ the phonon calculation with $\mathbf{q} \neq \mathbf{0}$ and $\mathbf{q} = \mathbf{0}$ are treated with two different approaches.^{7,18}

At $\mathbf{q} \neq \mathbf{0}$, the calculation is performed within the grand-canonical ensemble, with a constant electron chemical-potential (Fermi level) ϵ_F . In a metal, the limit

$$\lim_{\mathbf{q} \rightarrow \mathbf{0}} \Delta_{qs} = \Delta_{0+s} \quad (40)$$

is well defined and independent on the direction of $\mathbf{q}$. In general one has $\Delta_{0+s} \neq 0$.

At $\mathbf{q} = \mathbf{0}$, the calculation is performed in the canonical ensemble with a constant number of electrons. In this calculation the variation in the average Coulomb potential is conventionally set to zero, namely,

$$\Delta_{0s} = 0. \quad (41)$$

To keep constant the number of electrons the derivative of the Fermi energy with respect to the phonon displacement $\delta \epsilon_F / \delta \mathbf{u}_{0s}$ can be different from zero. In particular,^{7,18} it must be

$$\frac{\delta \epsilon_F}{\delta \mathbf{u}_{0s}} = -\Delta_{0+s}. \quad (42)$$

In the QUANTUM-ESPRESSO implementation³⁴ the $\delta v_{\text{SCF}}(\mathbf{r}) / \delta \mathbf{u}_{qs}$ stored on disk is discontinuous at $\mathbf{q} = \mathbf{0}$, since, in this case, it does not include (as it should) the contribution from the average Coulomb potential. As a consequence the electron-phonon matrix elements computed with $\delta v_{\text{SCF}}(\mathbf{r}) / \delta \mathbf{u}_{0s}$ are incorrect. Moreover such discontinuity deteriorates the localization properties of the electron-phonon matrix elements in real space. The problem is easily solved by redefining the self-consistent potential to be used in the

calculation of the deformation-potential matrix elements for $\mathbf{q}=\mathbf{0}$ as

$$\frac{\delta \tilde{v}_{\text{SCF}}(\mathbf{r})}{\delta \mathbf{u}_{0s}} = \frac{\delta v_{\text{SCF}}(\mathbf{r})}{\delta \mathbf{u}_{0s}} - \frac{\delta \epsilon_F}{\delta \mathbf{u}_{0s}}. \quad (43)$$

Note that since $\delta \epsilon_F / \delta \mathbf{u}_{0s}$ transforms under symmetry operation as a force, it is different from zero only for the atoms for which the internal coordinates are not fixed by symmetry. For this reason, $\delta \epsilon_F / \delta \mathbf{u}_{0s}$ is finite in CaC_6 , while it vanishes in MgB_2 .

We remark that the same problem occurs when a frozen-phonon calculation of $\frac{\delta v_{\text{SCF}}(\mathbf{r})}{\delta \mathbf{u}_{0s}}$ is carried out as in all the electronic-structure codes the average Coulomb potential is conventionally set to zero.

C. Wannier interpolation of the dynamical matrix at fixed phonon momentum

Steps 4, 5, and 6 of Sec. II G can be repeated using Wannier functions to interpolate at fixed phonon momentum $\mathbf{q}$ the quantity $\Pi_{sr}(\mathbf{q}, \omega, T_0)$ to obtain Eq. (23). The advantage of the Wannier-interpolation-based strategy with respect to the procedure explained in Sec. II G is that the time needed to calculate the matrix element is now negligible as there is no need to obtain, from first-principles, wave functions and energies on the dense $N_k(T_0)$ k -point grid. Still it is necessary to perform Fourier interpolation²⁹ to obtain dynamical matrices throughout the full BZ.

D. Wannier interpolation of the dynamical matrix

In what follows we outline a strategy to obtain dynamical matrices throughout the BZ using both Fourier interpolation²⁹ and Wannier functions. The method solves the main problem related to the presence of Kohn anomalies, originating from long-range interactions in the dynamical matrix. The idea is to separate in the force-constant matrix obtained in Eq. (22) in the short- and long-range components. The long-range force constants are associated to Kohn anomalies driven by Fermi-surface nesting, and, as such, they cannot be easily Fourier interpolated²⁹ and require an accurate sampling of the Fermi surface. This last part will be treated using the Wannier interpolation scheme explained in Sec. III A. On the contrary short-range force constants produce smooth phonon dispersions and can be safely Fourier interpolated²⁹ and do not require accurate sampling of the Fermi surface. Treating separately the two length scales permits to obtain converged phonon frequencies with respect to k -point sampling and electronic temperature, everywhere in the Brillouin zone.

This procedure is similar to the treatment of long-range dipolar forces due to the Born effective charges in polar semiconductors.^{7,9} In this case, these long-range forces generate a nonanalytical behavior of the dynamical matrix at zone center. While Fourier interpolation²⁹ of the dynamical matrices including the nonanalytical terms is impossible, it becomes possible if the long-range forces are subtracted to obtain short-range force constants. The nonanalytical part

subtracted to perform Fourier interpolation²⁹ is added again after Wannier interpolation.

In this spirit, we rewrite Eq. (22) as

$$\tilde{C}_{sr}(\mathbf{q}, \omega, T_0) = \Pi_{sr}(\mathbf{q}, \omega, T_0) - \Pi_{sr}(\mathbf{q}, 0, T_\infty) + \tilde{C}_{sr}(\mathbf{q}, 0, T_\infty), \quad (44)$$

where

$$\tilde{C}_{sr}(\mathbf{q}, 0, T_\infty) = C_{sr}(\mathbf{q}, 0, T_{\text{ph}}) + \Pi_{sr}(\mathbf{q}, 0, T_\infty) \quad (45)$$

and T_∞ is an electronic temperature large enough in order to have only short-range force constants named $\tilde{C}_{sr}(\mathbf{q}, 0, T_\infty)$, and no Kohn anomalies in the corresponding phonon branches. As a consequence, Fourier interpolation can be applied to $\tilde{C}_{sr}(\mathbf{q}, 0, T_\infty)$.

In practical implementation the procedure is the following:

- (1) Obtain $C_{sr}(\mathbf{q}, 0, T_{\text{ph}})$ from self-consistent linear-response phonon calculations. Such force constants are evaluated using a N_k^w k -point grid for the phonon momentum and a $N_k(T_{\text{ph}})$ k -point grid for the electron momentum.
- (2) Calculate $\Pi_{sr}(\mathbf{q}, 0, T_\infty)$ using the Wannier functions as described in Sec. III C.
- (3) Use Eq. (45) to compute $\tilde{C}_{sr}(\mathbf{q}, 0, T_\infty)$ on the N_k^w phonon-momentum grid.
- (4) Fourier interpolate²⁹ $\tilde{C}_{sr}(\mathbf{q}, 0, T_\infty)$ to obtain dynamical matrices at any desired phonon momentum at temperature T_∞ .
- (5) Obtain $\tilde{C}_{sr}(\mathbf{q}, \omega, T_0)$ in Eq. (44) by Wannier interpolation of $\Pi_{sr}(\mathbf{q}, \omega, T_0) - \Pi_{sr}(\mathbf{q}, 0, T_\infty)$ at any desired phonon momentum.
- (6) Diagonalize the dynamical matrix associated to $\tilde{C}_{sr}(\mathbf{q}, \omega, T_0, T_{\text{ph}})$ to obtain adiabatic, $\omega=0$, or nonadiabatic (in the clean limit) $\omega=\omega_{\mathbf{q}\nu}$, phonon frequencies. These phonon frequencies include Kohn anomalies as long-range terms are properly treated by the Wannier-functions approach.

IV. APPLICATIONS

We applied the theoretical and computational framework developed in the preceding sections to two well-known superconductors, namely, magnesium diboride (MgB_2) and calcium intercalated graphite (CaC_6). In these systems phonon, electron-phonon, and superconducting properties are extensively investigated from both theoretical and experimental point of view and a detailed comparison can be made. At the same time, they represent nontrivial examples, where convergence problems in first-principles approaches are relevant for the calculation of phonon and superconducting properties.

A. MgB_2

MgB_2 is, without doubts, one of the most studied and investigated materials, since 2001. The discovery of superconductivity at intermediate temperatures (40 K),³⁵ in this compound, represented an unexpected surprise in the scientific community. Easily available, a huge amount of experi-

mental characterizations were immediately possible. On the other hand, MgB_2 being composed of light elements in an hexagonal unit cell with only three atoms, allowed a first-principles computational approach for the theoretical description and understanding of its normal and superconducting properties. Density-functional theory and linear-response techniques, revealed an extraordinary high electron-phonon coupling between sp^2 bonding and antibonding boron orbitals, with a particular in-plane mode (E_{2g}) of the hexagonal boron sheet.^{36–38} Based on model calculations of the electron-phonon coupling parameter ($\lambda \approx 1$ in Ref. 37), the approximate critical temperature was estimated to be around 40 K. However, a subsequent careful investigation of the problem, revealed that the first-principles calculated values of λ , were too low to explain this high critical temperature, unless unphysical low Coulomb pseudopotentials were used.³⁹ The solution of this inconsistency, has come with the discovery of two-band superconductivity⁴⁰ in MgB_2 . Two different gaps develop on the σ and π bands of the boron sheets.³⁹ This allows to gain new scattering channels to enhance T_c still containing the average value of λ . At the moment, MgB_2 is classified as a two-band electron-phonon superconductor.^{41,42}

This continuous improvement of the theoretical explanation of the normal and superconducting properties of MgB_2 was in part due to some difficulties in the proper calculations of the electron-phonon coupling and of the phonon frequencies. Soon after the discovery of superconductivity in MgB_2 , the first theoretical papers (based on standard DFT codes) evidenced a relevant and anomalous difficulty to properly “converge” the E_{2g} phonon frequency and the electron-phonon coupling. The reason is now clear: due to the two-dimensional nature (almost cylindrical) of the σ^* Fermi-surfaces electron-phonon coupling calculations require a careful integration of the Fermi surface is needed. This translates, in practical calculations, with the necessity to use an extremely dense k -space integration for electronic and phononic degree of freedom.³² Although feasible, in principle, it would require a huge amount of resources and computational time.

So, still after about 10 years of calculations, the fundamental question about the value of the electron-phonon coupling in MgB_2 , remains unanswered. This information is fundamental in order to validate the electron-phonon origin of the superconductivity in MgB_2 and at the same time, include other, still unexplored pairing interactions.

The Wannier interpolation scheme, developed in the present paper, of phonon frequencies and electron-phonon matrix elements, represents the main tool to solve this problem. It retains the first-principles character but at the same time it is affordable from a computational point of view.

In MgB_2 the BZ-center phonon frequency, measured by Raman spectroscopy, lies between the adiabatic and clean-limit nonadiabatic phonon frequency¹² computed by DFT. Thus MgB_2 is in the intermediate regime (see Sec. II B and the relaxation time estimated in Ref. 12). Since the experimental frequency at BZ center is closer to the adiabatic than the clean-limit nonadiabatic value,¹² in MgB_2 we will not consider nonadiabatic effects, and we will present only the adiabatic dispersion. A proper treatment of nonadiabatic ef-

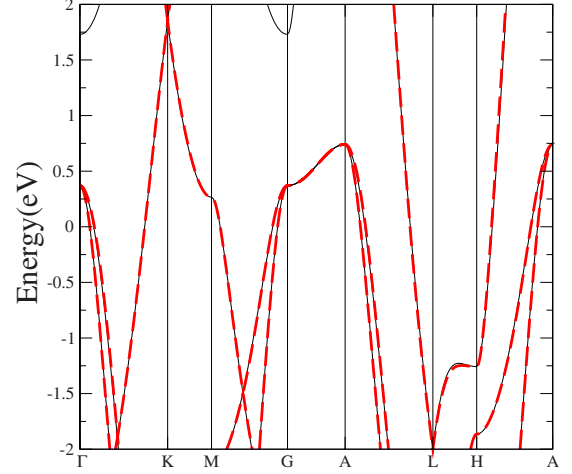


FIG. 2. (Color online) Wannier-interpolated (red dashed) and first-principles-calculated bands (black continuous) for MgB_2 . The band energies are plotted with respect to the Fermi level.

fects in this case would require a more complicate procedure such that applied in the framework of model Hamiltonian in Ref. 23.

1. Technical details

Wannier interpolation of the MgB_2 band structure is carried out using a $N_k^w = 6 \times 6 \times 4$ k -points grid centered at Γ using five Wannier functions starting from random projections. The Wannierized band structure is in excellent agreement with first-principles calculation in a 1.5 eV region from the Fermi level, as shown in Fig. 2.

The phonon dispersion and the electron-phonon matrix element are calculated using linear response^{7,34} on the irreducible part of the N_k^w k -points grid centered at Γ . The $\delta v_{\text{SCF}} / \delta \mathbf{u}_{\mathbf{q}s}$ on the full grid are obtained applying symmetry operations of the crystal. In the linear-response calculation we perform electronic integration using a $N_k = 16 \times 16 \times 12$ k -point grid in the Brillouin zone and an Hermite-Gaussian smearing $T_{\text{ph}} = 0.025$ Ry.

The interpolation of phonon frequencies is performed along the strategy outlined in Sec. III D and using $T_\infty = 0.11$ Ry to obtain smoothed “high-temperature” phonon frequencies.

2. Adiabatic phonon dispersion

The Wannier-interpolated adiabatic phonon dispersions on different k -point grids and smearings are compared to state-of-the-art electronic-structure calculations^{38,41,43} and experimental data^{5,44} in Fig. 3. In the top panel of Fig. 3 we compare the Wannier-interpolated phonon dispersion with $T_0 = 0.02$ Ry and $N_k(T_0) = 30^3$ with linear-response calculations performed on selected points in the Brillouin zone using the same mesh and the same electronic temperature. The error in the interpolation scheme is always smaller than 0.5 meV. In the bottom panel of Fig. 3 we compare Wannier-interpolated dispersion curves on $N_k(T_0) = 45^3$ at $T_0 = 0.01$ Ry with Fourier-interpolated²⁹ linear-response calculations from a $6 \times 6 \times 4$ phonon-momentum grid. As can be seen anomalies

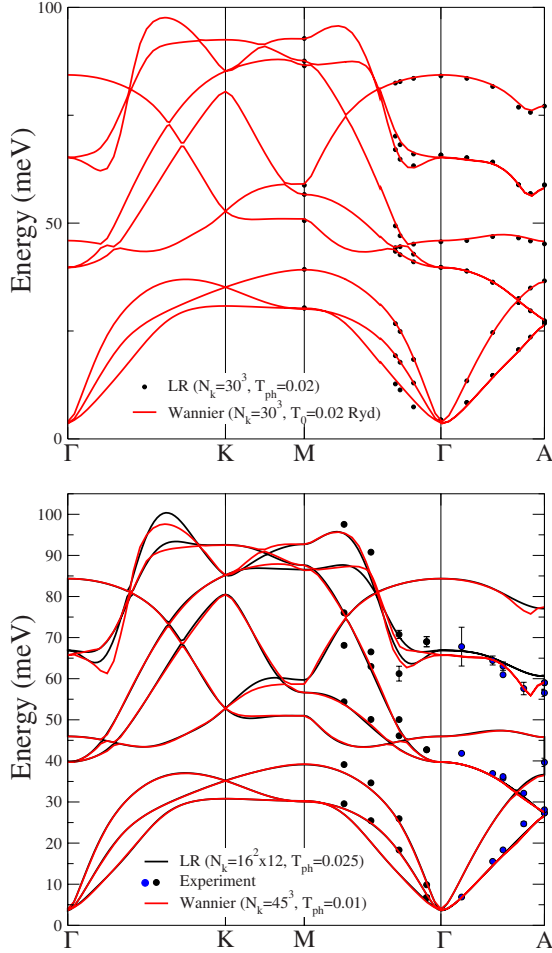


FIG. 3. (Color online) Top panel: Wannier-interpolated adiabatic phonon dispersion (red line) compared to standard linear-response calculations performed on selected points in the Brillouin zone (black dots). Bottom panel: comparison between state-of-the-art calculated phonon dispersion using Fourier interpolation (black line) and Wannier interpolation (red line). Both interpolation schemes start from the same linear-response calculation. Experimental data in the bottom panel are from Ref. 5 (blue circles) and from Ref. 44 (black circles). Electronic temperatures are in rydberg. The acoustic sum rule is not applied. Interpolated branches are obtained by connecting the points at which the interpolation has been carried out in the order of increasing energy.

are clearly found along ΓA using our new method but are completely missed by standard Fourier interpolation.²⁹ The main differences with respect to previous calculations^{38,41,43} are: (1) a prominent softening (Kohn anomaly) of the two E_{2g} modes at $\mathbf{q} \approx 0.25\Gamma K$ is seen. The Kohn anomaly is also present along the ΓM high symmetry direction and in a circular region around the zone center. Its origin is due to an in-plane nesting between the two σ cylinders. This Kohn anomaly could be probably inferred from previous calculations^{5,38,43} on smaller k -points grids although the softening of the E_{2g} modes in these works is weaker.

(2) A second Kohn anomaly, absent in previous calculations,^{5,38,43} is present on the E_{2g} and B_{1g} modes along the k_z direction at $\mathbf{q} \approx 0.8\Gamma A$. This Kohn anomaly is due to nesting between different cylinders along ΓA . As it can be

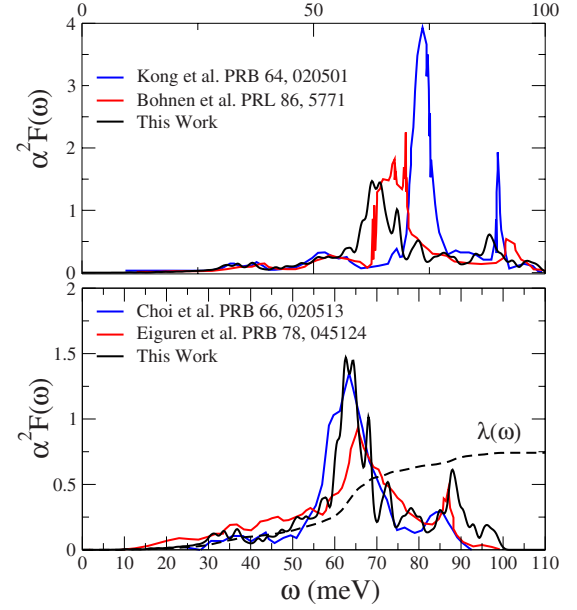


FIG. 4. (Color online) Comparison of our Wannier-interpolated MgB_2 Eliashberg function with previous calculations. Kong *et al.* (Ref. 38) used first-principles calculations and a particular treatment for $\lambda_{\mathbf{q}E_{2g}}$ for $\mathbf{q}$ along ΓA . Bohnen *et al.* (Ref. 43) used linear-response calculations while Choi *et al.* (Ref. 41) performed frozen-phonon calculations. Finally Eiguen *et al.* (Ref. 11) used a different implementation of Wannier interpolation on the electron-phonon matrix elements with 40^3 k -points grid for electron momentum and 40^3 k -points grid for phonon momentum, but did not interpolate phonon frequencies. In this work we Wannier interpolate both electron-phonon coupling (using 80^3 k -points grid for electron momentum and 20^3 k -points grid for phonon momentum) and phonon frequencies (using 30^3 k -points grid for electron momentum and 20^3 k -point grid for phonon momentum). The integrated $\lambda(\omega)$ from our work is also shown in the bottom panel.

seen by the comparison with previously available experimental data in Fig. 3, its presence is confirmed by inelastic x-ray scattering measurements of the phonon dispersion.^{5,44} The data at $\mathbf{q} \approx 0.8\Gamma A$ are indeed in disagreement with previous phonon-dispersion calculation^{5,38,41,43,44} even if this disagreement was overlooked in all previous publications.

(3) Overall the Wannier-interpolated phonon dispersion is in better agreement against experiments with respect to the linear-response calculated one. These differences point out the need of having an ultradense k -point sampling of the Brillouin zone not only for the electron-phonon coupling but also for the phonon dispersion.

3. Electron-phonon coupling

Having interpolated the electron-phonon matrix elements and the phonon frequencies it is possible to calculate the phonon linewidth and the electron-phonon coupling with a high degree of precision, eliminating source of errors coming from insufficient k -point sampling.

In Fig. 4 the Wannier-interpolated Eliashberg function is compared with previous calculations done with different approaches. There are two main improvements due to the better k -point sampling.

TABLE I. Comparison between different electron-phonon coupling calculations in MgB_2 using different first-principles methods. The label N_k (N_q) indicates the number of k point used for electron (phonon)-momentum integration.

Reference	λ	ω_{log} (meV)	N_k	N_q
Kong <i>et al.</i> (Ref. 38)	0.87	62.0	$12^2 \times 6$	6^3
Bohnen <i>et al.</i> (Ref. 43)	0.73	60.9	36^3	6^3
Choi <i>et al.</i> (Ref. 41)	0.73	62.7	$18^2 \times 12$	$18^2 \times 12$
Eiguren <i>et al.</i> (Ref. 11)	0.776		40^3	10^3
This work	0.741	58.8	80^3	20^3

First, several previous calculations^{11,38,43} on smaller k -point grids generally overestimate the position of the main peak in $\alpha^2F(\omega)$ (centered around $\omega \approx 63$ meV in our work) due to the coupling of σ bands with the E_{2g} phonon modes. This happens because in previous calculations the Kohn anomalies of the E_{2g} branches at $\mathbf{q} \approx 0.25\Gamma\text{K}$ was underestimated and because the anomaly along ΓA is missing. This crucial dependence of the Eliashberg function on the E_{2g} phonon frequency demonstrates the need of having both an accurate determination of λ and of the phonon frequencies to describe superconducting properties.

Second, in our work there is substantial more weight than in previous works^{11,38} in the 90–100 meV region. This energy region is dominated by the coupling of π electrons to the E_{2g} vibrations.

We now compare in more details our work with previous calculations. In the work of Bohnen *et al.*⁴³ all the peaks are upshifted not only by the limited k -points sampling but also by the choice of using the DFT-minimized crystal structure and not the experimental one. Kong *et al.*³⁸ have calculated $\lambda_{\mathbf{q}\nu}$ and $\omega_{\mathbf{q}\nu}$ on a $6 \times 6 \times 6$ phonon-momentum grid. Then for $\mathbf{q}$ of this grid belonging to the ΓA direction the corresponding $\lambda_{\mathbf{q}\nu}$ values were replaced with some of the $12 \times 12 \times 6$ k -point grid (see Ref. 38 for more details). Figure 4 shows that this approximation strongly overestimates the energy of the peak due to coupling between σ electronic states and the E_{2g} mode. Indeed the average electron-phonon coupling is much larger than the majority of the calculations present in literature (see Table I). Choi *et al.*⁴¹ used the local-density-approximation-minimized lattice structure but surprisingly obtained *softer* E_{2g} phonon frequencies at Γ than all other works using experimental lattice parameters. In Ref. 41 the electron-phonon coupling is calculated using an interpolation scheme that does not assure the localization properties of the electron-phonon matrix element in real space. Nevertheless the position of the main peak in $\alpha^2F(\omega)$ is similar to what we obtain. On the contrary the secondary peak related to coupling between π states and the E_{2g} mode is at too low energy. Finally, Eiguren *et al.*¹¹ used a Wannier interpolation scheme that requires an explicit calculation of the wave functions for any phonon momentum. The interpolation scheme was used to calculate the average electron-phonon coupling but not to interpolate phonon frequencies as they were obtained by Fourier interpolation.²⁹ As a consequence the phonon dispersion does not present the two observed Kohn anomalies and

the main peak of the $\alpha^2F(\omega)$ is at higher energies respect to our work. This difference reflects the need of having an accurate determination of the phonon frequency in order to have converged Eliashberg functions. This appears in the lower phonon frequency logarithmic average obtained in our work with respect to previous calculations as shown in Table I.

B. CaC_6

Graphite intercalated compounds represent a wide class of compounds. Due to the particular bonding properties of carbon atoms, with strong and stable sp^2 bonds and weak van der Waals π_z bonds, graphite allows incorporation of many different atomic species between the hexagonal C sheets. Alkali metals and alkaline-earth metals are the most common, but even H, Hg, Tl, Bi, As, O, S, and halogens are reported.⁴⁵

The possibility to change the number of electrons in the covalent C-C bonds, always stimulated the search of superconductivity in intercalated graphite, but only in 2005 calcium intercalated graphite (CaC_6) was found to superconduct at temperatures as high as 11.5 K.⁴⁶

First-principles theoretical investigations on CaC_6 revealed that the superconducting critical temperature can be explained considering only the electron-phonon mechanism,^{47,48} even if other pairing mechanisms were proposed (excitonic and plasmonic).

The pairing originates from the electron-phonon interaction between intercalant Fermi surface and the C out-of-plane modes and Ca in-plane modes.⁴⁷ These last modes, with very low frequencies (≈ 15 meV), account for about one half of the total λ . In this section, we re-examine the phonon and electron-phonon properties of CaC_6 by means of the computational framework based on the Wannier interpolation. In fact, from a computational point of view, the calculation of the energy position and $\mathbf{q}$ dispersion of the low-energy Ca modes requires very high precision, not obtainable with the state-of-the-art phonon and electron-phonon calculations.

CaC_6 is well described by the clean limit regime. Indeed, the CaC_6 zone-center phonon frequency measured by Raman,^{16,49,50} is significantly larger than the DFT adiabatic one but agrees very well with the DFT clean-limit nonadiabatic frequency.^{12,16,49,50} For this reason we will discuss both the adiabatic and the nonadiabatic dispersion.

1. Technical details

Wannier interpolation of the CaC_6 band structure is carried out using a $N_k^w = 6 \times 6 \times 6$ k -points grid centered at Γ . We use seven Wannier functions starting from an initial configuration with one s state on calcium and one p_z state on each carbon. The Wannierized band structure as compared to first-principles calculations is shown in Fig. 5.

We perform one linear-response calculation for each point of the irreducible N_k^w k -point grid using $N_k(T_{\text{ph}}) = 8 \times 8 \times 8$ and Hermitian-Gaussian smearing $T_{\text{ph}} = 0.05$ Ry. We then obtain $\delta v_{\text{SCF}} / \delta \mathbf{u}_{\mathbf{q}s}$ on the full grid applying the symmetry operations of the crystal. At zone center, we added a Fermi-level shift to the $\mathbf{q} = 0$ component of $\delta v_{\text{SCF}} / \delta \mathbf{u}_{\mathbf{q}s}$ to obtain an

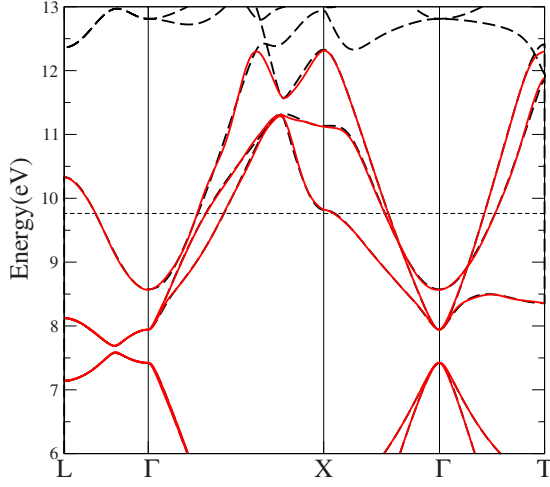


FIG. 5. (Color online) Wannierized (red dashed) and first-principles-calculated bands (black continuous) for CaC_6 . The horizontal dashed line marks the Fermi level.

analytical behavior at $\mathbf{q}=0$ (see Sec. III B for more details).

The interpolation of phonon frequencies is performed along the strategy outlined in Sec. III D and using $T_\infty = 0.075$ Ry to obtain smoothed high-temperature phonon frequencies.

For the calculation of nonadiabatic phonon frequencies we use $N_k(T_0)=50^3$, $T_0=0.01$ Ry, and $\eta=0.01$ Ry in Eq. (23). In principle, Eq. (8) should be solved self-consistently since the dynamical matrix should be computed at the frequency obtained from the solution of the determinant equation. However we have numerically verified that solving iteratively Eq. (8) or simply replacing the adiabatic phonon frequency of the E_{2g} mode at Γ in the dynamical matrix of Eq. (8) leads to variation in the optical-phonon frequencies that are smaller than 1 meV.

2. Adiabatic phonon dispersion

The phonon dispersions of CaC_6 as obtained from Fourier interpolation and from Wannier interpolation are illustrated

in Fig. 6. The Fourier interpolate phonon dispersion is in agreement with previous linear-response calculations.^{47,51,52} When compared with the more converged calculations performed using Wannier interpolation several differences are found. The largest deviation concerns the high-energy modes at ≈ 160 – 185 meV, in particular, along ΓL . These modes involve carbon vibrations parallel to the graphite layers (C_{xy} vibrations). There is a substantial hardening of the two highest optical phonon modes approaching zone boundary and a somewhat weaker softening close to zone center. The shape of the phonon dispersion of the two highest optical modes along ΓL recalls the typical behavior of the real part of the phonon self-energy due to electron-phonon coupling [see, for example, for the case of MgB_2 , Ref. 32, Fig. 3(a)]. The electron-phonon coupling to these optical modes comes essentially from π^* states and mostly from intraband coupling⁵³ (small Fermi surface) so that a quite accurate BZ sampling is necessary to display this behavior. This explains the strong k -point dependence of the result.

Moreover the relevance of having an accurate sampling of the Fermi surface is evident from the large number of Kohn anomalies (arrows in Fig. 6 mark the occurrence of a Kohn anomaly) present in the Wannier-interpolated branches and almost always absent in the Fourier-interpolated ones. At high energy (150–180 meV) we count a large number of anomalies, no one of which is present in Fourier-interpolated branches. These anomalies are mostly located close to the X and χ points. At low energy we count eight more softenings, six of which involve points close to the X point (although on different branches) and two occur at the χ point. In Fourier-interpolated calculations²⁹ only a very broad anomaly is visible in the low-energy modes, located exactly at the X point, nothing in other energy modes. The facts that close to the X point (i) several anomalies at the same vector occur on different modes and that (ii) the phonon frequencies associated to the anomaly are strongly dependent on the electronic temperature suggest an origin dependent from the Fermi-surface geometry. Indeed this is the case and the anomaly is illustrated in the nesting vector in Fig. 7.

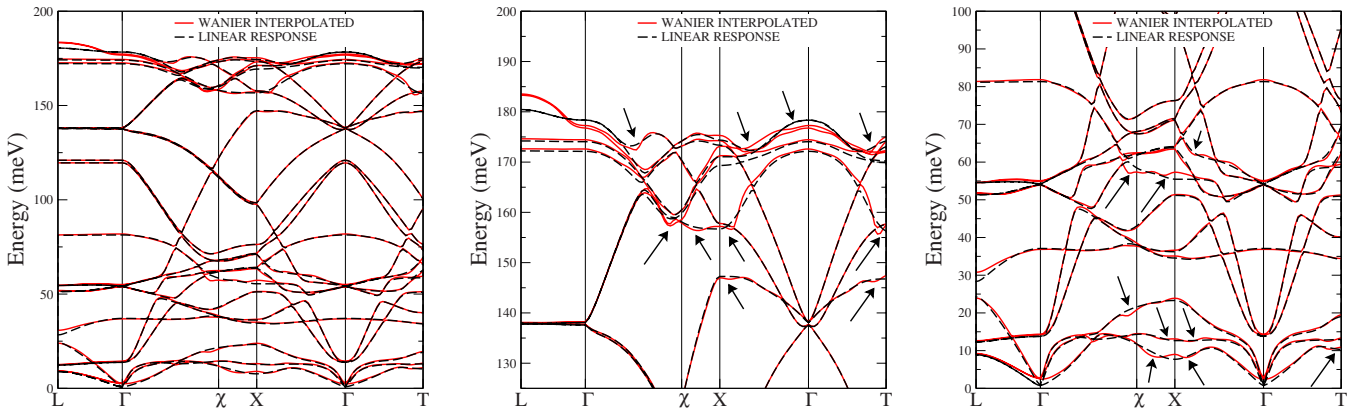


FIG. 6. (Color online) Wannier-interpolated (red continuous) and Fourier-interpolated (black dashed) adiabatic phonon dispersion in CaC_6 . The center and right panels are zooms to the high- and low-energy parts of the phonon dispersion. The Fourier-interpolated phonon branches are obtained from the dynamical matrices calculated on a $N_k^{\text{ph}}=6^3$ phonon grid, using $N_k=8^3$ and Hermite-Gaussian smearing $T_{\text{ph}}=0.05$ Ry. The Wannier-interpolated bands are obtained on a $N_k=40^3$ and Hermitian-Gaussian smearing $T_{\text{ph}}=0.01$ Ry. The Kohn anomalies are indicated by arrows.

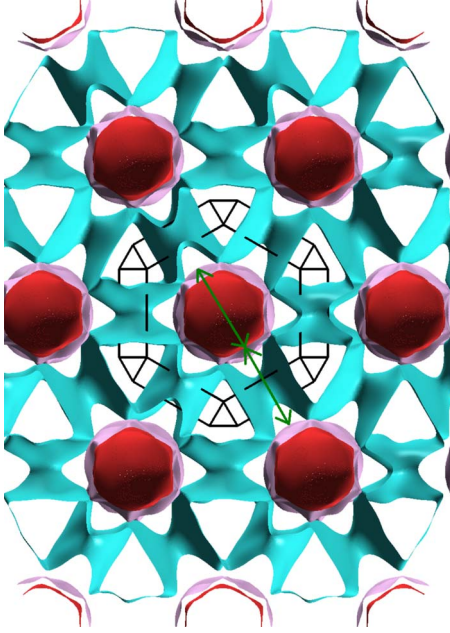


FIG. 7. (Color online) Fermi surface of CaC_6 calculated using Wannier functions on a 100^3 k -points grid. The green arrows mark the nesting vectors responsible for the Kohn anomaly close to X.

3. Nonadiabatic phonon dispersion

Nonadiabatic effects occur in CaC_6 close to zone center.^{12,16} However it is unknown how strong are these effects far from zone center, namely, what is the degree of localization of nonadiabatic effects around the Γ point. The question is meaningful as if nonadiabatic effects extend substantially in the Brillouin zone then they can be relevant for superconductivity and transport as the average electron-phonon coupling and the critical temperature could be affected.

In order to test the convergence with respect to the parameter η in Eq. (23), we calculate the nonadiabatic phonon dispersion along the symmetry lines $L\Gamma$ and $\Gamma\chi$ using for $T_0=0.01$ Ry, $N_k(T_0)=50 \times 50 \times 50$, and various values of η . As shown in Fig. 8, when the parameter η becomes smaller then the phonon frequency $\omega \approx 0.013$ Ry, then the dispersion are weakly dependent on η .

In Fig. 9 we plot the Wannier-interpolated nonadiabatic phonon dispersion. At Γ we obtain $\omega^{\text{NA}}=190$ meV (≈ 1532 cm^{-1}), in good agreement with what found in Ref. 12.

The most interesting result of the nonadiabatic calculation in Fig. 9 is that the full E_{2g} branch is shifted to higher energies (particularly along ΓL , the k_z direction) by the nonadiabatic effects. Even at halfway to the zone border the correction is sizable and it can be easily measured with inelastic x-ray or neutron-scattering experiments. In the case of CaC_6 as the high-energy modes are weakly coupled to electrons the nonadiabatic correction, even if large, probably does not affect the critical temperature. The situation can be substantially different in other superconductors so that nonadiabatic effects have to be taken into account to describe the electron-phonon interaction in layered superconductors.

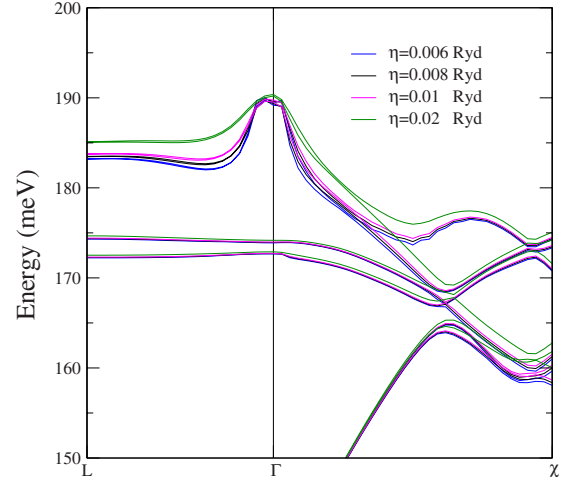


FIG. 8. (Color online) Wannier-interpolated nonadiabatic phonon dispersion in CaC_6 for $T_0=0.01$ Ry, $N_k(T_0)=50 \times 50 \times 50$ and various values of η .

4. Electron-phonon coupling

The Eliashberg function calculated with the adiabatic phonon frequencies and the integrated electron-phonon coupling for CaC_6 are illustrated in Fig. 10. The situation is very similar to previous works in what concern the average value of the electron-phonon coupling, as shown in Table II.

Previous calculations performed using standard linear-response methods report similar values of λ and a 13% variation is present on $\omega_{\log}$ (see Table II). Our calculation confirms the largest value reported in literature.

V. CONCLUSIONS

In this work we developed a first-principles scheme to calculate adiabatic and nonadiabatic phonon frequencies in the full Brillouin zone. We demonstrated how the method

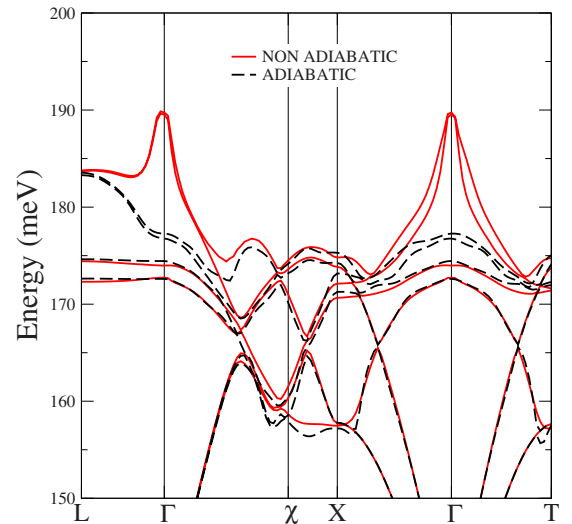


FIG. 9. (Color online) Wannier-interpolated nonadiabatic (red continuous) and adiabatic (black dashed) phonon dispersion in CaC_6 .

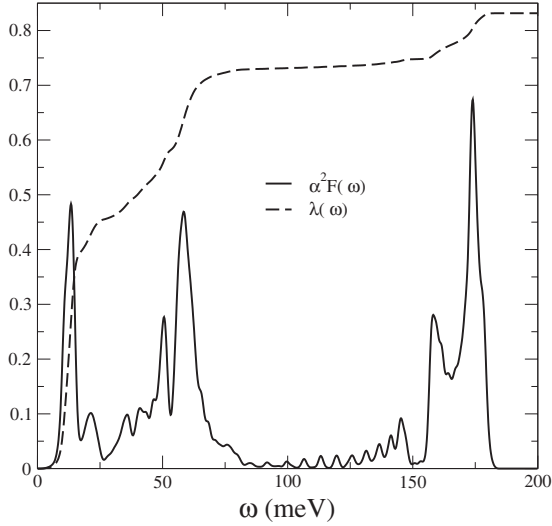


FIG. 10. Wannier-interpolated Eliashberg function and integrated Eliashberg functions for CaC_6 . Note that the wiggles in the 80–150 meV region are not due to poor convergence but to the presence of many well-separated dispersive branches in this energy region.

permits the calculation of phonon-dispersion curves free from convergence issues related to Brillouin-zone sampling. Our approach also justifies the use of the static screened potential in the calculation of the phonon linewidth due to decay in electron-hole pairs.

We apply the method to the calculation of the phonon dispersion and electron-phonon coupling in MgB_2 and CaC_6 . In both compounds we demonstrate the occurrence of several Kohn anomalies, absent in previous works, that are manifested only after careful electron and phonon-momentum integration. In MgB_2 , the presence of Kohn anomalies on the E_{2g} branches improves the agreement with measured phonon spectra and affects the position of the main peak in the Eliashberg function. In CaC_6 we show that the nonadiabatic

TABLE II. Comparison between different electron-phonon coupling calculations for CaC_6 using different first-principles methods. The label N_k (N_q) indicates the number of k point used for electron (phonon)-momentum integration.

Reference	λ	$\omega_{\log}$ (meV)	N_k	N_q
Calandra <i>et al.</i> (Ref. 47)	0.83	24.7	$6 \times 6 \times 6$	$4 \times 4 \times 4$
Kim <i>et al.</i> (Ref. 52)	0.84	26.28	$8 \times 8 \times 8$	$4 \times 4 \times 4$
Sanna <i>et al.</i> (Ref. 48)	0.85	28.0	$6 \times 6 \times 6$	$6 \times 6 \times 6$
This work	0.829	27.9	59^3	20^3

effects on in-plane carbon vibrations are not localized at zone center but are sizable throughout the full Brillouin zone. Thus NA effects can be relevant for the determination of the superconducting properties of layered superconductors. In general our work underlines the importance of obtaining accurate (well-converged) phonon frequencies to determine the electron-phonon coupling and superconducting properties in a reliable way.

The large gain in the computational time necessary to obtain phonon dispersion provided by our theoretical scheme opens perspectives in large-scale first-principles calculations of dynamical properties and electron-phonon interaction. Furthermore, the stationary property of the force constants functional with respect to the first-order perturbation of the electronic charge density is a property that can be generalized to the calculation of other response functions such as optical properties and the calculation of Knight shifts as measured in nuclear magnetic resonance.⁵⁴

ACKNOWLEDGMENTS

We acknowledge fruitful discussion with J. Yates and support from ANR PNANO-ACCATTONE. G.P. acknowledges support from CNRS. Calculations were performed at the IDRIS supercomputing center and at Cineca (Bologna, Italy) through an INFM-CNR supercomputing.

¹J. M. Ziman, *Electron and Phonons* (Clarendon Press, Oxford, 2001).

²G. Grimvall, *The Electron-Phonon Interaction in Metals* (North Holland, Amsterdam, 1981).

³J. R. Schrieffer, *Theory of Superconductivity* (Addison Wesley, Reading, MA, 1988).

⁴R. E. Peierls, *Quantum Theory of Solids* (Oxford University Press, New York, 2001).

⁵A. Shukla, M. Calandra, M. d'Astuto, M. Lazzeri, F. Mauri, C. Bellin, M. Krisch, J. Karpinski, S. M. Kazakov, J. Jun, D. Daghero, and K. Parlinski, *Phys. Rev. Lett.* **90**, 095506 (2003).

⁶M. Born and J. R. Oppenheimer, *Ann. Phys.* **84**, 457 (1927).

⁷S. Baroni, S. de Gironcoli, A. Dal Corso, and P. Giannozzi, *Rev. Mod. Phys.* **73**, 515 (2001).

⁸S. Y. Savrasov and D. Y. Savrasov, *Phys. Rev. B* **54**, 16487 (1996).

⁹X. Gonze and C. Lee, *Phys. Rev. B* **55**, 10355 (1997).

¹⁰F. Giustino, M. L. Cohen, and S. G. Louie, *Phys. Rev. B* **76**, 165108 (2007).

¹¹A. Eiguren and C. Ambrosch-Draxl, *Phys. Rev. B* **78**, 045124 (2008).

¹²A. M. Saitta, M. Lazzeri, M. Calandra, and F. Mauri, *Phys. Rev. Lett.* **100**, 226401 (2008).

¹³M. Lazzeri and F. Mauri, *Phys. Rev. Lett.* **97**, 266407 (2006), see Ref. 15 of this paper.

¹⁴F. Giustino, Jonathan R. Yates, I. Souza, M. L. Cohen, and G. Louie, *Phys. Rev. Lett.* **98**, 047005 (2007).

¹⁵N. Marzari and D. Vanderbilt, *Phys. Rev. B* **56**, 12847 (1997).

¹⁶M. P. M. Dean, C. A. Howard, S. S. Saxena, and M. Ellerby, *Phys. Rev. B* **81**, 045405 (2010).

¹⁷See, e.g., N. W. Ashcroft and N. D. Mermin, *Solid State Physics* (Holt, Rhinehard and Winston, New York, 1976), Chap. 26, p. 529.

- ¹⁸S. de Gironcoli, *Phys. Rev. B* **51**, 6773 (1995).
- ¹⁹A. A. Quong and B. M. Klein, *Phys. Rev. B* **46**, 10734 (1992).
- ²⁰S. Y. Savrasov, *Phys. Rev. Lett.* **69**, 2819 (1992).
- ²¹E. Maksimov and S. V. Shulga, *Solid State Commun.* **97**, 553 (1996).
- ²²M. Calandra, M. Lazzeri, and F. Mauri, *Physica C* **456**, 38 (2007).
- ²³E. Cappelluti, *Phys. Rev. B* **73**, 140505 (2006).
- ²⁴H. Hellmann, *Einführung in die Quantenchemie* (Deuticke, Leipzig, 1937).
- ²⁵R. P. Feynman, *Phys. Rev.* **56**, 340 (1939).
- ²⁶M. Di Ventura and S. T. Pantelides, *Phys. Rev. B* **61**, 16207 (2000).
- ²⁷X. Gonze, D. C. Allan, and M. P. Teter, *Phys. Rev. Lett.* **68**, 3603 (1992).
- ²⁸In principle, the force-constant matrix depends implicitly on the temperature used in the self-consistent calculation of $n_0(\mathbf{r})$, $\epsilon_{\mathbf{k},i}$, and $\psi_{\mathbf{k},i}(\mathbf{r})$ (Ref. 17). Moreover, the dependence of force constants on this last temperature is weak and thus it is usually taken (as in the present derivation) equal to T_{ph} . However, it should be set equal to the physical temperature, T_0 as a single standard self-consistent calculation does not poses relevant problems in k -point convergence.
- ²⁹D. D. Koelling and J. H. Woodb, *J. Comput. Phys.* **67**, 253 (1986).
- ³⁰I. Souza, N. Marzari, and D. Vanderbilt, *Phys. Rev. B* **65**, 035109 (2001).
- ³¹P. B. Allen, *Phys. Rev. B* **6**, 2577 (1972); P. B. Allen and R. Silbergliitt, *ibid.* **9**, 4733 (1974).
- ³²M. Calandra and F. Mauri, *Phys. Rev. B* **71**, 064501 (2005).
- ³³A. A. Mostofi, J. R. Yates, Y.-S. Lee, I. Souza, D. Vanderbilt, and N. Marzari, *Comput. Phys. Commun.* **178**, 685 (2008).
- ³⁴P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G. L. Chiarotti, M. Cococcioni, I. Dabo, A. Dal Corso, S. de Gironcoli, S. Fabris, G. Fratesi, R. Gebauer, U. Gerstmann, C. Gougoussis, A. Kokalj, M. Lazzeri, L. Martin-Samos, N. Marzari, F. Mauri, R. Mazza-relo, S. Paolini, A. Pasquarello, L. Paulatto, C. Sbraccia, S. Scandolo, G. Sclauzero, A. P. Seitsonen, A. Smogunov, P. Umari, and R. M. Wentzcovitch, *J. Phys.: Condens. Matter* **21**, 395502 (2009).
- ³⁵J. Nagamatsu, N. Nakagawa, T. Muranaka, Y. Zenitani, and J. Akimitsu, *Nature (London)* **410**, 63 (2001).
- ³⁶J. Kortus, I. I. Mazin, K. D. Belashchenko, V. P. Antropov, and L. L. Boyer, *Phys. Rev. Lett.* **86**, 4656 (2001).
- ³⁷J. M. An and W. E. Pickett, *Phys. Rev. Lett.* **86**, 4366 (2001).
- ³⁸Y. Kong, O. V. Dolgov, O. Jepsen, and O. K. Andersen, *Phys. Rev. B* **64**, 020501(R) (2001).
- ³⁹A. Y. Liu, I. I. Mazin, and J. Kortus, *Phys. Rev. Lett.* **87**, 087005 (2001).
- ⁴⁰F. Giubileo, D. Roditchev, W. Sacks, R. Lamy, D. X. Thanh, J. Klein, S. Miraglia, D. Fruchart, J. Marcus, and P. Monod, *Phys. Rev. Lett.* **87**, 177008 (2001).
- ⁴¹H. J. Choi, D. Roundy, H. Sun, M. L. Cohen, and S. G. Louie, *Nature (London)* **418**, 758 (2002); *Phys. Rev. B* **66**, 020513 (2002).
- ⁴²A. Floris, G. Profeta, N. N. Lathiotakis, M. Lüders, M. A. L. Marques, C. Franchini, E. K. U. Gross, A. Continenza, and S. Massidda, *Phys. Rev. Lett.* **94**, 037004 (2005).
- ⁴³K. P. Bohnen, R. Heid, and B. Renker, *Phys. Rev. Lett.* **86**, 5771 (2001).
- ⁴⁴M. d'Astuto, M. Calandra, S. Reich, A. Shukla, M. Lazzeri, F. Mauri, J. Karpinski, N. D. Zhigadlo, Alexei Bossak, and Michael Krisch, *Phys. Rev. B* **75**, 174508 (2007).
- ⁴⁵N. Emery, C. Hérold, J.-F. Marêché, and P. Lagrange, *Sci. Technol. Adv. Mater.* **9**, 044102 (2008).
- ⁴⁶T. E. Weller, M. Ellerby, S. S. Saxena, R. P. Smith, and N. T. Skipper, *Nat. Phys.* **1**, 39 (2005).
- ⁴⁷M. Calandra and F. Mauri, *Phys. Rev. Lett.* **95**, 237002 (2005).
- ⁴⁸A. Sanna, G. Profeta, A. Floris, A. Marini, E. K. U. Gross, and S. Massidda, *Phys. Rev. B* **75**, 020511 (2007).
- ⁴⁹J. Hlinka, I. Gregora, J. Pokorny, C. Hérold, N. Emery, J. F. Marêché, and P. Lagrange, *Phys. Rev. B* **76**, 144512 (2007).
- ⁵⁰A. Mialitsin, J. S. Kim, R. K. Kremer, and G. Blumberg, *Phys. Rev. B* **79**, 064503 (2009).
- ⁵¹M. Calandra and F. Mauri, *Phys. Rev. B* **74**, 094507 (2006).
- ⁵²J. S. Kim, L. Boeri, R. K. Kremer, and F. S. Razavi, *Phys. Rev. B* **74**, 214513 (2006).
- ⁵³L. Boeri, G. B. Bachelet, M. Giantomassi, and O. K. Andersen, *Phys. Rev. B* **76**, 064510 (2007).
- ⁵⁴M. d'Avezac, N. Marzari, and F. Mauri, *Phys. Rev. B* **76**, 165122 (2007).