Electron-Phonon Renormalization of the Direct Band Gap of Diamond

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We calculate from first principles the temperature-dependent renormalization of the direct band gap of diamond arising from electron-phonon interactions. The calculated temperature dependence is in good agreement with spectroscopic ellipsometry measurements, and the zero-point renormalization of the band gap is found to be as large as 0.6 eV. We also calculate the temperature-dependent broadening of the direct absorption edge and find good agreement with experiment. Our work calls for a critical revision of the band structures of other carbon-based materials calculated by neglecting electron-phonon interactions.

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The calculation of quasiparticle band structures from first principles has reached a very high level of accuracy. Standard calculations based on density-functional theory (DFT) are improved by including many-electron self-energy effects using a variety of techniques ranging from the *GW* approach [1,2] to dynamical mean-field theory [3], and the best band structures agree with measured photoemission spectra within a few tens of an eV. While significant efforts have been devoted to improving the description of electron-electron interactions, it appears that in comparison, the effect of lattice vibrations on the quasiparticle band structures has been mostly neglected within the community working on first-principles electronic structure methods. One possible reason is that electron-phonon effects are generally assumed to yield quasiparticle energy shifts of the order of 10–50 meV, thereby falling within the precision of the best electronic-structure calculations. In addition, the calculation of electron-phonon interactions has been traditionally very challenging, and only recently novel approaches have rendered accurate electron-phonon calculations accessible; see Ref. [4] and references therein.

In the case of diamond, several studies including empirical pseudopotential calculations [5], fitting of optical data [6], and path-integral Monte Carlo simulations [7] all point to a surprisingly large electron-phonon renormalization of the band gaps of up to 0.7 eV. If confirmed, such large renormalization would be of the same order of magnitude of *GW* corrections [1] to the DFT band structure of diamond, and hence should be taken into account on the same footing as electron-electron interactions.

In this Letter we calculate from first principles the electron-phonon renormalization of the direct band gap $\Gamma'_{25v} \rightarrow \Gamma_{15c}$ of diamond using the Allen-Heine theory of the temperature dependence of electronic band structures [8]. The unperturbed band structures are obtained within the *GW* approximation, and the lattice dynamics is described within density-functional perturbation theory [9]. The calculated temperature dependence of the direct band gap and the broadening of the direct absorption edge are found to be in good agreement with synchrotron-based spectroscopic ellipsometry measurements [10]. The zero-point renormalization of the gap is found to be as large as 615 meV. This value is comparable to self-energy corrections obtained from electron-electron interactions [1], and calls for a reexamination of the band structures of related materials which neglect electron-phonon effects.

The Allen-Heine theory [8] describes the thermal shift of the electronic energies using second-order perturbation theory within the harmonic and adiabatic approximations. The electron-phonon correction $\Delta\epsilon_{n\mathbf{k}}$ to the one-particle energy $\epsilon_{n\mathbf{k}}$ of the electronic state $|n\mathbf{k}\rangle$ with wave vector $\mathbf{k}$ and band n is

$$\Delta\epsilon_{n\mathbf{k}} = \Delta^{\rm SE}\epsilon_{n\mathbf{k}} + \Delta^{\rm DW}\epsilon_{n\mathbf{k}}, \tag{1}$$

where $\Delta^{\rm SE}\epsilon_{n\mathbf{k}}$ and $\Delta^{\rm DW}\epsilon_{n\mathbf{k}}$ are the so-called phonon-induced self-energy (SE) or Fan term [11] and Debye-Waller (DW) term, respectively. The SE term is obtained by considering first-order phonon-induced perturbations to the electron energies up to the second-order in the ionic displacements, and involves the electron-one phonon interaction twice. The DW term is obtained by considering second-order phonon-induced perturbations to the electron energies and involves the electron-two phonon interaction once [Fig. 1]. In the present Letter we neglect the effect of the thermal expansion of the lattice, which is negligible in diamond due to the small thermal expansion coefficient ($<$ 10 meV at 700 K) [5]. The Allen-Heine theory exploits the translational invariance of the thermal shift which results in expressing *both* the SE and DW corrections using only the first-order variations $\Delta_{\mathbf{q}\nu}V$ of the self-consistent potential associated with a phonon of wave vector $\mathbf{q}$, branch ν, and frequency $\omega_{\mathbf{q}\nu}$. The SE term is [4,12]

$$\Delta^{\rm SE}\epsilon_{n\mathbf{k}} = \sum_{m\neq n,\nu}\int\frac{d\mathbf{q}}{\Omega_{\rm BZ}}\frac{2n_{\mathbf{q}\nu}+1}{\epsilon_{n\mathbf{k}}-\epsilon_{m\mathbf{k}+\mathbf{q}}}|g_{mn,\nu}(\mathbf{k},\mathbf{q})|^2, \tag{2}$$

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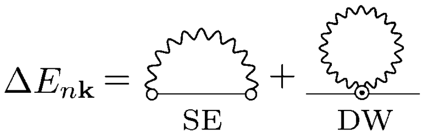

FIG. 1. Electron-phonon diagrams leading to the temperature dependence of the electron energy: self-energy diagram (left) and Debye-Waller diagram (right). Solid and curved lines represent the electron and phonon Green's function, respectively. The circles in the SE diagram represent the standard electron-phonon matrix element, the circle in the DW diagram represents a one electron-two phonons matrix element.

where $n_{\mathbf{q}\nu}$ is the Bose-Einstein occupation factor and $\Omega_{\rm BZ}$ the volume of the Brillouin zone. The electron-phonon matrix element $g_{mn,\nu}(\mathbf{k},\mathbf{q})$ in Eq. (2) is calculated as $\langle m\mathbf{k}+\mathbf{q}|\Delta_{\mathbf{q}\nu}V|n\mathbf{k}\rangle$. After algebraic manipulations we were able to recast the DW term of Ref. [8] in a form which parallels the SE expression

$$\Delta^{\rm DW}\epsilon_{n\mathbf{k}} = -\sum_{m\neq n,\nu}\int\frac{d\mathbf{q}}{\Omega_{\rm BZ}}\frac{2n_{\mathbf{q}\nu}+1}{\epsilon_{n\mathbf{k}}-\epsilon_{m\mathbf{k}}}[g^{\rm DW}_{mn,\nu}(\mathbf{k},\mathbf{q})]^2, \quad (3)$$

where we have introduced a "Debye-Waller electron-phonon matrix element" defined as follows:

$$[g^{\rm DW}_{mn,\nu}(\mathbf{k},\mathbf{q})]^2 = \frac{1}{2\omega_{\mathbf{q}\nu}}\sum_{\mu\mu'}t^{\nu}_{\mu\mu'}(\mathbf{q})h^{*}_{mn,\mu}(\mathbf{k})h_{mn,\mu'}(\mathbf{k}), \quad (4)$$

$$t^{\nu}_{\kappa\alpha,\kappa'\alpha'}(\mathbf{q}) = u^{*}_{\nu,\kappa\alpha}(\mathbf{q})u_{\nu,\kappa\alpha'}(\mathbf{q}) + u^{*}_{\nu,\kappa'\alpha}(\mathbf{q})u_{\nu,\kappa'\alpha'}(\mathbf{q}), \quad (5)$$

$$h_{mn,\mu}(\mathbf{k}) = \sum_{\nu}u^{-1}_{\mu\nu}(\mathbf{0})\omega^{1/2}_{\mathbf{0}\nu}g_{mn,\nu}(\mathbf{k},\mathbf{0}). \quad (6)$$

The quantities $u_{\mu\nu}(\mathbf{q})$ appearing in Eqs. (5) and (6) are the mass-scaled phonon eigenvectors, and the Greek indices κ, α refer to atomic species and Cartesian direction, respectively. Using these expressions the rigid translations of the crystal correctly yield a vanishing total shift, as required by the Allen-Heine theory [8].

In this Letter we describe the broadening of the direct absorption edge by using the linewidth $\gamma_{n\mathbf{k}}$ of the conduction band edge Γ_{15c} [4]

$$\begin{aligned}\gamma_{n\mathbf{k}} = {}& \pi\sum_{m,\nu}\int\frac{d\mathbf{q}}{\Omega_{\rm BZ}}|g_{mn,\nu}(\mathbf{k},\mathbf{q})|^2 \\ & \times[(n_{\mathbf{q}\nu}+f_{m\mathbf{k}+\mathbf{q}})\delta(\epsilon_{n\mathbf{k}}-\epsilon_{m\mathbf{k}+\mathbf{q}}-\omega_{\mathbf{q}\nu}) \\ & +(n_{\mathbf{q}\nu}+1-f_{m\mathbf{k}+\mathbf{q}})\delta(\epsilon_{n\mathbf{k}}-\epsilon_{m\mathbf{k}+\mathbf{q}}+\omega_{\mathbf{q}\nu})], \quad (7)\end{aligned}$$

where $f_{m\mathbf{k}+\mathbf{q}}$ is the Fermi-Dirac occupation factor. Our choice can be justified based on the following observations. (1) The linewidth of the electronic states at the valence band top Γ'_{25v} is vanishing as there are no available final hole states. (2) The linewidth of the conduction band edge Γ_{15c} arising from electron-electron interactions is vanishing because the energy threshold for the decay into electron-hole pairs (corresponding to the band gap) exceeds the separation between the initial state Γ_{15c} and the lowest conduction state near X_{1c}. The decay into plasmons is forbidden for a similar reason. The electron-hole interaction is not taken into account as it does not modify qualitatively the line shapes of the absorption edge [10,13].

We perform DFT calculations using the local density approximation (LDA) [14,15], and account for the core-valence interaction by using norm-conserving pseudopotentials [16,17]. The electronic wave functions are expanded in a plane wave basis [18] with a kinetic energy cutoff of 60 Ry. The relaxed lattice parameter is 3.52 Å. We obtain vibrational frequencies and eigenmodes, as well as electron-phonon matrix elements, within density-functional perturbation theory [9], using a $10\times10\times10$ Brillouin-zone sampling. In order to evaluate the Brillouin zone integral in Eq. (7) we employ the first-principles interpolation method [4] based on maximally localized Wannier functions [19] using 27 000 inequivalent points in the Brillouin zone and replacing the Dirac deltas by Lorentzians of width 10 meV.

The evaluation of the thermal shifts in Eqs. (2) and (3) is complicated by the presence of slowly decaying energy denominators. This problem is the same as encountered in quasiparticle *GW* calculations and is a general feature of calculating the real part of self-energy operators. Extensive tests show that an energy cutoff of 500 eV in the denominator (300 conduction bands) is required to converge the thermal shifts. This aspect is important because the convergence of the DW term with this energy cutoff is nonmonotonic. For the thermal shifts the sampling of the Brillouin zone plays a secondary role and the electron-phonon interpolation of Ref. [4] is not required. In this case we smooth the energy denominators by introducing a small imaginary component of 100 meV following Ref. [5]. The calculations are based on the QUANTUM ESPRESSO [20], WANNIER90 [21], and EPW [22] codes. The Allen-Heine theory has been implemented in a modified version of the EPW.

In Ref. [10] the authors report spectroscopic ellipsometry measurements of the complex dielectric function of diamond using synchrotron radiation in the energy region 5–10 eV. In order to extract the direct band gap and the broadening of the absorption edge as a function of temperature, the authors fit the dielectric function using analytic line shapes and extract the leading edge and its width using first- and second-derivative analysis. The fitting procedure shows that an excitonic line shape and one based on a two-dimensional critical point yield similar results, and the data for the latter analysis are reported. The first- and second-derivative analysis yield band gaps differing by a constant shift of ~60 meV, and broadening parameters differing by ~30 meV. These values can be taken as an estimate of the experimental uncertainty. The inability to distinguish between an interband critical point and an excitonic line shape indicates that, in the presence of bound excitons, the binding energy must be smaller than the linewidth of the absorption onset (< 150 meV). This observation is supported by first-principles calculations of the optical absorption edge in diamond using the Bethe-Salpeter equation, which indicate a redistribution of spectral weight upon inclusion of excitonic effects, but no sizeable shift of the absorption onset [13].

Figure 2 shows the calculated temperature dependence of the direct band gap of diamond and compares our results with the experimental data of Ref. [10]. The agreement between our calculation and experiment is excellent. The calculated magnitude of the zero-point renormalization is extremely large and amounts to 615 meV. This value is 1 to 2 orders of magnitude larger than what is typically expected for tetrahedral semiconductors [6] and is the signature of a very strong electron-phonon interaction in diamond. Our first-principles calculations support previous studies [5] based on the empirical pseudopotential method [23] which find a zero-point renormalization of $\sim$680 meV. In order to estimate the error introduced in our calculations by the use of the LDA eigenvalues in Eqs. (2) and (3), we repeated our calculations by using a scissor operator corresponding to the *GW* correction of the direct band gap of diamond (2.04 eV). The zero-point renormalization of the band gap calculated after scissor correction is 605 meV, i.e., less than 2% smaller than the value of 615 meV obtained in LDA.

Figure 3 shows a breakdown of the band gap renormalization into SE and DW contributions. Both the SE and the DW corrections are negative and tend to reduce the unperturbed band gap. The band gap renormalization is dominated by the SE term at low temperature (81% of the total shift at $T = 0$ K), while the DW term becomes relatively more important at high temperature (40% of the total at $T = 700$ K). The temperature dependence and the relative importance of the SE and DW terms are in agreement with the findings of Ref. [5].

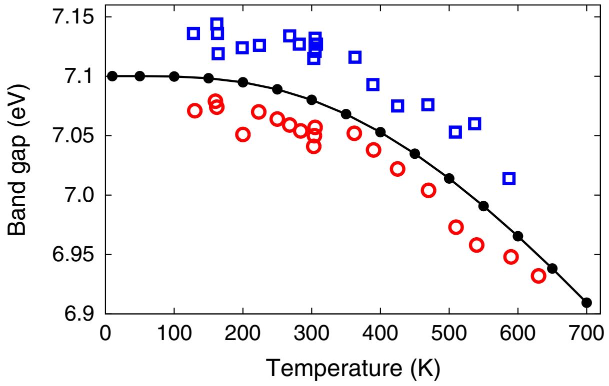

FIG. 2 (color online). Temperature dependence of the direct band gap of diamond: calculated gap (black disks), and experimental data from Ref. [10]. The calculated band gap is obtained by adding the SE and DW thermal shifts to our *GW* gap $E_g^{GW} = 7.715$ eV. The *GW* gap is calculated using the method of Ref. [1] as implemented in the BERKELEYGW code [33]. The experimental data are from the first-derivative line shape analysis of the type IIA sample [(red) circles] and from the second-derivative line shape analysis of the same sample [(blue) squares].

The temperature dependence of the band gap can be described approximately using a simple Bose-Einstein law as $\Delta E_g(T) = -a[1 + 2(e^{\Theta/T} - 1)^{-1}]$ (with a and Θ fitting parameters) [10]. By fitting our calculated shifts we extract an effective temperature $k_B\Theta = 118$ meV (black solid line in Fig. 3, k_B is the Boltzmann constant). This indicates that in diamond the optical phonons provide the main contribution to the gap renormalization, similarly to what happens in superconducting diamond [24].

Figure 4 shows the calculated broadening of the absorption edge as a function of temperature. The large effective phonon frequency Θ of diamond makes the broadening rather insensitive to temperature, and the zero-point effect accounts for most of the linewidth. Our calculated broadening is in good agreement with the line shape analysis of Ref. [10]. The fact that our calculations are on the upper end of the measured broadening suggests that other broadening effects due to impurities, surface scattering, or Auger processes [10], should be of secondary importance.

We note that the good agreement between our calculations and experiment may be somewhat fortuitous since the Allen-Heine theory does not take into account dynamical effects, such as the dependence on the phonon frequencies of the SE denominators in Eq. (2) or the quasiparticle renormalization parameter Z [1]. We also point out that

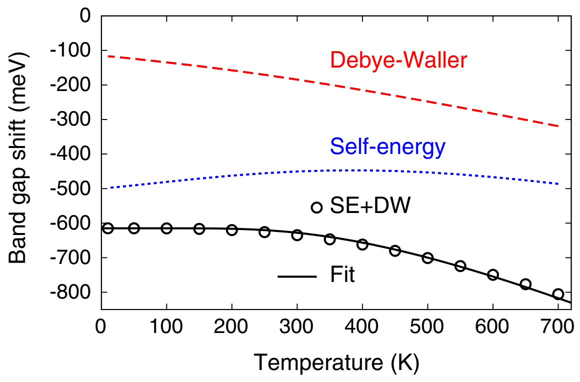

FIG. 3 (color online). Breakdown of the temperature shift of the direct band gap of diamond in terms of SE [(blue) dotted line] and DW [(red) dashed line] contributions. The circles are the total shift as in Fig. 2 and the solid black line is the fit with a Bose-Einstein law $\Delta E_g(T) = -a[1 + 2(e^{\Theta/T} - 1)^{-1}]$, with $a = 615$ meV and $k_B\Theta = 118$ meV. The nonmonotonic behavior of the SE term results from the slightly different temperature dependence of the Γ'_{25v} and the Γ_{15c} states, and from the fact that the gap renormalization is obtained through their difference. The different temperature dependence can be traced back to different electron-phonon couplings in Eq. (2), and hence to the different character of the Γ'_{25v} and Γ_{15c} states in diamond.

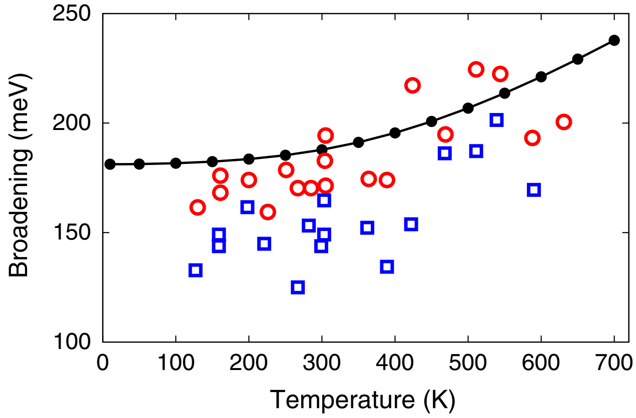

FIG. 4 (color online). Temperature-dependent broadening of the direct absorption edge of diamond. The black disks are our data calculated using Eq. (7). The (red) circles and (blue) squares are the experimental data from the first- and second-derivative line shape analysis of the type IIA sample in Ref. [10], respectively.

our electron-phonon matrix elements are obtained within DFT, and a more accurate description of the screening may lead to a slight modification of the quantitative aspects of our results [25].

In the present case, the 0.6 eV electron-phonon renormalization of the band gap of diamond is comparable in magnitude to the corresponding *GW* correction of ~2 eV. This indicates that electron-phonon effects are non-negligible in carbon-based materials and should be considered in future band structure calculations.

The large calculated zero-point renormalization of the band gap in diamond is consistent with the strong electron-phonon interaction leading to superconductivity in B-doped diamond [24,26–29] and the predicted superconductivity of graphane and diamond nanorods [30], and with the strong electron-phonon effects observed in carbon nanotubes [31] and graphene [32].

With the suggestion of a move from silicon electronics to carbon electronics, a detailed atomistic description of the electron-phonon effects in carbon materials as reported here may prove important for the development of novel device concepts. On a more fundamental level, our work demonstrates the truly significant role of electron-phonon renormalizations on the quasiparticle excitations of diamond, bearing important implications on many related properties.

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