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Ab initio calculation of the low-frequency Raman cross section in silicon

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The macroscopic polarizability of silicon is calculated from first principles as a function of the lattice distortion induced by a zone-center optical phonon. The electronic response to the electric field is dealt with by dielectric matrices, and the lattice distortion is treated by frozen-phonon techniques. Our results compare quite well with the most recent measurements of the one-phonon Raman cross section.

I. INTRODUCTION

The one-phonon Raman cross section of a solid is directly related to the derivative of its macroscopic electronic polarizability with respect to the atomic displacements from equilibrium.[1]

Although Raman spectroscopy is a standard tool nowadays in many areas of solid-state physics, accurate measurement of the absolute one-phonon cross section in silicon has been carried out only recently.[2]

On the theoretical side, the calculation of the Raman efficiency of Si has been the subject of several studies,[3] none of which, however, has been performed from first principles. In particular, all of them have completely neglected local-field and exchange-correlation effects, whose crucial role in phonon physics is well known.[4-6] The experience gathered in recent years has proved that the local-density approximation (LDA) to the density-functional theory (DFT)[7] provides a powerful tool to calculate completely *ab initio* a number of properties of the electronic ground state of real materials.[8] In particular, the LDA calculations of structural, lattice-dynamical, and elastic properties of covalent semiconductors have been very successful.[9]

The purpose of the present paper is twofold: On one hand, we demonstrate that such a quantity as the derivative of the macroscopic polarizability with respect to some external parameter can be successfully calculated completely from first principles. On the other hand, our calculation, which includes all the state-of-art ingredients of modern DFT calculations, provides a useful test of the LDA beyond its traditional field of application.

II. CALCULATIONS

Let $\Delta\chi_{\alpha\beta}$ be the variation of the macroscopic polarizability tensor due to the presence of an optical phonon at the zone center; then to the first order in the atomic displacements we have

$$\Delta\chi_{\alpha\beta} \simeq \chi^{(1)}_{\alpha\beta} = \frac{1}{\Omega_c} \sum_s \sum_\nu P_{\alpha\beta\nu} u_\nu(s) \ , \tag{1}$$

where $\mathbf{u}(s)$ is the displacement of the sth atom in the unit cell, Ω_c is the unit-cell volume, and the third-rank tensor $P_{\alpha\beta\nu}$ is by definition the Raman tensor. We have omitted in Eq. (1) any dependence on the energy of the incident light, and we are assuming throughout that such energy is much smaller than the direct energy gap of the material. In fact, the present calculation is performed within the framework of DFT, which applies to the electronic ground state only.[7]

In the diamond structure the s index in Eq. (1) runs over two values; let us indicate them as + and −. Because of symmetry, for the zone-center optical mode one has $\mathbf{u}(+) = -\mathbf{u}(-)$; furthermore, it can be proved that the Raman tensor has only one independent component P:

$$P_{\alpha\beta\nu}(s) = |\varepsilon_{\alpha\beta\nu}| P \operatorname{sgn}(s) \ , \tag{2}$$

where $\varepsilon_{\alpha\beta\nu}$ is the Levi-Civita tensor. According to Eq. (2), if the macroscopic electric field is parallel to x and the phonon is polarized along y, the macroscopic electric polarization is parallel to z. It turns out that, for computational reasons, a more suitable geometry is one with the phonon polarization along (1,1,1). In this case, the macroscopic field and polarization are parallel to each other when the field is chosen either parallel or perpendicular to (1,1,1). Let us define the dimensionless amplitude u through

$$\mathbf{u}(\pm) = \pm u a (1,1,1) \ , \tag{3}$$

where a is the lattice constant. Replacement of Eqs. (2) and (3) in Eq. (1) yields

$$\chi^{(1)}_{\alpha\beta} = (1-\delta_{\alpha\beta}) 8Pu/a^2 \ . \tag{4}$$

We calculate the electronic polarizability tensor for the crystal with phononlike distortions of several amplitudes. Because of symmetry, for any value of u there are only two independent elements:

$$\Delta\chi_{\alpha\beta}(u) = \eta(u)\delta_{\alpha\beta} + \gamma(u)(1-\delta_{\alpha\beta}) \ . \tag{5}$$

To leading order, η is quadratic in u and γ is linear, whence we extract the value of P according to Eq. (4). A typical value of u, providing good linearity and still giving no cancellation problems, is $u = 10^{-4}$.

We now wish to discuss how the macroscopic polarizability tensor $\overleftrightarrow{\chi}_{\text{macro}}$, whose elements we have indicated with $\chi_{\alpha\beta}$, is obtained from the microscopic theory of dielectric response.[4] It proves better to switch to the macroscopic dielectric tensor $\overleftrightarrow{\epsilon}_{\text{macro}}$, simply related to $\overleftrightarrow{\chi}_{\text{macro}}$ by

$$\overleftrightarrow{\epsilon}_{\text{macro}} = \overleftrightarrow{1} + 4\pi\overleftrightarrow{\chi}_{\text{macro}} \quad . \tag{6}$$

The most basic microscopic linear-response operator in a periodic medium is the *inverse* dielectric matrix $\epsilon^{-1}(\mathbf{q}+\mathbf{G}, \mathbf{q}+\mathbf{G}')$; this is a matrix in the indices $\mathbf{G}$ and $\mathbf{G}'$ (reciprocal lattice vectors), and depends parametrically on $\mathbf{q}$ in the first Brillouin zone. The matrix ϵ^{-1} has nonvanishing off-diagonal elements—due to lattice periodicity—which generate "umklapp" effects in the electronic response. These are generally referred to as local-field effects.[5]

Within DFT, as well as in any self-consistent scheme, the response function which is most directly accessible to calculations is the independent-electron polarizability χ_0. This is defined as the density response to a given change in the *self-consistent* (Kohn-Sham) potential; its expression is

$$\chi_0(\mathbf{q}+\mathbf{G},\mathbf{q}+\mathbf{G}') = -\frac{4}{(2\pi)^3}\sum_{v,c}\int_{\text{BZ}} \frac{\langle \mathbf{k}+\mathbf{q},c|e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|\mathbf{k},v\rangle\langle \mathbf{k},v|e^{-i(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}}|\mathbf{k}+\mathbf{q},c\rangle}{E_c(\mathbf{k}+\mathbf{q})-E_v(\mathbf{k})}\, d^3\mathbf{k} \quad , \tag{7}$$

where $E_b(\mathbf{k})$ and $|\mathbf{k},b\rangle$ are, respectively, the eigenvalues and eigenvectors (either valence or conduction) of the one-electron Hamiltonian. In terms of χ_0, the *exact* expression for the direct dielectric matrix reads (in shorthand notation for matrices)

$$\epsilon = 1 - v_C(\chi_0^{-1} - f_{\text{xc}})^{-1} \quad , \tag{8}$$

where v_C is the Coulomb potential (diagonal) matrix and f_{xc} is the functional derivative of the exchange-correlation (xc) potential with respect to the electron density.

Assuming $f_{\text{xc}}=0$, Eq. (8) yields the standard random-phase approximation (RPA),[10] which corresponds to complete neglect of xc effects in the dielectric response. Within LDA, the operator f_{xc} is local in $\mathbf{r}$ space and can be easily expressed in terms of the electronic density.[11,12]

For the purposes of this work, the relevant local-field effect concerns the $\mathbf{G}=\mathbf{G}'=0$ elements of the matrices ϵ^{-1} and ϵ:

$$\epsilon^{-1}(\mathbf{q},\mathbf{q}) \neq 1/\epsilon(\mathbf{q},\mathbf{q}) \quad . \tag{9}$$

The link to the macroscopic response is given by the long-wavelength limit ($\mathbf{q}\rightarrow 0$) of $\epsilon^{-1}(\mathbf{q},\mathbf{q})$, which is related to the *inverse* of the tensor $\overleftrightarrow{\epsilon}_{\text{macro}}$. Because of the long-range nature of the Coulomb interaction, $\epsilon^{-1}(\mathbf{q},\mathbf{q})$ is, in general, nonanalytic at $\mathbf{q}=0$; its leading term in $\mathbf{q}$ gives $\overleftrightarrow{\epsilon}^{-1}_{\text{macro}}$ through the relationship

$$\epsilon^{-1}(\mathbf{q},\mathbf{q}) \simeq \frac{1}{q^2}(\mathbf{q}\cdot\overleftrightarrow{\epsilon}^{-1}_{\text{macro}}\cdot\mathbf{q}) \quad . \tag{10}$$

For each of the lattice distortions considered here, the self-consistent electronic charge density and energy bands involved in the evaluation of dielectric matrices, Eqs. (7) and (8), have been calculated using norm-conserving pseudopotentials[13,14] and plane-wave basis sets corresponding to a kinetic energy cutoff of 14 Ry (i.e., about 250 plane waves). The electron-gas data used as input for the LDA are those of Ceperley and Alder,[15] as interpolated by Perdew and Zunger.[16] We first calculate Eq. (8), and then we account for local-field effects considering the $\mathbf{G}=\mathbf{G}'=0$ element of its inverse. We find full convergence using a dielectric matrix of order 181. The main problems occurring in the practical evaluation of χ_0 are the same as for undistorted crystals, namely, the summation of slowly convergent perturbation series and Brillouin-zone integration. Convergence in the sum over conduction states has been found using 210 of them. The Brillouin-zone integration is performed using the special-point technique.[17] We use the (8,8,8) Monkhorst-Pack[18] integration mesh which, for the undistorted crystal, reduces to the 10-point Chadi-Cohen[17] set, while, for the distorted geometry considered here, it gives 30 inequivalent points in the irreducible wedge of the Brillouin zone.

We have recently performed[19] analogous calculations for the unperturbed crystal, where—taking advantage of symmetry—larger meshes have been used. We found that the integration mesh used here is very accurate for the "body" of the matrix ($\mathbf{G}$ and $\mathbf{G}'=0$), while for the "wings" ($\mathbf{G}=0$ or $\mathbf{G}'=0$) and the head ($\mathbf{G}=\mathbf{G}'=0$), the error is rather small but not negligible. Based upon this experience, we estimate that a larger special-point set for Brillouin-zone integration would yield a value of P smaller by 5%–10% than the one calculated here. Given that the present experimental error bar for the absolute Raman cross section[2] is of the order of 15%, we decided not to perform time-consuming integrations over larger special-point sets.

Finally, the $\mathbf{G}=\mathbf{G}'=0$ element of the inverse microscopic dielectric matrix, Eq. (10), has been calculated for both $\mathbf{q}$ parallel and perpendicular to the (1,1,1) phonon polarization. From this, the values of $\gamma(u)$ and $\eta(u)$ are straightforwardly obtained using Eqs. (5) and (6).

III. RESULTS AND DISCUSSION

The term in $\gamma(u)$ which is linear in u is proportional to the Raman cross section, as discussed in Sec. II. We display in Table I our calculated values for $\gamma(u)/u$ for several values of the phonon amplitude u. Inspection of Table I shows, first of all, that the values of u used in the calculations ensure a very good linearity, without giving cancellation problems. The quadratic behavior of $\eta(u)$ has also been checked.

The final results are shown in the last column of Table I;

TABLE I. Calculated values of $\gamma(u)/u$, Eq. (5), for several values of the lattice distortion.

	LFE neglected		LFE included	
u	RPA	LDA	RPA	LDA
0.0001	7.06	8.08	6.57	7.15
−0.0001	6.95	7.94	6.49	7.06
Average	7.00	8.01	6.53	7.10
0.0002	7.12	8.16	6.61	7.20
−0.0002	6.90	7.86	6.44	7.01
Average	7.01	8.01	6.53	7.11
Expt.				6.2 ± 1

these correspond to the use of the response matrix which is, in principle, exact at the LDA level and can only be affected by numerical roundoff errors, most of which come from the finite-mesh Brillouin-zone integration. Our result agrees with the experiment, being, however, at the upper limit of the experimental error bar. According to our previous discussion, the use of a more accurate integration scheme would yield a calculated value lower by 5%–10%, in even better agreement with the experiment.

The first three columns of Table I are reported to display separately the effects of neglecting, in the calculation of the dielectric response, either xc effects (column 3), local-field effects (LFE) (column 2), or both (column 1). Some calculations of the Raman tensor exist in the literature;[3] all of them are performed within the RPA and completely neglect local-field effects: i.e., they are at the same level of approximation as in column 1 of Table I. Furthermore, none of the existing calculations uses a first-principles band structure.

An interesting feature emerging from this work is that the errors due to neglect of xc effects and local-field effects are of the order of 15% but opposite in sign, thus nearly canceling each other.

To the best of our knowledge, macroscopic dielectric properties were never attacked before within the framework of modern DFT. We have shown in this work that even a ticklish quantity like the Raman tensor—which is the derivative of the macroscopic electronic response with respect to an external parameter—can be predicted with remarkable accuracy.

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