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Tight-binding calculations of microscopic screening of ion-ion interaction and phonon dispersion in germanium

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A set of extreme tight-binding states for the valence and conduction bands in germanium, consistent with its observable electronic dielectric properties, is used to calculate the effective ion-ion interaction and phonon dispersion relations in the material. The agreement with experimental dispersion curves is comparable with other elaborate calculations.

In an earlier paper,[1] referred to hereafter as I, we have shown that it is possible to obtain meaningful results for the nonresonant part of the self-consistent microscopic optical dielectric matrix, the local dielectric function and microscopic fields induced by a long-wavelength transverse-optical field in crystals like diamond or germanium, even if we use the extreme tight-binding electronic states, i.e., the molecular bonding and antibonding states for the valence and conduction bands, in their calculations. This simple line of approach is based on the belief that the molecular-orbital model is expected to give fairly accurate results for quantities which only depend upon the average properties[2] of the electrons in a full band. In this paper we show that this simple approach can also be used to calculate microscopic response to rapidly varying static longitudinal external fields. We demonstrate this by finding the effective ion-ion interaction in germanium, and by comparing the resulting phonon dispersion relations with the existing experimental data. While calculating the optical fields in I, it was enough to restrict ourselves to the calculation of the microscopic response function $\overleftrightarrow{\epsilon}^T(\vec{q}+\vec{G},\vec{q}+\vec{G}',\omega)$ for an external transverse field, in the long-wavelength limit $(\vec{q}\rightarrow 0)$, where $\vec{G}$ is any reciprocal-lattice vector of the crystal and $\vec{q}$ is the wave vector of the external field. In the phonon dispersion studies, we are required to calculate the microscopic static longitudinal dielectric function $\epsilon^L(\vec{q}+\vec{G},\vec{q}+\vec{G}',0)$ for all $\vec{q}$ values lying in the first Brillouin zone, in order to find the net effective ion-ion interaction because of the screening by the valence electrons.

In the context of the calculation of the effective ion-ion interaction in metals and semiconductors, screening properties of such systems have been recently studied by several workers.[3–7] Martin,[4] in his calculation of phonon dispersion relations in silicon, used the Phillips bond-charge model to find the contribution to screening due to the off-diagonal elements $\epsilon^L(\vec{q}+\vec{G},\vec{q}+\vec{G}',0), \vec{G}\neq\vec{G}'$. For completely delocalized electrons, ϵ^L is, of course, almost diagonal. The bond-charge magnitude is taken as an adjustable parameter to obtain a good fit for the calculated dispersion curves with the experimental ones. Sinha,[5] on the other hand, has used a factorization scheme in which the dielectric matrix $\epsilon^L(\vec{q}+\vec{G},\vec{q}+\vec{G}',0)$ is written approximately in terms of the state-independent average form factors $f(\vec{q}+\vec{G}), f(\vec{q}+\vec{G}')$ for the valence electrons, and a $\vec{q}$-dependent polarizability tensor $\overleftrightarrow{a}(\vec{q})$. Parameters introduced in the simplified forms for f and $\overleftrightarrow{a}$, are obtained by using the acoustic sum rule, and by comparing with the experimental dispersion curves (best fit).

For any $\vec{q}$ in the first Brillouin zone, the dynamical matrix $D^{ss'}_{\alpha\beta}(\vec{q})$ which enters into the theory of phonon dispersion relations is given by[3–5]

$$D^{ss'}_{\alpha\beta}(\vec{q}) = \phi^{ss'}_{\alpha\beta}(\vec{q}) - \delta_{s,s'} \sum_{s''} \phi^{ss''}_{\alpha\beta}(0)\,, \tag{1}$$

where α and β are the three-dimensional Cartesian components. The force constants $\phi^{ss'}_{\alpha\beta}(\vec{q})$ are defined as

$$\phi^{ss'}_{\alpha\beta}(\vec{q}) = \sum_{\vec{G},\vec{G}'} (\vec{q}+\vec{G})_\alpha (\vec{q}+\vec{G}')_\beta \frac{|\vec{q}+\vec{G}|}{|\vec{q}+\vec{G}'|} \epsilon^{-1}_{\vec{G}\vec{G}'}(\vec{q}) \times V^0_{ss'}(\vec{q}+\vec{G}')\, e^{i(\vec{G}\cdot\vec{R}_s - \vec{G}'\cdot\vec{R}_{s'})}\,, \tag{2}$$

where $V^0_{ss'}(\vec{q}+\vec{G})$ represents the Fourier component of the bare interaction between the charged ions including the core electrons, $\vec{R}_s$ denotes the position of the sth basis atom with respect to the position of the unit cell in which it is located, and $\epsilon^{-1}_{\vec{G}\vec{G}'}(\vec{q})$ is the $(\vec{G},\vec{G}')$ matrix element of the matrix $\epsilon^{-1}(\vec{q})$ obtained by taking the inverse of the longitudinal dielectric matrix $\epsilon^L_{\vec{G}\vec{G}'}(\vec{q}) \equiv \epsilon^L(\vec{q}+\vec{G},\vec{q}+\vec{G}',0)$. In terms of the single-particle Bloch states, $\epsilon^L_{\vec{G}\vec{G}'}(\vec{q})$ is given by[8]

$$\epsilon^L_{\vec{G},\vec{G}'}(\vec{q}) = \delta_{\vec{G},\vec{G}'} - \frac{1}{\Omega}\frac{4\pi e^2}{|\vec{q}+\vec{G}|\,|\vec{q}+\vec{G}'|} \sum_{m,m'} f_m \left[\left(\frac{\langle m|e^{i(\vec{q}+\vec{G}')\cdot\vec{r}}|m'\rangle}{E_m - E_{m'}} \times \langle m'|e^{i(\vec{q}+\vec{G})\cdot\vec{r}}|m\rangle\right) - (m \longleftrightarrow m')\right], \tag{3}$$

where E_m is the electron energy corresponding to the Bloch state $|m\rangle$; the label m stands for the band index b, the electronic wave vector $\vec{k}$ and spin s.

We calculate $\epsilon^L_{\vec{G}\vec{G}'}(\vec{q})$ in Ge for all $\vec{q}$ values in the first Brillouin zone by using the approximate extreme tight-binding electronic states, which have already been discussed and defined completely, without any parameter left, in I. In this molecular-orbital model,[9] the eight valence electrons per unit cell of Ge crystal are assumed to form four equivalent tetrahedral bonds along the crystallographic $\langle 111\rangle$ directions. The bonding and antibonding wave functions $\psi_{v\vec{t}}$ and $\psi_{c\vec{t}}$, respectively, for the electrons in a bond in the direction $\vec{t}$ are

$$\psi_{v\vec{t}}(\vec{r}) = \tfrac{1}{2}\sqrt{2}\,(\Phi^A_{\vec{t}} + \Phi^B_{\vec{t}}) , \tag{4}$$

$$\psi_{c\vec{t}}(\vec{r}) = \tfrac{1}{2}\sqrt{2}\,(-\Phi^A_{\vec{t}} + \Phi^B_{\vec{t}}) , \tag{5}$$

$$\Phi^A_{\vec{t}} = \tfrac{1}{2}(\phi^A_{ns} + \sqrt{3}\,\phi_{np\vec{t}}) , \tag{6}$$

$$\Phi^B_{\vec{t}} = \tfrac{1}{2}(\phi^A_{ns} - \sqrt{3}\,\phi_{np\vec{t}}) , \tag{7}$$

where $\phi^{A,B}_{ns}$ and $\phi^{A,B}_{np\vec{t}}$ are s- and p-type hydrogenlike normalized atomic wave functions centered on atoms A and B, with $n=4$.

In the extreme tight-binding approximation in which the interaction between any two different bonds is neglected, we have two flat bands (energy independent of $\vec{k}$), the valence band and the conduction band, each fourfold degenerate. The corresponding electronic wave functions in the crystal, in this approximation are

$$\Psi_{v\vec{t}}(\vec{k},\vec{r}) = (\tfrac{1}{2}N)^{-1/2} \sum_j e^{i\vec{k}\cdot\vec{R}_j}\,\psi_{v\vec{t}}(\vec{r}-\vec{R}_j) , \tag{8}$$

$$\Psi_{c\vec{t}}(\vec{k},\vec{r}) = (\tfrac{1}{2}N)^{-1/2} \sum_j e^{i\vec{k}\cdot\vec{R}_j}\,\psi_{c\vec{t}}(\vec{r}-\vec{R}_j) , \tag{9}$$

where $\tfrac{1}{2}N$ is the number of unit cells in the crystal and $\vec{R}_j$ is the position of the jth cell. In I, the two parameters entering in the characterization of the unperturbed states, namely, E_g, the average energy gap between the valence band and the conduction band, and the common effective Z value for the s- and p-type hydrogenlike wave functions for Ge, are fixed self-consistently by requiring that the resultant macroscopic dielectric function (including local field corrections) must be equal to the experimental one, and by requiring that electron wave functions satisfy the f-sum rule. For germanium one has $E_g = 3.9$ eV, $Z_{\text{eff}} = 12.4$, with $\epsilon_{00}(0) = 17.0$, and $\langle\psi_{v\vec{t}}|x|\psi_{c\vec{t}}\rangle = 0.992$ Å. As discussed in I, the self-consistent values for Z_{eff} are not very much different from appropriate averages of the values given by Slater for 4s and 4p orbitals, and the average energy gap E_g is also very close to the value for Ge in the theory of covalent crystals by Phillips.

Using this approximate band structure for Ge, $\epsilon^L_{\vec{G}\vec{G}'}(\vec{q})$ can be written

$$\epsilon^L_{\vec{G}\vec{G}'}(\vec{q}) = \delta_{\vec{G},\vec{G}'} + \frac{8\pi N e^2}{|\vec{q}+\vec{G}|\,|\vec{q}+\vec{G}'|}\,\frac{1}{E_g}\sum_{\vec{t}} \langle\psi_{v\vec{t}}|\sin(\vec{q}+\vec{G})\cdot\vec{r}\,|\psi_{c\vec{t}}\rangle\langle\psi_{c\vec{t}}|\sin(\vec{q}+\vec{G}')\cdot\vec{r}\,|\psi_{v\vec{t}}\rangle . \tag{10}$$

The summation over $\vec{t}$ in this expression simply implies summation over all the four bonds. Based on the above expression, we have calculated $\epsilon^L_{\vec{G}\vec{G}'}(\vec{q})$ for $\vec{G}$ vectors up to $\langle 400\rangle$; for beyond these values the off-diagonal elements $(\vec{G}\neq\vec{G}')$ and the diagonal elements $(\vec{G}=\vec{G})$ are close to 0 and 1, respectively. The inverse of the matrix $\epsilon^L(\vec{q})$ in $\vec{G}$ space which enters in the calculation of the force constants $\phi^{ss'}_{\alpha\beta}(\vec{q})$ of Eq. (2) is then calculated approximately by using standard numerical techniques. We separate the force constant $\phi^{ss'}_{\alpha\beta}(\vec{q})$ into two parts

$$\phi^{ss'}_{\alpha\beta}(\vec{q}) = \phi^{(c)ss'}_{\alpha\beta}(\vec{q}) + \phi^{(e)ss'}_{\alpha\beta}(\vec{q}) , \tag{11}$$

$$\phi^{(c)ss'}_{\alpha\beta}(\vec{q}) = \sum_{\vec{G}} (\vec{q}+\vec{G})_\alpha(\vec{q}+\vec{G})_\beta \times V^0_{ss'}(\vec{q}+\vec{G})\,e^{i\vec{G}\cdot(\vec{R}_s-\vec{R}_{s'})} , \tag{12}$$

$$\phi^{(e)ss'}_{\alpha\beta}(\vec{q}) = \sum_{\vec{G}}\sum_{\vec{G}'} (\vec{q}+\vec{G})_\alpha(\vec{q}+\vec{G}')_\beta \frac{|\vec{q}+\vec{G}|}{|\vec{q}+\vec{G}'|} \times[\epsilon^{-1}_{\vec{G}\vec{G}'}(\vec{q}) - 1]\,V^0_{ss'}(\vec{q}+\vec{G}') \times e^{i(\vec{G}\cdot\vec{R}_s - \vec{G}'\cdot\vec{R}_{s'})} . \tag{13}$$

The Coulomb term $\phi^{(c)ss'}_{\alpha\beta}(\vec{q})$, due to ions including electrons other than the valence electrons, is very slowly convergent and is calculated by using the standard method of Ewald.[10] The electronic term $\phi^{(e)ss'}_{\alpha\beta}(\vec{q})$ corresponds to the contribution to the effective ion-ion interaction due to the presence of the valence electrons.

To obtain $\phi^{ss'}_{\alpha\beta}(\vec{q})$, we take a simple analytic form of the pseudopotential $V^0(\vec{Q})$ due to a bare ion of charge Z^0e:

$$V^0(\vec{Q}) = (4\pi Z^0 e^2/Q^2)\,\sin Qr_c/Qr_c , \tag{14}$$

where r_c is a parameter. This form of the potential was used by Sinha *et al.*[5] in their phonon dispersion

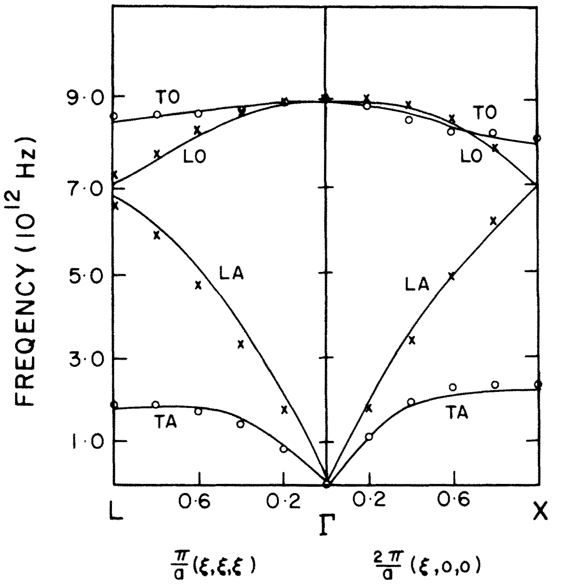

FIG. 1. Phonon dispersion curves for germanium in [111] and ⟨100⟩ directions. The experimental points are from Nilsson and Nelin (Ref. 12).

calculations for Si and Ge. They adjusted the value of the parameter r_c in such a way that the first node in the profile of $V^0(\vec{Q})$ obtained from Eq. (14) coincided with the Heine and Abarenkov potential, as modified by Shaw.[11] In our calculation, we, however, fix the value of r_c by using the acoustic sum rule, which states that all acoustic-mode frequencies tend to zero in the limit $\vec{q} \to 0$. In the microscopic theory of lattice vibrations this condition is equivalent to[4,5]

$$\lim_{\vec{q}\to 0} \sum_{\vec{G}} \vec{q}\cdot(\vec{q}+\vec{G}) \frac{|\vec{q}+\vec{G}|}{q} \epsilon^{-1}_{0\vec{G}}(\vec{q}) V^0(\vec{q}+\vec{G}) e^{i\vec{G}\cdot\vec{R}_s} = 0 . \tag{15}$$

It is reassuring that the value of $r_c \simeq 0.19\, a$ (a is the lattice constant) obtained by us is not very different than that used by Sinha *et al.*[5] It is then straightforward to obtain the electronic term $\phi^{(e)ss'}_{\alpha\beta}(\vec{q})$ numerically from Eq. (13), and the Coulomb term from Eq. (12).

The phonon dispersion curves in Ge are obtained for the crystallographic directions ⟨100⟩ and ⟨111⟩. These are plotted in Fig. 1. Experimental numbers given by Nilsson and Nelin[12] are also plotted. We find that there is a fairly close agreement between the theoretical curves obtained in our model with the experimental curves. Note that we have obtained good agreement for the acoustic modes even for large wave vectors, where it is usually difficult to get such flat dispersion curves.

Compared to more elaborate calculations of Sinha *et al.*[5] and Martin,[4] our approach is simple. Nevertheless, it gives agreement with experimental results which is comparable with their success. We feel that our model would give reliable results for phonon dispersions in other group IV-IV crystals also.

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