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Local-field effects and zone-center phonons in Si, Ge, GaAs, and ZnSe

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We present a microscopic lattice-dynamics calculation of the zone-center phonons in Si, Ge, GaAs, and ZnSe based on first-principles dielectric matrices. Our results compare favorably with the experimental data and show that local-field effects are essential to explain the trends with increasing ionicity.

The calculation of phonon energies by self-consistent distorted-crystal band-structure calculations (self-consistent microscopic theory) has scored in very recent times quite remarkable success.[1,2] The linear microscopic theory of lattice dynamics[3,4] on the other side, which is formulated in terms of dielectric matrices (DM's), has mainly been applied in model calculations.[4,5,6] Truly first-principles linear-response calculations reported to date are only a few[7,8]; they refer to Si only and give conflicting results on the accuracy obtainable in this way. Furthermore, according to Ref. 7, off-diagonal dielectric screening raises the zone-center TO frequency in Si whereas the opposite effect is found in model calculations.[5] In view of these facts, a wider first-principles investigation of phonon frequencies within the linear microscopic theory becomes necessary. Very accurate DM's[9-11] have recently been obtained for some covalent and partly ionic semiconductors. Here we apply these first-principles DM's to the calculation of the zone-center phonon energies. We will present and discuss our results after having defined some basic quantities useful in the discussion.

The dynamical matrix of a zinc-blende crystal is nonanalytic at $\vec{q}=0$, and its nonanalytic part is responsible for the L-T splitting of the optic modes for $\vec{q}\rightarrow 0$. Its matrix elements at small $\vec{q}$ are given by the microscopic theory of lattice dynamics as[3]

$$D_{SS'}^{\alpha\beta}(\vec{q})\cong(M_S M_{S'})^{-1/2}\left[\bar{C}_{SS'}^{\alpha\beta}(0)-\delta_{SS'}\sum_{S''}\bar{C}_{SS''}^{\alpha\beta}(0)\right.$$
$$\left.+\frac{4\pi Z_S^* Z_{S'}^*}{\Omega\epsilon_0}\,\frac{q^\alpha q^\beta}{q^2}\right], \quad (1a)$$

where the subscripts refer to atoms in the unit cell, superscripts indicate Cartesian components, Ω is the cell volume, and ϵ_0 is the static electronic dielectric constant.[12] Since our materials are cubic with two atoms in the unit cell, we only need in evaluating Eq. (1) the Born effective charges Z_S^* and the $S\neq S'$ force-constant tensor $\bar{C}_{SS'}^{\alpha\beta}(0)$ which is diagonal. In a pseudopotential formulation[4,7] these quantities are related to the bare pseudopotentials $V_S(\vec{q}+\vec{G})$ and to the inverse dielectric matrix (IDM) as follows:

$$Z_S^*=Z_S-\frac{\Omega\epsilon_0}{4\pi}\lim_{\vec{q}\rightarrow 0}\sum_{\vec{G}\neq 0}\vec{q}\cdot\vec{G}\,\epsilon^{-1}(\vec{q},\vec{q}+\vec{G})V_S(\vec{G})e^{i\vec{G}\cdot\vec{R}_S}, \quad (1b)$$

$$\bar{C}_{SS'}^{\alpha\alpha}(0)=\frac{1}{3}\left[-4\pi Z_S Z_{S'}/\Omega+(\Omega/4\pi)\sum_{\vec{G},\vec{G}'\neq 0}\vec{G}\cdot\vec{G}'\,|\vec{G}|^2[\epsilon^{-1}(\vec{G},\vec{G}')-\delta_{\vec{G},\vec{G}'}]\right.$$
$$\left.\times V_S(\vec{G})V_{S'}(\vec{G}')\exp(-i\vec{G}\cdot\vec{R}_S+i\vec{G}'\cdot\vec{R}_{S'})\right], \quad S\neq S' \quad (1c)$$

where $\vec{R}_S$ is the position of the Sth ion in the unit cell, Z_S is the bare ion charge, and $\vec{G}$ are reciprocal-lattice vectors.

Owing to symmetry reasons, the 6×6 dynamical matrix, Eq. (1), factorizes in three 2×2 blocks, one for longitudinal phonons and two (identical) for transverse phonons. These 2×2 matrices become very meaningful after transformation to the normal coordinates which correspond to the acoustic and optic modes. Let us define

$$\eta=(Z_A^* M_C - Z_C^* M_A)/(M_A M_C)^{1/2} , \tag{2}$$

$$\omega_{\mathrm{TO}}^2 = -\bar{C}_{AC}^{\alpha\alpha}(0)/m , \tag{3}$$

where $1/m = 1/M_A + 1/M_C$, and the A (C) label refers to the anion (cation). The quantity η is simply related[13] to the macroscopic field $\vec{\mathrm{E}}$ associated to LO phonons and vanishes by symmetry in the diamond lattice. The 2×2 dynamical matrices are then

$$\tilde{D} = \begin{bmatrix} 0 & 0 \\ 0 & \omega_{\mathrm{TO}}^2 \end{bmatrix} + \Theta \frac{4\pi}{\Omega\epsilon_0} \frac{1}{M_A + M_C} \times \begin{bmatrix} (Z_A^* + Z_C^*)^2 & (Z_A^* + Z_C^*)\eta \\ (Z_A^* + Z_C^*)\eta & \eta^2 \end{bmatrix} , \tag{4}$$

where the Θ factor assumes the value of 0 for the transverse modes and 1 for the longitudinal ones.

The frequencies of the transverse modes are therefore $\omega_{\mathrm{TA}}=0$ and ω_{TO} given by Eq. (3). For longitudinal modes the constraint imposed by the acoustic sum rule (ASR) is very important.[3] If the ASR is satisfied we have $Z_C^* = -Z_A^* = Z^*$ and $\tilde{D}$ is diagonal. The frequencies of the longitudinal modes are then

$$\omega_{\mathrm{LA}} = 0, \qquad \omega_{\mathrm{LO}} = [\omega_{\mathrm{TO}}^2 + 4\pi (Z^*)^2/(\Omega\epsilon_0 m)]^{1/2} . \tag{5}$$

Previous calculations for the diamond structure[7,14] have proved that it is difficult to satisfy the ASR in a first-principles calculation without adjustable parameters. Also in the present calculation the ASR is not exactly verified, the deviations being of the same order of magnitude as those found in previous works. Violation of the ASR results in the fact that the eigenvectors of the dynamical matrix correspond to mixed modes and *not* to pure LA and LO modes. Such a mixing is not present in the diamond structure, due to the vanishing of η. A further unphysical consequence of ASR violation, present in both diamond and zinc-blende structures, is that $\omega_{\mathrm{LA}} \neq 0$.

The IDM's of some diamond—[10] and zinc-blende—structure[11] semiconductors have previously been calculated within the empirical pseudopotential scheme[15] both for $\vec{q}=0$ and $\vec{q}\rightarrow 0$. Bare potentials compatible with this scheme, however, are not known and we will use the Appelbaum-Hamann atomic pseudopotentials[16,17] in our lattice-dynamics calculation. A violation of the ASR is therefore to be expected.

TABLE I. Anion and cation Born effective charges calculated from Eq. (1b).

	Si	Ge	GaAs	ZnSe
Z_A^*	0.49	0.60	-1.24	-0.96
Z_C^*	0.49	0.60	2.19	2.21

The Born effective charges Z_S^* of Si, Ge, GaAs, and ZnSe have been calculated including the lowest 113 reciprocal-lattice vectors in the summation of Eq. (1b). The results are reported in Table I. ASR violations are comparable to those found in previous work.[14,18] Their maximum value is 16% in the case of ZnSe.

The force constants $\bar{C}_{AC}^{\alpha\beta}(0)$ needed in Eq. (3) in order to obtain ω_{TO} have been calculated following Eq. (1c) and using IDM's obtained from numerical inversion of $\vec{q}=0$ DM's (Ref. 19) of order 113. Diagonal terms corresponding to 116 additional reciprocal vectors have been added wtih the use of the free-electron $\epsilon^{-1}(\vec{G},\vec{G})$ values.[20] This free-electron contribution is well converged; inclusion of further $\vec{G}$ vectors contributes less than 1×10^{24} s^{-2} to ω_{TO}^2, except for Si where the contribution is 1.9×10^{24} s^{-2}.

The numerical importance of the various terms in Eq. (1c) contributing to ω_{TO}^2 is shown in the upper portion of Table II. The off-diagonal terms, line (c), are responsible for most of local-field effects in ω_{TO}. We stress that these terms always give a *lowering* of the TO frequency with respect to the diagonal approximation, and that this lowering is more important in more ionic materials, consistently with the general trend of other local-field effects within the Ge isoelectronic series.[11] The local-field induced lowering of all TO frequencies we have found is in agreement with the results of model phonon calculations in Si,[5] and the fact that the off-diagonal and the diagonal electronic polarization densities are in phase over most of the unit cell during a TO vibration in Si.[21]

A calculation analogous to the present one has recently been reported for Si,[7] based on a dielectric matrix of order 59 and on a bare ionic pseudopotential different from the one used here. The main result of that paper is that off-diagonal screening *increases* ω_{TO}, clearly at variance with our findings. We have therefore repeated our calculations starting from *direct* DM's of order 59 and 89. The di-

TABLE II. Partial contributions to ω_{TO}^2 in Eq. (1c) ($10^{24}\ \mathrm{s}^{-2}$). (a) bare ions; (b) diagonal IDM contribution up to 113 $\vec{G}$ vectors; (c) off-diagonal IDM contribution up to 113 $\vec{G}$ vectors; (d) diagonal free-electron contribution from 116 additional $\vec{G}$ vectors. The lower portion of the table gives the (b) and (c) contributions resulting from DM's of order 59 and 89.

	Si	Ge	GaAs	ZnSe
a	415.9	142.1	135.3	108.7
b	−137.4	−69.2	−59.5	−33.2
c	−14.4	−19.0	−31.5	−64.0
d	32.9	11.5	11.4	11.6
b(59)	−122.3	−63.4	−53.5	−26.3
c(59)	82.1	22.6	13.2	−10.6
b(89)	−95.2	−56.2	−46.2	−19.0
c(89)	59.1	11.1	0.9	−22.3

TABLE III. Phonon frequencies at the Brillouin zone center, in THz. For each mode, the first line gives the result of the present calculation and the second line the experimental frequency, from Ref. 22.

	Si	Ge	GaAs	ZnSe
ω_{TA}	0	0	0	0
	0	0	0	0
ω_{LA}	1.32	0.82	0.74	1.19
	0	0	0	0
ω_{TO}	17.23	8.09	7.47	4.81
	15.53	9.11	8.06	6.09
ω_{LO}	17.23	8.09	8.00	6.51
	15.53	9.11	8.75	7.55

agonal and off-diagonal contributions to ω_{TO}^2 are given in the lower portion of Table II. The off-diagonal contribution to ω_{TO}^2 in Si using a direct DM of order 59 is $+82.1$, a figure close to that of Ref. 7 (despite the difference in the bare potentials used), but opposite in sign and very different in magnitude from that obtained with a DM of order 113. Table II shows that, upon increasing the order of the direct DM, the off-diagonal contribution to ω_{TO}^2 changes considerably also in Ge, GaAs, and ZnSe. We conclude that large DM's are needed in lattice dynamics even when dealing with soft-core pseudopotentials.[16] We remark here that the other available first-principles calculation within linear microscopic theory[8] uses a DM of order 27.

Our final results for the phonon frequencies are reported in Table III, together with the experimental data, taken from Ref. 22. The overall agreement is good, considering our first-principles scheme without adjustable parameters. The most striking fact is, of course, the nonvanishing of ω_{LA} due to the ASR violation discussed above. The acoustic-optic mode mixing, however, is small: 0.1% in GaAs and 2.9% in ZnSe.

For the optical frequencies we reproduce the experimental *L-T* splitting and the trend of the TO frequencies with increasing ionicity. As discussed above, the latter mostly results from local-field contributions. In fact, calculating ω_{TO} with the simple free-electron dielectric function[20] we obtain in THz units 16.52, 8.00, 8.22, and 8.40 in Si, Ge, GaAs, and ZnSe, respectively. These figures are quite good for Si and Ge, a fact first noted many years ago,[4] but are at variance with experimental trends in polar semiconductors.

The relative error on the value of ω_{TO} is about 10% (20% in ZnSe). The partial contributions reported in Table II suggest that more accurate values require the use of larger dielectric matrices (of order ~200). Line (d) of the table shows in fact that the diagonal contribution due to vectors beyond the first 113 is non-negligible and therefore from the same vectors we expect some off-diagonal contributions which we have neglected here. We note that available calculations[1,2] within the self-consistent microscopic theory have found it necessary to use at least 200 plane waves to achieve sufficient convergence in the total energy.

In conclusion, in this paper we have shown that lattice-dynamics calculations within the linear microscopic theory can successfully predict phonon energies in both covalent and partly ionic semiconductors. This, however, requires the use of larger dielectric matrices than suspected up to now. The use of small matrices can even lead to severe qualitative errors.

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Zn: $\alpha = 0.61$, $v_1 = 2.896$, $v_2 = -0.924$;
Ga: $\alpha = 0.61$, $v_1 = 2.768$, $v_2 = -1.080$;
Ge: $\alpha = 0.61$, $v_1 = 2.640$, $v_2 = -1.237$;
As: $\alpha = 0.61$, $v_1 = 2.511$, $v_2 = -1.394$;
Se: $\alpha = 0.61$, $v_1 = 2.383$, $v_2 = -1.550$.

The resulting self-consistent energy bands of Ge, GaAs, and ZnSe have accuracy comparable to that found by the local empirical pseudopotential method (Ref. 15).

[18] Results published in Ref. 7 imply $Z^* \simeq 0.23$ in Si.

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