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Full-potential linear-muffin-tin-orbital calculation of phonon frequencies in semiconductors

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The optical-phonon frequencies in compound semiconductors are obtained from total-energy calculations using the local-density approximation in conjunction with a newly developed full-potential version of the linear-muffin-tin-orbital (LMTO) method. In this scheme the full nonsphericity of the potential is included throughout the self-consistency cycle. The results agree well with experiments and with the results of first-principles pseudopotential calculations. A linear correlation is found between the force constants and the sp^3 bond orders as obtained, for instance, from conventional LMTO calculations for the undistorted crystals. This allows us to derive the optical-phonon frequencies for all zinc-blende-type semiconductors from those of only two materials, e.g., Si and Ge.

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I. INTRODUCTION

During the last decade it has become possible to calculate phonon frequencies with high accuracy and without adjustable parameters by using the density-functional formalism in conjunction with either first-principles pseudopotentials or the linear augmented-plane-wave (LAPW) method. The basis sets used in the linear methods[1,2] generally have the advantages of being relatively small and of being equally applicable to narrow- and broady-band materials. A disadvantage is that they lead to simple matrix elements only for the so-called muffin-tin (MT) part of the one-electron potential. In frozen-phonon calculations, however, where the atoms are being moved away from the high-symmetry positions, the full potential—not merely its muffin-tin part—must be included in the self-consistency cycle. This has been done within the LAPW scheme,[3–5] and recently one of us showed[6] how this can be done with linear-muffin-tin orbitals (LMTO's) as well, and in Ref. 7 the scheme is applied in the calculation of ferroelectric instabilities of ABO_3 compounds.

Whereas the LAPW method requires about 50 basis functions per atom, the LMTO scheme needs only about 10, and this is of great importance when systems with large unit cells are treated. On the other hand, whereas LAPW's form a complete set of functions in the interstitial region between the atoms (between the muffin-tin spheres), solid-state LMTO's do not, because they are chosen to satisfy Laplace's equation in that regime.[8] It follows, therefore, that a full-potential method employing the basis set of solid-state LMTO's is bound to be relatively economical and generally applicable, but a crucial question is whether it is accurate enough for calculations of the small-energy changes caused by small, symmetry-breaking distortions. This is the first question addressed in this paper where we present frozen-phonon calculations for C (diamond), Si, Ge, GaAs, and AlAs using the full-potential LMTO (LMTO-FP) method.[6]

Nearly all existing LMTO band-structure calculations have made use of the so-called atomic-sphere approximation[1,9] (ASA), which is similar to, but simpler than, the MT approximation. In the ASA *total-energy functional* all integrals over space are substituted by sums of integrals over Wigner-Seitz spheres, and the electron density is taken to be spherically symmetric inside each sphere. Minimization of this ASA functional leads to a self-consistent one-electron problem in which the potential is a superposition of spherically symmetric atomic-sphere contributions[10] derived from spherically symmetric densities. Since the LMTO's are differentiable, it is obvious that a band-structure calculation for such an AS potential will generate differentiable Bloch functions, and hence, a differentiable, nonspherical density. Earlier calculations of elastic shear moduli for transition metals[11] indicated that whereas the ASA functional is not sufficiently accurate for frozen-phonon calculations, the nonsphericalized density obtained from a self-consistent LMTO-ASA calculation does yield reasonable results if inserted in the *proper* (i.e., not the ASA) functional. This is consistent with the demonstration[12] that, albeit for undistorted Si, the nonsphericalized LMTO-ASA density is almost identical with the density resulting from a full-potential LAPW calculation. This approximation of restricting the potential, but *not* the energy functional, to the AS form may be referred to as ASA-V. Most recently, a study of deformation potentials related to band splitting induced by uniaxial strains found the accuracy of also ASA-V to be insufficient.[13]

In the analysis of the bonding properties in a large number of compound semiconductors, it was found[14] that the so-called sp^3 bond order is a convenient measure of the degree of covalent bonding. It was claimed that this quantity is a measure of the strength of the sp^3 bond in the zinc-blende-type crystals. A second purpose of the present work is to show that this is true, and we find that the "force constant" related to bond stretching appears to be linearly related to the bond order. Consequently, knowing the TO(Γ)-phonon frequency for *only two* semiconductors, we can derive the phonon frequency for any other zinc-blende-type compound just be calculating the bond order; this merely requires a LMTO-ASA self-consistent calculation for the undistorted crystal.

The details of the LMTO-FP method and its application to the TO(Γ)-phonon mode of Si are given in Ref. 6. This presentation is somewhat technical so we thought it worthwhile to include a general description of the method in Sec. II of the present paper. The results of the calculations are given in Sec. III.

II. OUTLINE OF THE LMTO-FP METHOD

In spite of its name, the full-potential LMTO method still employs a division of space into *spheres,* either muffin-tin (MT) spheres or atomic spheres (AS's). These spheres, however, only serve the purpose of defining the *basis functions* that are used in the variational procedure of calculating the one-electron band structure. By MT spheres we mean spheres that are centered on the atomic sites and which do not intersect each other. In the present case, where we calculate the total energy as a function of distortions in the optical-phonon mode, the radii are so small that the spheres do not overlap for any of the distortions applied. Atomic spheres, on the other hand, are space filling, and they do therefore, even in the undistorted geometry, overlap slightly. The calculations reported here only use the MT spheres. When applied to open structures, like that of zinc blende, the LMTO-FP still, as does the usual LMTO method (e.g., Ref. 15), needs the introduction of empty spheres in the lattice. Thus, the primitive cell of GaAs, for example, contains *four* atomic positions, Ga, As, E_1, and E_2, with the following undistorted positions: $(0,0,0)$, $(1,1,1)(a/4)$, $(-1,-1,-1)(a/4)$, and $(1,1,1)(a/2)$, respectively (a being the lattice constant). The labels E_1 and E_2 refer to the two, in general inequivalent, empty spheres.

The MT spheres thus divide the crystal into two regions, an *atomic* region, inside the spheres, and an *interstitial* region, the space between the MT spheres. The basis functions are chosen to be Bloch sums of muffin-tin orbitals (MTO's). A MTO is made up of solutions (for certain energies,[1] E_ν) to the Schrödinger-like equation for a *muffin-tin* potential which is spherically symmetric in the atomic regions and spatially constant in the interstitial region. The MTO's in the interstitial region are thus very simple, namely, the solutions to Laplace's equation (see, for example, Refs. 1, 6, and 16). These *pseudo*-MTO's can be represented by superpositions of plane waves and lead to a convenient Fourier representation of the electron density in the interstitial region.[16,17,6] The MTO's in the atomic region are ϕ-$\dot{\phi}$-augmented[1] functions matching the pseudo-MTO's at the sphere surfaces, with ϕ being the solution, at the linearization energy E_ν, to the radial wave equation with the spherical symmetric potential, and $\dot{\phi}$ the energy-derivative of ϕ. In order to utilize the advantages of a Fourier representation of the density associated with the pseudo-MTO's, we let these extend over the entire space, i.e., also inside the atomic regime. Thereby, the MTO of wave number $\mathbf{k}$ related to the partial waves of angular momentum (l,m) and centered on the sites $\mathbf{R}_q$ has the form

$$\chi^{\mathbf{k}}_{\Lambda}(\mathbf{r})=\hat{\chi}^{\mathbf{k}}_{\Lambda}(\mathbf{r})+\tilde{\chi}^{\mathbf{k}}_{\Lambda}(\mathbf{r}) , \tag{1}$$

where Λ is a combined index representing $(l,m,\mathbf{R}_q)$, and $\hat{\chi}$ is

$$\hat{\chi}^{\mathbf{k}}_{\Lambda}(\mathbf{r})=\chi^{1,\mathbf{k}}_{\Lambda}(\mathbf{r})-\tilde{\chi}^{1,\mathbf{k}}_{\Lambda}(\mathbf{r}) , \tag{2}$$

a function that is only nonzero inside the sphere with which it is associated. The χ functions on the right-hand side are the *one-center* (thus the superscripts 1) expansions[1,16] truncated at a certain maximum l value ($l_{\max}$) of the real (including the $\phi,\dot{\phi}$) and pseudo-MTO's, respectively. The wave function of the state $(j,\mathbf{k})$, where j is a band index, is

$$\Psi^{j,\mathbf{k}}=\sum_{\Lambda}a^{j,\mathbf{k}}_{\Lambda}\chi^{\mathbf{k}}_{\Lambda} , \tag{3}$$

where the eigenvectors $\mathbf{a}$ are obtained from the eigenvalue problem,

$$[\underline{H}^{\mathbf{k}}-\varepsilon_j(\mathbf{k})\underline{O}^{\mathbf{k}}]\mathbf{a}^{j,\mathbf{k}}=0 . \tag{4}$$

In (4) $\underline{H}$ and $\underline{O}$ are the Hamiltonian and overlap matrices. This is where the *nonspherical* potential enters into the formalism. In order to calculate the matrix elements involving the full potential $[V(\mathbf{r})]$, this is split into a *local* part, $\hat{V}(\mathbf{r})$, and a *pseudocontribution,* $\tilde{V}(\mathbf{r})$, which can be represented by a Fourier series:

$$V(\mathbf{r})=\hat{V}(\mathbf{r})+\tilde{V}(\mathbf{r}) , \tag{5}$$

with

$$\tilde{V}(\mathbf{r})=\sum_{\mathbf{G}}\tilde{V}(\mathbf{G})\exp(i\mathbf{G}\cdot\mathbf{r}) . \tag{6}$$

The local potential, $\hat{V}(\mathbf{r})$, is only nonzero in the atomic region, and there it is represented by an expansion in radial functions multiplied by spherical harmonics. The matrix elements of $\underline{H}$ and $\underline{O}$ are given explicitly in Ref. 6.

The total charge density is separated into two parts, a *local* part, only nonzero in the atomic region, $\rho_{\text{loc}}(\mathbf{r})$, and a remainder, $\rho_{\text{rem}}(\mathbf{r})$:

$$\rho_{\text{tot}}(\mathbf{r})=\rho_{\text{loc}}(\mathbf{r})+\rho_{\text{rem}}(\mathbf{r}) , \tag{7}$$

and this division is made in such a way that the local density does not produce any electric fields outside the spheres. Therefore the two charge contributions are given by

$$\rho_{\text{loc}}=\hat{\rho}+\rho_{c,N}-\Delta \tag{8}$$

and

$$\rho_{\text{rem}}=\tilde{\rho}+\Delta , \tag{9}$$

where the charge density $\Delta=\Delta(\mathbf{r})$ that is subtracted and added is the density needed to ensure that the *local* density alone produces no field outside the spheres. This can be expressed in terms of a Fourier series which is convenient in (9), where it is added to the *pseudocharge.* The first term on the right-hand side of (8) is due to the $\hat{\chi}$ part of the MTO's [Eq. (1)], whereas the second term represents the contributions from the nuclei plus the *core* electrons. (We consider as *core* electrons those which are low lying in energy and well localized inside the MT spheres; their density is kept frozen during the self-consistency iterations, and their density is taken to be spherically symmetric in the atomic region.)

With the definition of the *local* density as given in Eq. (8), the calculation of the local, nonspherical Hartree potential becomes particularly simple, due to the boundary condition imposed at the MT-sphere surfaces[6,13] (vanishing of all multipole fields). The plane-wave part of the potential is easily obtained as a Fourier series, once the Fourier coefficients of $\tilde{\rho}$ and Δ are known:

$$\tilde{V}_H(\mathbf{r})=\sum_{\mathbf{G}}\frac{8\pi}{G^2}[\tilde{\rho}(\mathbf{G})+\Delta(\mathbf{G})]\exp(i\mathbf{G}\cdot\mathbf{r}) \ . \tag{10}$$

The exchange-correlation potential (we use the LDA parametrization by von Barth and Hedin[18]) is nonlinear in the electron density. Also, this contribution is split into a local part and the exchange-correlation potential for the pseudodensity alone.[6] The local contribution is only nonzero in the atomic regime; it vanishes with zero slope at the MT-sphere surfaces and can be expanded as a Taylor series in the (nonspherical) deviation from the spherically averaged electron density in the atomic regime. The pseudopart is represented by a Fourier series, where the coefficients are determined by numerical integration over the cell.

The total energy is calculated within the frozen-core approximation, as indicated above. This means that we only calculate the valence energy, and this quantity is given by

$$F[\rho]=T_s+F^C_{\text{loc}}+\tilde{F}^C+E_{\text{xc}}[\rho]-E_{\text{xc}}[\rho^c] \ , \tag{11}$$

where the kinetic energy T_s is calculated as

$$T_s=\sum_{j,\mathbf{k}}^{\text{occ}}\varepsilon_j(\mathbf{k})-\int_{\Omega_c}V(\mathbf{r})\rho^v(\mathbf{r})d\mathbf{r} \ , \tag{12}$$

Ω_c being the cell volume and ρ^v the valence charge density. The second term in (11) is a *local* Coulomb-type contribution consisting of a summation over all MT spheres, q, in the primitive cell of

$$F^C_{\text{loc}}(q)=\tfrac{1}{2}F^C_1(q)+F^C_2(q)+F^C_3(q) \ , \tag{13}$$

where each of the terms on the right-hand side are of the form

$$F^C_i(q)=\int\int_{\text{MT}_q}\frac{2\rho_a(\mathbf{r})\rho_b(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}\,d\mathbf{r}' \ . \tag{14}$$

The charge densities in these three types of Coulomb integrals are, for $i=1$,

$$\rho_a=\hat{\rho}^q+\Delta^q, \quad \rho_b=\hat{\rho}^q-\Delta^q \ ,$$

for $i=2$,

$$\rho_a=\hat{\rho}^q, \quad \rho_b=\rho^q_{c,N} \ ,$$

and for $i=3$,

$$\rho_a=\tilde{\rho}^q, \quad \rho_b=\hat{\rho}^q-\Delta^q+\rho^q_{c,N} \ .$$

The *pseudo* contribution is

$$\tilde{F}^C=4\pi\Omega_c\sum_{\mathbf{G}}\frac{|\tilde{\rho}(\mathbf{G})+\Delta(\mathbf{G})|^2}{G^2} \ ,$$

and the last two terms in (11) are the exchange-correlation energies evaluated for the total and core densities, respectively. Note that in (10) and the expression for the total energy above, we have referred to the V's as *potentials* and the ρ's and Δ's as *charge* densities, although we in fact mean *potential energies* and *electron* densities. The equations are written in Ry atomic units, i.e., the magnitude $|e|$ of the electronic charge is $\sqrt{2}$.

III. RESULTS

The application of the LMTO-FP method to the calculation of the TO(Γ)-phonon frequencies is now, in principle, straightforward. The atomic positions of the undistorted zinc-blende–type crystal are given at the beginning of Sec. II, and we just have to calculate (self-consistently) the total energy, Eq. (11), as a function of the displacement $2u$ in the [111] direction of the anion with respect to the cation. There is no way in which we unambiguously can specify how the MT spheres associated with the interstitial positions (the empty spheres) should be moved when the distortion is introduced. We have therefore tried various possibilities: (i) E_1 and E_2 are moved along with the sublattices to which they may be associated, (ii) they are kept in fixed positions, and (iii) they are moved *opposite* to case (i). In all three cases we find the same frequencies, i.e., the use of empty spheres for the definition of the basis set does not lead to ambiguities in the LMTO-FP scheme.

For small distortions the deviation ΔF of the total energy from that of the undistorted crystal is

$$\Delta F=A(u/a)^2+B(u/a)^3 \ , \tag{15}$$

where the coefficient A of the second-order term naturally will be referred to as the *force constant*. Knowing this, we then get the phonon frequency ν_{TO} as

$$\nu_{\text{TO}}=(2\pi a)^{-1}\left[\frac{A}{2\mu}\right]^{1/2} \ , \tag{16}$$

where μ is the anion-cation reduced mass. Typically three to five values of u are chosen, and A and B in (15) are determined by a least-squares procedure.

The values of A and B obtained for five semiconductors are listed in Table I. The phonon frequencies de-

TABLE I. The calculated values of the second- and third-order coefficients A and B in the total-energy variation with distortion in the optical-phonon mode. The values are given in units of keV.

	A	B
C	1.103 10	−1.0200
Si	0.821 00	−10.410
Ge	0.749 90	−10.736
GaAs	0.621 87	−8.7603
AlAs	0.524 41	−11.034

TABLE II. Optical-phonon frequencies (in THz) as obtained directly from the full-potential LMTO total-energy calculations (LMTO-FP) derived from the linear relation between the force constants (A) and the sp^3 bond order (LMTO-FP*) are compared to experiments and values resulting from other theoretical works.

	LMTO-FP	LMTO-FP*	Expt.[a]	Other calc.
C	42.25	42.29	39.9	38.98[e]
Si	15.57	15.46	15.53	17.10,[d] 15.64[c]
Ge	8.89	8.82	9.02	9.05[c]
AlAs	10.06	10.11	10.84	
GaAs	8.11	8.15	8.064	8.29,[b] 8.09[c]
BN		36.77	31.62	
AlP		12.30	13.17	
ZnSe	6.46[f]	6.48	6.39	
InSb		4.76	5.49	
CdTe		4.20	4.20	
InAs		6.33	6.51	
InP		8.76	9.09	
SiC		19.72	23.86, 23.11	

[a] Reference 19.
[b] Reference 21.
[c] Reference 22.
[d] Reference 24.
[e] Reference 23.
[f] Reference 25.

rived from A for the same five semiconductors are given in the first column of Table II (LMTO-FP). These may be compared to the experimental data[19] (third column, Table II) and to the results of other theoretical calculations (the last column). The first-principles, norm-conserving, pseudopotential[20] calculations[21–23] yield frequencies that are in excellent agreement with experiments. For Si, Ge, and GaAs our values agree equally well with the measured data, but our value for C is 3.3 THz higher[26] than that calculated by Nielsen,[23] and 2.3 THz too high as compared to the frequency measured (at room temperature). In the case of AlAs, where we have no pseudopotential calculation to compare to, the LMTO-FP value is in good agreement with experiment. We take these results as an indication that the LMTO-FP method is well suited for calculation on the energy changes induced by small, symmetry-breaking distortions, and that for the semiconductors its accuracy is comparable to that of the best pseudopotential calculations. In that context it should be noted that a strict ASA calculation gives *negative* values of A.

It was suggested in Ref. 14 that the theoretically calculated sp^3 *bond-order* parameter should represent a measure of the strength of the covalent bond in the tetrahedrally bonded compound semiconductors. The distortions which we are considering here consist of the stretching of the bond, and it might then be assumed that the force constant A would be simply related to this parameter, b. It follows from Fig. 1, where we have plotted A as a function of b, that this is indeed the case. To a very good approximation the relation appears to be linear. Making a best linear fit to $A=A(b)$ on the basis of the LMTO-FP calculations for the five compounds discussed above, we can then use the b values tabulated in Ref. 14 to derive A, and thus the phonon frequencies for other compounds. The results of this procedure are listed in the second column (LMTO-FP*) of Table II, and the frequencies agree extremely well with the experiments. Thus, using this (still empirically found) linear relation between A and b, we, in principle, only needed to calculate ν_{TO} for *two* semiconductors, that might even be two homopolar (Si and Ge) semiconductors, in order to determine the TO(Γ) frequency in any zinc-blende–type compound. It is stressed again that the calculations that produced the bond orders are of the ASA type, i.e., they did not apply the computationally much heavier LMTO-FP scheme. These observations suggest that a reformulation of the total-energy functional that breaks the various terms up in a way that relates directly to a certain orbital basis (in this case sp^3) may be very useful for an improved physical picture of the bonding properties.

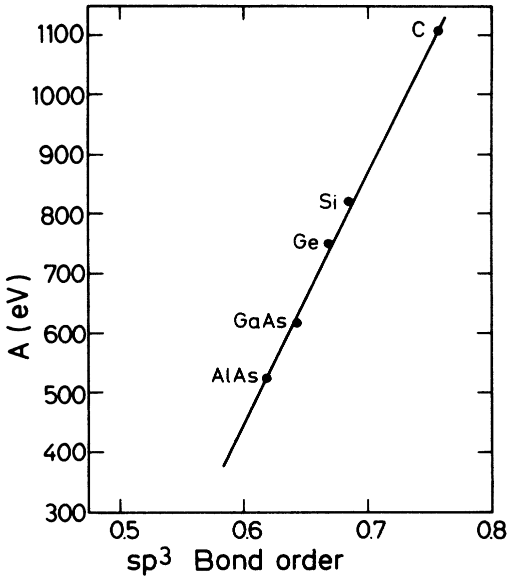

FIG. 1. The force constant A vs the sp^3 bond order.

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