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# Real-space convergence of the force series in the lattice dynamics of germanium

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It is shown how phonon dispersion in germanium along the [100] and [111] directions can be described in terms of planar force constants, which are determined *ab initio* by using the local-density-functional theory. Anharmonicity, real-space extent, and physical origins of the above forces are discussed.

## I. INTRODUCTION

Since the *ab initio* force-constant method for determination of phonon dispersion in covalent semiconductors was proposed,[1-3] little interest has been paid to the force constants themselves, i.e., to the forces connecting the distinct atomic planes perpendicular to the selected propagation direction. Yet we are in possession of first-hand information which, for the first time, can be obtained without any adjustable parameters: The sets of forces have a figurative meaning in direct space and their knowledge can bring us new insight into the nature of crystal bonding. In this paper we apply the *ab initio* force-constant method to germanium and, using the local-density-functional (LDF) technique, we calculate planar forces that determine complete phonon dispersion $\omega(\mathbf{k})$ and $\mathbf{u}(\mathbf{k})$ in [100] and [111] directions. The main part of the work consists of discussing different aspects of behavior of the bonding forces obtained in this way, and their physical meaning. The *ab initio* approach is applied to the [111] direction for the first time.

After a brief reminder of the method (Sec. II), the *anharmonicity* of the forces is quantitatively discussed in Sec. III; it is shown how the information relevant to harmonic lattice dynamics is to be extracted. Section IV examines *spatial variation* of the interactions and, as different lattice dynamical quantities can be expressed in terms of planar forces, convergence properties of the respective series are examined; the convergence itself is a mathematical expression of what we intuitively feel as *spatial extent* of forces. Besides giving quantitative results pertinent to germanium, Secs. III and IV provide the methodic details necessary for systematic application of the *ab initio* force-constant method, which have only been evoked in the previous works.[1-3] Peculiar features of the convergence of lattice-dynamical quantities with range of forces, which are shown in Sec. IV, have a more general significance and apply, as well, to compounds "similar" to Ge; these particularities are then shown in Sec. V to originate from alternation of signs of the transverse forces which, in turn, reflects presence of *angular interactions* characteristic of covalent bonding. We finally demonstrate in Sec. V how the transverse forces arise through screening of the electrostatic core-core interactions by electronic terms, and we show the analogy between this screening and composition of energies of frozen phonons.

## II. METHOD

The *ab initio* force-constant approach to lattice dynamics of *homopolar* semiconductors was proposed on the example of germanium in Ref. 1 and generalized to *heteropolar* compounds in Ref. 2. Procedures similar to previous work,[1] which was originally restricted to homopolar substances, were independently applied in Ref. 3 to silicon. The method is based upon realization that a monochromatic plane wave propagating through a periodic structure does *not* destroy the crystal's translational symmetry in the direction perpendicular to the phonon propagation. This means that in a crystal through which an arbitrary plane wave of wave vector $\mathbf{k}$ propagates, the atoms of every plane perpendicular to $\mathbf{k}$ vibrate in phase; with planes moving as rigid units, the crystal vibrations can be described as those of a linear chain.

Two examples of such chains are given in Fig. 1. The atomic planes are connected by interplanar force constants $k_n$ and, for symmetric choices of propagation direction, the equations of motion of the "linear chain" lead to a simple secular equation $2\times2$, whatever the range of forces;[4] different sets $\{k_n\}$ are needed for different choices of polarization and of propagation direction.

The above picture of linear chain is not new; the new ingredient is the faculty to determine the force constants *ab initio*, independent of any phenomenological model for the interactions, and without assumptions limiting their range *a priori*. This became possible only recently with the development of the local-density-functional (LDF) theory[5] and with the demonstration[6,7] that the Hellmann-Feynman theorem applied to the self-consistent charge densities can precisely provide the restoring forces equivalent to energy changes defining the corresponding "frozen phonons."[7,8] In the present paper we apply the LDF in very much the same way as in our previous works on phonon energies in GaAs (see, e.g., Ref. 7). In particular the Fourier expansions of all quantities include plane waves with kinetic energy up to $E_2=9.15$ Ry; only those with $E_1\leq2.55$ Ry are treated exactly, while the remaining

 

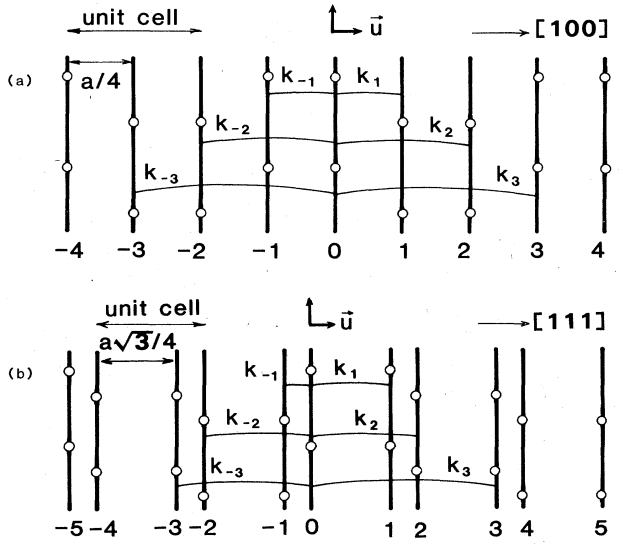


FIG. 1. Linear chains representing the vibrations in Ge propagating in the [100] and [111] directions. The origin (plane 0) and positive sense of the [100],[111] directions are chosen as defined in Fig. 2. The interplanar force constants $k_n$ connecting the planes determine the phonon dispersion $\omega(\mathbf{k})$ along the propagation direction perpendicular to the planes. The relation $k_n = k_{-n}$ holds for even $n$ (and with longitudinal [100] forces for any $n$).

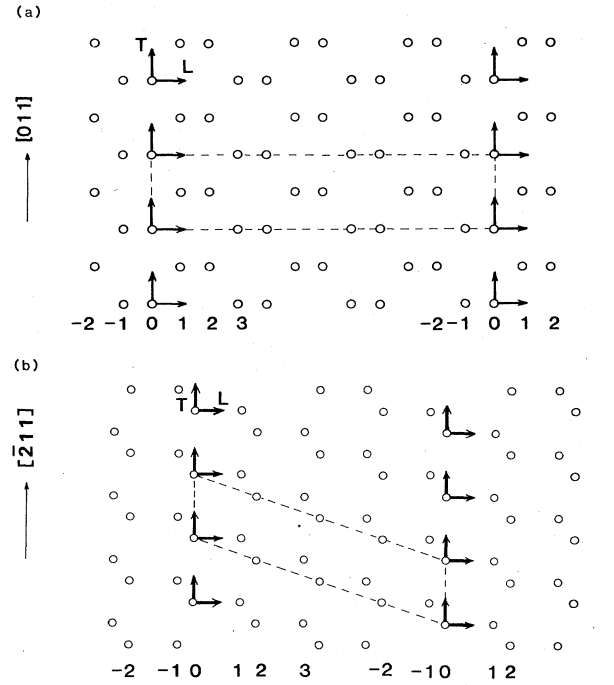


FIG. 2. Supercells and displacement patterns used for the calculation of planar force constants connecting the atomic planes of Ge shown in Fig. 1. The origin of coordinates is chosen so that the atom (0,0,0) is in the plane 0; positive directions [100] and [111] are such that the atom at $(a/4)(1,1,1)$ is in the plane $+1$, atoms $(a/4)(-1,1,-1)$ and $(a/4)(-1,-1,1)$ in the plane $-1$.

ones are dealt with by Löwdin perturbation theory.

In order to conserve the freedom of dealing with supercells of medium and large sizes, we are using a *local* pseudopotential[9] for Ge (together with the Slater $X\alpha$ exchange[10])—even if this choice implies giving up part of the rigor and accepting large numerical uncertainties; it turns out that in the final results it is essentially only the TA modes that are affected. Unlike in Ref. 1, we choose for Ge an *average* of pseudopotentials for Ga and As, which were defined in Ref. 11 and used in our previous works.[12,13] The main advantage of this choice (over the Ge pseudopotential from Ref. 11 used in Ref. 1) is that the predicted equilibrium lattice constant is close to the experiment ($-1.6\%$ error)[14]—a quality which is crucial for all lattice-dynamical calculations; the convergence properties with number of plane waves are expected to be similar to those of GaAs.

In order to evaluate the force constants we choose periodic supercells likes those in Fig. 2, which repeat the elementary unit cell $m$ times along the direction of propagation; entire planes of atoms are then given a small (longitudinal or transverse) displacement $\mathbf{u}$ and, after the self-consistent charge densities are found within the LDF framework, the Hellmann-Feynman theorem provides us with forces acting on all atoms in the supercell. The interplanar force constant $k_n$ is then defined as the negative of the force acting on the atom in the plane $n$ per unit displacement of the plane 0:

$$-F(n) = k_n u_0 \ , \tag{1a}$$

or, in analogy with the more conventional notation,[15]

$$-F(l,\kappa) = K(l,\kappa;l',\kappa')u(l',\kappa') \ ; \tag{1b}$$

different sets of force constants are obtained for longitudinal and transverse vibrations, as well as for different propagation directions. The origin of coordinates is chosen so that the atom at (0,0,0) is in the plane 0; positive directions [100] or [111] are such that the atom $(a/4)(111)$ is in the plane $+1$, atoms $(a/4)(-1,1,-1)$ and $(a/4)(-1,-1,1)$ in the plane $-1$. The symmetry of the structure implies that $k_n = k_{-n}$ only for *even* $n$; for longitudinal vibrations in [100], however, $k_n = k_{-n}$ holds for any $n$.

Present calculations were performed on supercells with $m = 4$ to 8 (quadrupled to octupled) and with displacements $|\mathbf{u}|$ ranging from $0.01a$ to $0.02a$. The results from different supercells are consistent within $\lesssim 0.004 \times 10^5$ dyn/cm, and the force constants summarized in Table I are those obtained on the smallest of the supercells tried (which we expect to limit the roundoff errors and thus to be more reliable); they will be discussed later. Writing down the equations of motion for the linear chains shown schematically in Fig. 1 leads to $2 \times 2$ secular equations, which have as solutions the phonon dispersion shown in Fig. 3; before reaching this point, however, two problems require an adequate treatment: *anharmonicity* and *spatial extent of forces*. They are the topics of the next two sections.

## III. ANHARMONICITY

A characteristic feature inherent to all "direct" approaches to lattice dynamics is that the harmonic terms

TABLE I. Interplanar force constants $k_n$ defined by Eq. (1) as obtained from the *ab initio* self-consistent calculations; the anharmonic contributions of the lowest order are eliminated. The transverse [100] force constants were determined on a $6\times Ge_2$ supercell, all other on $4\times Ge_2$; the last decimal is not guaranteed. The values in parentheses were not used in calculation of the phonon dispersion in Fig. 3. All force constants in $10^5$ dyn/cm.

| | [100] | | [111] | |
|---|---|---|---|---|
| $n$ | Longitudinal | Transverse | Longitudinal | Transverse |
| 0 | +2.248 | +1.806 | +2.161 | +1.931 |
| +1 | −1.050 | −1.695 | −1.142 | −0.101 |
| −1 | −1.050 | −0.203 | −0.900 | −1.899 |
| ±2 | −0.083 | +0.086 | −0.054 | +0.048 |
| +3 | (−0.006) | −0.035 | −0.020 | −0.044 |
| −3 | (−0.006) | −0.094 | −0.029 | −0.024 |
| ±4 | (+0.014) | +0.029 | (+0.020) | (+0.021) |
| +5 | | −0.007 | | |
| −5 | | −0.023 | | |
| ±6 | | (+0.015) | | |

appear intertwined with the anharmonic contributions: As the response to *finite* displacements **u** is computed, care has to be taken to correctly isolate the harmonic part. It has either to be verified that the **u** in question is small enough to give rise to any noticeable anharmonic effects or to be ascertained that the anharmonic contribution is properly eliminated; this can readily be done by repeating all procedures with several magnitudes of the displacement. The entire process may thus become somewhat heavy—but it is shown below how symmetry considerations can be used. Unless the study of anharmonic terms is a goal for itself, one usually finds that only the lowest order of anharmonicity, if any, is numerically important: cubic or quartic, according to the symmetry of the mode.[17]

Anharmonic contributions to the vibrational energies of semiconductors have already been studied *ab initio* in Refs. 8 and 18, within the frozen-phonon approach. In the present force-constant method the anharmonicity can show up in two different ways: (1) The relation between the force and displacement may not be exactly linear as given in Eq. (1); (2) the force may not have exactly the same direction as the displacement.

The first case, which was expected from analogy with frozen-phonon calculations,[7,8] requires working with different values of $|\mathbf{u}|$, so that the linear part of the varia-

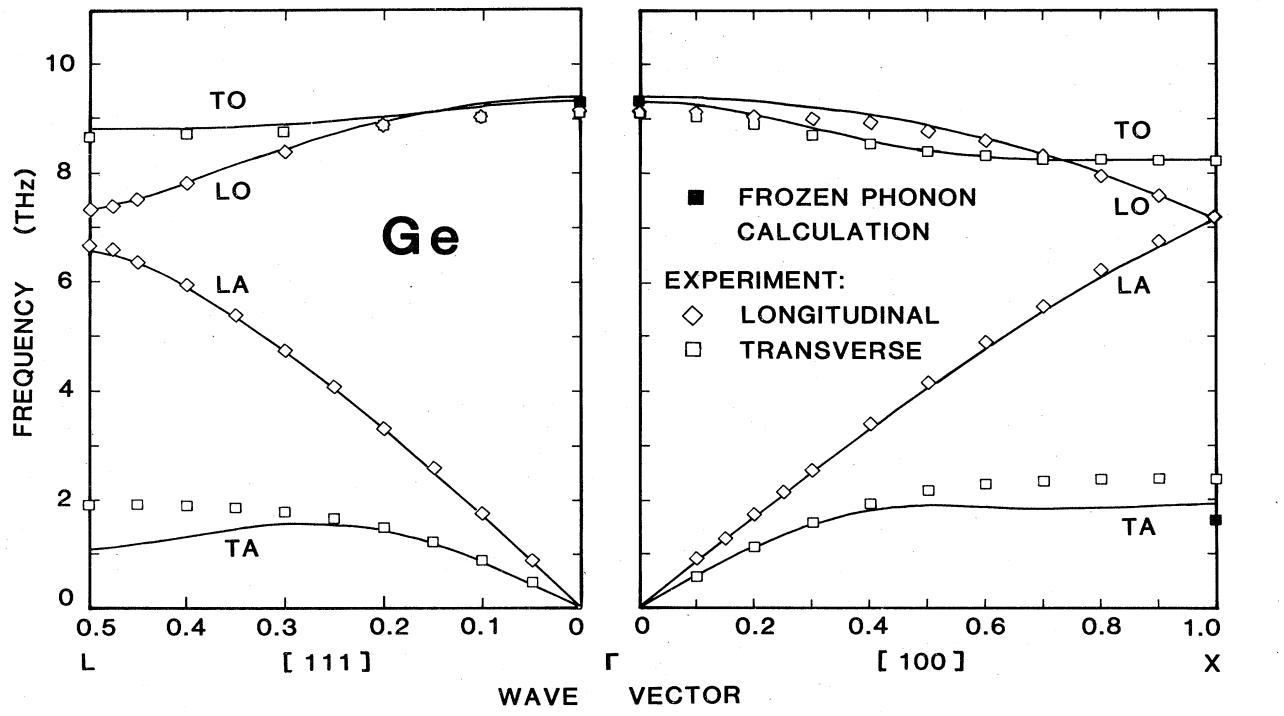


FIG. 3. Phonon dispersion $\omega(\mathbf{k})$ in germanium calculated from the planar force constants determined *ab initio* and summarized in Table I. Experimental points from Ref. 16. The $\Gamma$—$X$ part of this figure has already been shown in Ref. 12.

tion can be extracted. In the second case, one only retains the projection of **F** onto the direction of **u** before writing Eq. (1) or before checking its linearity. Here the anharmonic terms emerge to remind us of the limited validity of the one-dimensional representations: The symmetry-suggested decoupling into longitudinal and transverse modes is only exact within the limits of the harmonic approximation.

Among the modes studied here, the longitudinal [100] vibrations belong to the first category: We find $F_y=F_z=0$ at all atomic sites $\kappa$, but a perceptible cubic anharmonicity makes $F_x(u_x)$ deviate from linearity

$$-F=ku+lu^2+\cdots . \tag{2}$$

In the general case, the contribution $lu^2$ would be eliminated by repeating calculations twice, with $u_x=+u$ and $u_x=-u$ and by averaging the two results for $F_x/u_x$. In the longitudinal [100] geometry, however, the symmetry simplifies the task by imposing not only the equality $k_{+n}=k_{-n}$ for the harmonic part at *any* $n$, but also by making the force at the site $\kappa=-n$, $|\mathbf{F}(\kappa=-n)|$ computed with the displacement $+u$ equal to $|\mathbf{F}(\kappa=+n)|$ obtained with $-u$; consequently, only one calculation with a single $u$ is sufficient and the harmonic $k_n$ is obtained by *averaging* "$k_n$" and "$k_{-n}$" evaluated naively as $F/u$.

In a calculation with $|\mathbf{u}|=0.01a$ we have obtained the force constants the harmonic part of which is given in Table I; the anharmonic contributions $|\text{"}k_{+1}\text{"}-\text{"}k_{-1}\text{"}|/2$ and $|\text{"}k_2\text{"}-\text{"}k_{-2}\text{"}|/2$ are, at this displacement, respectively, $\approx 3\%$ of $k_1$ and $\leq 2\%$ of $k_{\pm 2}$.

The *transverse* [100] vibrations illustrate the other manifestation of anharmonicity. The displacement $\mathbf{u}=(0,\alpha,\alpha)$ produces forces with components $F_y,F_z$ equal, but with a small nonzero component $F_x$ orienting **F** slightly *off* the direction **u**: for $\mathbf{u}=0.007a(0,1,1)$—the value used in our calculations—this "longitudinal" component of **F** is roughly 10% of the transverse one at the first-neighbor sites, 3.5% at second-neighbor ones. We found that this contribution is a consequence of cubic anharmonicity and it is readily eliminated by projecting **F** onto **u**—which, in this case, simply means not considering the $F_x$ component. After this "projection" is accomplished, there is no cubic anharmonicity left because, as one finds from symmetry, every $k_n$ evaluated as above is exactly the same, whether determined with trial displacement $+u$ or $-u$. We also took care to verify[1] that the contribution of the quartic anharmonicity to $k_n$ is numerically negligible: By repeating the same calculations (on a smaller supercell) with $|\mathbf{u}|=0.01a$ and $0.005a$, the largest variation in $k_n$ found was $-0.005\times 10^5$ dyn/cm in $k_{+1}$; it could not be distinguished from the background noise of the calculation.

The anharmonicity turns out to be markedly stronger in the [111] direction, and not even approximate results could be expected from a single calculation, with only one value of the displacement. In order to determine longitudinal [111] force constants, two calculations with displacements $\mathbf{u}=\pm 0.006a(1,1,1)$ were performed on supercell shown in Fig. 2(b); a simplification of the kind used with the longitudinal [100] configuration is not possible here. The resulting forces are all parallel with the direction [111], but rather different for the $+$ and $-$ displacements: With the above $|\mathbf{u}|$, the cubic term $lu^2$ in (2) represents 14% of the harmonic one for $k_{+1}$, 3% for $k_{-1}$: like in the TO($\Gamma$) frozen phonon, not the same energy is required for stretching as for compressing the bonds (see Fig. 7 in Ref. 7). Averaging the two results obtained with $+\mathbf{u}$ and $-\mathbf{u}$ eliminates the cubic anharmonicity and yields the force constants given in Table I; they can, at worst, contain some quartic contributions, which the analogy with the TO($\Gamma$) frozen phonon (Fig. 8 in Ref. 7) suggests to be small.

The most complicated anharmonic terms are found in the transverse [111] configuration, where both "forms" mentioned at the beginning of this section appear at the same time: Forces are not parallel to the displacement, and their variation is not linear. Two calculations were first performed with $\mathbf{u}=\pm 0.004a(1,1,-2)$, and the calculated forces were projected on the three perpendicular directions [11$\bar{2}$], [111], and [$\bar{1}$10]. Whereas all projections on [$\bar{1}$10] are zero, the longitudinal [111] component of the force at the first-neighbor site ($\kappa=+1$) is, with the above $|\mathbf{u}|$, as much as 46% of the transverse [11$\bar{2}$] one; at the sites $\kappa=-1,\pm 2$, the nonparallel components are still, respectively, 13% and 20% of the parallel ones. For obtaining the harmonic force constants, only the "parallel" [11$\bar{2}$] projection of the force was retained, and (in contrast to the transverse [100] case) a noticeable anharmonic behavior was still found: $k_n$ determined with displacements $+u$ and $-u$ were averaged, in order to eliminate the cubic contributions, because they still differed considerably—for $k_{-1}$ the cubic term $lu^2$ in (2) represents 7% of the harmonic one.

As the behavior of the nonparallel [111] projection at $\kappa=-1$ suggested that not only the cubic but also a nonvanishing quartic anharmonicity is present, two more calculations with displacements twice as large, $\mathbf{u}=\pm 0.008a(1,1,-2)$ were accomplished. Processed as above, the forces provided $k_n$ which differed very little from the previous set: $-0.010$ and $-0.006$ variation in $k_{-1}$ and $k_{+1}$, and less than the error margins for all other $k_n$. Although a presence of quartic potential is clearly demonstrated, it is sufficiently weak to be neglected in our present applications, and no further effort was made to isolate it. The harmonic force constants given in Table I are those found with the smaller displacements $\mathbf{u}=\pm 0.004a(1,1,-2)$.

The force constants summarized in Table I represent the harmonic terms of Eqs. (1) or (2). It is clear that the anharmonic contributions, whose presence has been in this study an unpleasant perturbation to be eliminated, carry in themselves a considerable amount of valuable information, which still remains to be explored.

## IV. CONVERGENCE IN REAL SPACE

The first question one naturally asks when addressing lattice dynamics of any solid, by any method, is that of the actual range of forces: How far do the forces extend? The answer is getting a new meaning in the context of *ab initio* calculation of these quantities. In contrast to the

phenomenological model treatments where the range of forces is limited "technically" by the number of parameters which the numerical fitting procedures can handle and by the volume of experimental information that is available or that one wishes to incorporate into the model, the *ab initio* methods allow one, at least in principle, to determine forces acting on arbitrarily distant neighbors. However, as the size of the computations increases very quickly with the size of the supercells used—i.e., with the range of interactions sought—the unrestricted amount of accessible first-hand information is still limited by the computational effort one is ready to invest. Thus, awareness of the spatial extent of interactions helps one to choose the supercells which are, for a given purpose, no larger than necessary; it allows one to judge whether a calculation in question is at all feasible.

The main problem of this section is the question beyond which point the additional information gained is not worth the increased effort or cost. It is clear that it would be pointless, for example, to look for forces that are smaller than the numerical uncertainty of the calculations; it is not necessary to deal with supercells which are much larger than the minimum required by the range of interactions. On the other hand, even if the sets of meaningful force constants are obtained, the convergence properties of one physical quantity or another may be such that the last terms contribute only slightly to the quantity in question and are thus beyond practical interest.

Unlike most LDF calculations, the convergence of force series examined in this section is *not* convergence with the number of plane waves, but that with the extent of forces in real space; as for the other type of convergence, we rely on tests performed in the context of our previous works.[7,8]

The notion *convergence* expresses mathematically what we intuitively feel as "range of forces," because, strictly speaking, the spatial extent of forces is infinite. Thus, rather than asking "how far do the forces extend," a more rigorous formulation of the question is "what error do we incur by neglecting forces beyond the $n$th neighboring plane?" As the answer obviously depends on the quantities studied, we concentrate on phonon frequencies, elastic constants, and few related quantities, briefly, on phonon dispersion.

Let us note that phenomenological models of lattice dynamics can shed very little light on the issue, because they start by assuming some range of forces and end by skillfully, often successfully, *minimizing* the disagreements with the experiment. An excellent fit of experimental data thus *cannot* be considered as the ultimate justification of any force-constants set; at best the *relative* physical realism of different models can be judged on this basis.

Comparing the results obtained on supercells of different sizes, we found in Sec. II that differences in the force constants can be as large as $0.004\times10^5$ dyn/cm; this is the estimated numerical precision of our method. It concerns namely the small forces, and it suggests that at the present stage all calculated $k_n \leq 0.004$ have to be viewed as effective *absences* of interaction; consequently, the last figure given in Table I is not guaranteed.

A good estimate for the "significant" range of forces is provided by the self-consistent electronic charge density $n(\mathbf{r})$, viz. by modification of its distribution due to the displacement of one atomic plane. This is shown in Fig. 4 for a longitudinal [100] displacement in Ge; so as to retain only that part of the information that is relevant to $k_n$, the picture was made one-dimensional by averaging the $\Delta n(\mathbf{r})$ over the remaining two coordinates $y,z$. The perturbation in charge density produced by the displacement is strong at the first neighbor plane, weak at the second, and negligible at the third. This agrees with the values of the forces found *ab initio* and given in Table I. $k_3$ is of the same order as the error margin and the roundoff errors made $|k_4| > |k_3|$; thus, only $k_1$ and $k_2$ are to be considered as meaningful interactions.

The longitudinal [100] dispersion $\omega(\mathbf{k})$ shown in Fig. 3 was calculated with $k_1$ and $k_2$ only; the inclusion of $k_3$ does not produce any "visible" modification of $\omega(\mathbf{k})$, but neglect of $k_2$ does: the frequency of the LOA($X$) mode falls by 8%. The role of distant forces is even better judged on the elastic constants which determine the slope at the origin, because the force constants enter the expression for $c_{ij}$ as $n^2k_n$. The values of $c_{11}$ calculated with cutoffs after first, second, and third neighbors are, respectively, 9.28, 12.21, and 12.67 (the experiment:[19] $13.11\times10^{11}$ dyn cm$^{-2}$); apparently, $k_3$ still can alter the $c_{11}$ by 4%, which provides an estimate for error margins of the calculated $c_{ij}$. We conclude that the longitudinal [100] forces extend to second neighbors; presence of the third ones is uncertain and their role negligible.

Much more interesting is the spatial extent of the [100] *transverse* forces, and interactions up to the *fifth* neighbors were included for calculation of the phonon dispersion in Fig. 3. The choice of $n=5$ deserves some attention.

The most sensitive part of the transverse dispersion is the TA branch. A fairly steep slope at the origin (elastic constant $c_{44}$) becomes a *flat* dispersion near the Brillouin-zone edge, behavior which is characteristic for covalent bonding. In Fig. 5(a) the calculated frequency $\nu$(TA($X$)) is plotted versus the range of forces $n$. The frequency of the mode is given in terms of the transverse force constants as

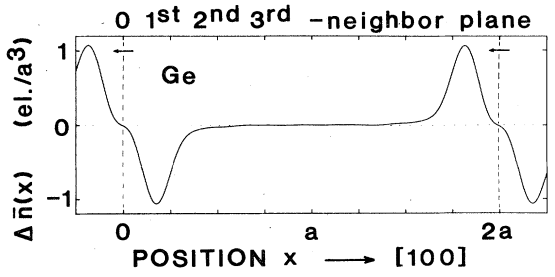


FIG. 4. Modification in electronic charge density $n(\mathbf{r})$ of Ge caused by a longitudinal displacement $u=-0.01a$. (In electrons/$a^3$; the $\Delta n(\mathbf{r})$ was averaged over $y$ and $z$ in planes perpendicular to [100].)

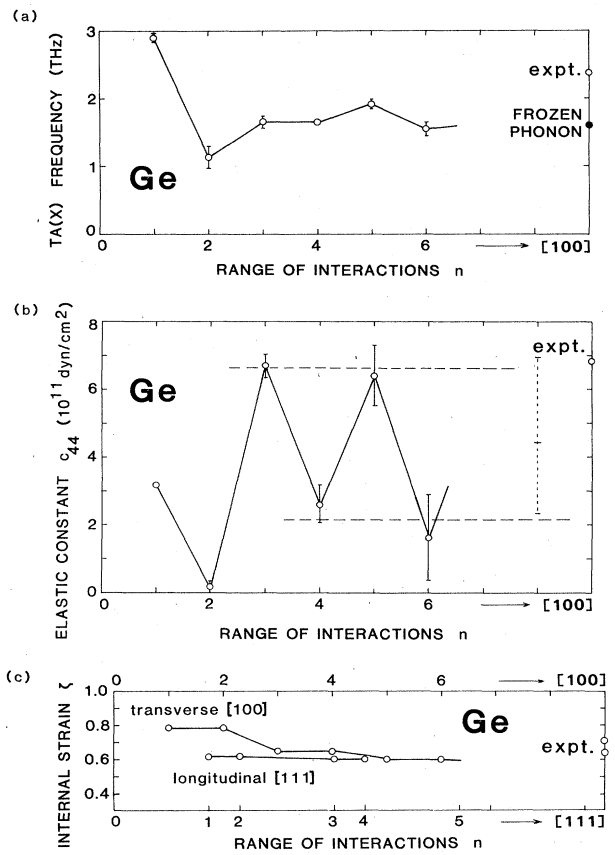


FIG. 5. Convergence with spatial extent of forces in Ge: different quantities are evaluated, with forces included up to the $n$th neighbor plane. Error bars at $n$ correspond to $\pm 0.004 \times 10^5$ dyn/cm in $k_n$ and $k_{-n}$. (a) The TA($X$) frequency given by Eq. (3). The $n \to \infty$ limit of the force-constant method is the frozen-phonon result. The experimental value from Ref. 16. (b) The elastic constant $c_{44}(n)$ evaluated from the transverse [100] forces through Eq. (4). The reason for the "zig-zag" convergence is that the expression for $c_{44}$ in terms of force constants is an alternating series. Experimental value from Ref. 19. (c) The internal strain parameter $\zeta$ calculated from transverse [100] and longitudinal [111] force constants using Eqs. (5) and (6). (Error bars are smaller than the circles.) Experimental values form Refs. 20 and 21.

$$M\omega^2(\mathrm{TA}(X)) = -2(k_{-1} + 2k_2 + k_{+3} + k_{-5} + 2k_6 + k_{+7} + k_{-9} + \cdots), \quad (3)$$

and the values of frequency in Fig. 5(a) represent partial sums of the series (3), from $k_{-1}$ through $k_{\pm n}$. The mathematically rigorous limit of (3) for $n \to \infty$ is known: It is the calculated frequency of the *frozen phonon,* which is shown in Fig. 5(a) by a black dot. This alternative approach, proceeding via energies, includes *all* force interactions up to infinite neighbors within the same physical approximations.

Inspection of Fig. 5(a) suggests that the limiting value is already attained at $n = 3$ although as many as 6 to 7 neighbor forces may be needed to "stabilize its evolution," i.e., in order to achieve convergence. Note that fourth- and eighth-neighbor forces do not contribute at all to vibrations at the Brillouin-zone edge.

In Figs. 6(a) and 6(b) we have plotted, with different cutoffs $n$, the entire sensitive branch TA($\Delta$), results corresponding to *even* and *odd* $n$ are plotted separately. At first sight all "partial sums" with even $n$ have to be eliminated; the dispersions with odd $n$ shown in Fig. 6(a) then allow us to choose between $n = 3$, 5, and 7, values which Fig. 5(a) left us with. Judged merely by a sum of least squares, the $n = 3$ and $n = 5$ curves match experiment to about the same degree. Nevertheless the curve with $n = 3$ misses an important physical feature: the characteristic *flatness* of the TA branch. The value $n = 5$ is thus the smallest $n$ reproducing this flatness adequately. Including an even more distant force ($k_{\pm 7}$) appears desirable in order to remove a small, barely visible bow on the flat part of the $n = 5$ dispersion. Unfortunately, the values we found on the octupled supercell are less reliable and $k_{\pm 7}$ turns out to be of the same order as the present precision of the method. We choose therefore $n = 5$ as an acceptable compromise and conclude that transverse forces extend *at least* to the fifth-neighbor plane. Limiting the expansion to $n = 3$ might, nevertheless, be justified in complex situations, if only *rough estimates* of the transverse dispersion were acceptable.

A possibly unexpected feature of Fig. 6 is that including *one* more interaction does not necessarily improve the result: *two* have to be added. This is a remarkable property of the slope at point $\Gamma$, the origin of which can be traced back to the nature of transverse forces in covalent crystals.

The elastic constant $c_{44}$, giving the slope of the TA($\Delta$) branch, is given,[22] in terms of interplanar force constants, as

$$4ac_{44} = -\sum_{n=-\infty}^{+\infty} n^2 k_n + \left[\sum_{\text{odd}n} n k_n\right]^{+2} \left[\sum_{\text{odd}n} k_n\right]^{-1} \quad (4a)$$

$$= -\sum_{n=-\infty}^{+\infty} n^2 k_n + \zeta^2 \sum_{\text{odd}n} k_n , \quad (4b)$$

where

$$\zeta = \left[\sum_{\text{odd}n} n k_n\right] \left[\sum_{\text{odd}n} k_n\right]^{-1} \quad (5)$$

is the internal strain parameter. All the summations are infinite, and for finite cutoffs $n$ the expression (4) is evaluated in Fig. 5(b); the error bars correspond to an uncertainty of 0.004 in $k_n$. The conspicuous zig-zag behavior of $c_{44}(n)$ is not surprising once we notice (see Table I) that expression (4) is an alternating series.

The physical meaning of the alternation of signs of $k_n$ will be discussed in Sec. V. In the meantime we notice that $c_{44}(n)$ with *odd* $n$'s, $n > 1$, seems to converge to a different value than the series with $n$ even. This behavior should not be surprising: As there is no evidence that Eq. (4) converges *absolutely,* we recall a well-known property of alternating series, viz., that their convergence can be accelerated by an appropriate grouping of the terms. Despite the increasingly large roundoff errors in the partial sums, Fig. 5(b) merely suggests that the rate of con-

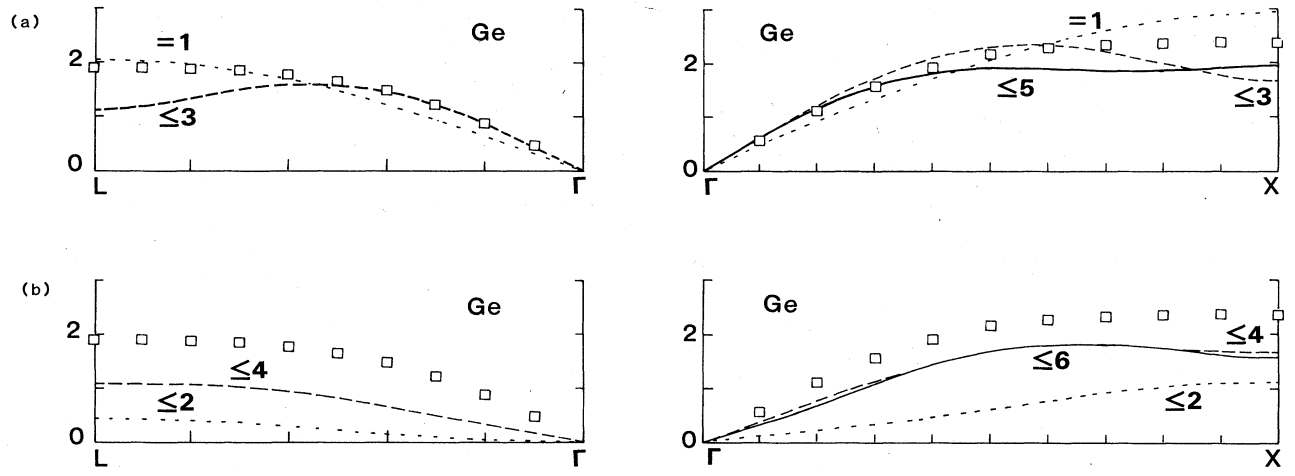


FIG. 6. Convergence with spatial extent of forces in Ge: dispersion $\omega(\mathbf{k})$ of the most sensitive branches TA($\Lambda$) and TA($\Delta$) is calculated from the planar force constants given in Tab. I. (a) Odd-$n$ cutoffs; (b) Even-$n$ cutoffs.

vergence for the upper dotted line is more favorable than for the lower one. It is understood that for large $n$ both of them should reach the same limit.

The optimal "grouping" of terms in the series (4), which is suggested by Fig. 5(b), is thus in pairs, and with the cutoff after an *odd*-neighbor interaction. A clear physical meaning of this rule is not obvious, but it is reminiscent of assembling terms in the expression for Madelung energy in the way that makes them correspond to electrically neutral shells.

Behavior of $c_{44}(n)$ does not bring any new light upon the question of the range of forces: For both $n=3$ and $n=5$, the $c_{44}$ has about the same value; the $n^2$ weighting which, obviously, concerns the error bars, too, makes it meaningless to speculate what $c_{44}$ might be with $k_{\pm 7}$ included. We notice by the way that, in absence of any "frozen shear" calculation for $c_{44}$, the reasoning above is based on physical rather than purely mathematical grounds, viz., on the assumption that the $n \to \infty$ limit of (4) will be close to the experimental value $c_{44}$.

In the [111] direction, the behavior of the longitudinal [111] dispersion was found similar to the longitudinal [100] one, except that forces at third and fourth neighbors are still sizeable. The $\omega(\mathbf{k})$ shown in Fig. 3 was calculated with $k_{\pm 1}$ through $k_{\pm 3}$; neglect of $k_{\pm 3}$ makes the LA($L$) frequency drop by as little as 1%, but the value of $c_{11}+2c_{12}+4c_{44}$, controlling the slope at the origin, decreases by 16% if only $k_{\pm 1}$ and $k_{\pm 2}$ are employed and even with the cutoff after third neighbors, this quantity is not yet completely converged, despite a reasonable agreement with experiment.[23]

Finally the transverse [111] dispersion is similar in all respects to the transverse [100], and the $\Gamma$—$L$ part of Fig. 6 indicates that also the same rule for optimizing the convergence will apply here: Cutoffs after *odd*-neighbor interactions are to be preferred. The conclusion that third-neighbor forces are not sufficient to describe adequately the flat TA dispersion applies in [111] direction as well. As the most sensitive part of Fig. 6, the slope at the origin, visualizes the value of $c_{11}-c_{12}+c_{44}$, it is, again, the shear elastic constant that is to be questioned. The dispersion shown in Fig. 3 was calculated with forces up to the third neighbors included; the sensitive TA branch is still far from being flat and it points out that also in the [111] direction the transverse forces extend *beyond* the third-neighbor plane. Further calculations on larger supercells are needed.

The conclusion reached in this section, viz. that the transverse forces extend *at least* over a distance $\approx 1.6a$ (to the fifth-neighbor plane) is in itself not shocking, nevertheless, it brings a certain surprise, because several valence-force-field (VFF) models have demonstrated that excellent phonon dispersion in Ge, including the flat TA branches, can be obtained with forces extending to the *third*-neighbor [100] plane only, while neglecting all more distant interactions.[24,25] Also the result of Herman[26]—that at least the fifth-neighbor inter*atomic* force constants are needed—is consistent, despite first impressions, with other phenomenological models: If we denote by $\{\Phi(n)\}$ the set of interatomic force constants between atom 0 and the shell of its $n$th neighbors, then the [100] interplanar $k_{\pm 3}$ can be written as a linear combination of $\{\Phi(3)\}$, $\{\Phi(5)\}$, $\{\Phi(7)\}, \ldots,$ and is, according to Herman, "needed;" on the other hand, it follows from geometry that $k_{\pm 5}$ is only composed of $\{\Phi(7)\}$, $\{\Phi(9)\}, \ldots,$ and is thus zero when all $\Phi(n)$, $n>5$ are zero.

Different approaches give clear but different answers to a question as simple as "how far?" We note that phenomenological results generally do not carry much weight if any disagreement with *ab initio* results occurs. The *assumption* at the spatial extent of forces, which every model treatment starts with, is not necessarily confirmed or disproved when the good agreement with experiment is limited to $\omega(\mathbf{k})$ *only*. A recent experience[7,8] has taught us that, for example, models fitted to phonon dispersion, and matching the experimental values of frequencies excellently can be completely unreliable in predicting quantities other than the information fed in. The force constants (and, *a fortiori*, their range) are certainly such data, and any set of fitted parameters should

thus be taken with reservation, as to its physical meaning. On the other hand, since present calculations use a rather low-quality pseudopotential, some reservation is not out of place here either.[27] Although our calculations support the conclusion $n \geq 5$ unambiguously, an error bar $\pm 2$ cannot be presently made smaller; it would be decreased, at best, by more exact *ab initio* calculations in the future. Nevertheless, a limited number of checks on the available data can be proposed at this stage already. Predicted eigenvector dispersion along $\Gamma-X$ or $\Gamma-L$ would *not* be, in the case of Ge, a sufficiently sensitive test for comparison of different representations;[28] a testing ground might be found, however, in comparing different predictions for the $\Gamma-K$ and namely $K-W$ directions. Also, it would be interesting to see a deconvolution of the bond-charge model[29]—the most realistic among all phenomenological descriptions of Ge—before any new and more precise *ab initio* determinations are performed.

To close this section, we have also plotted in Fig. 5(c) the convergence of the internal strain parameter $\zeta$ which, in terms of transverse [100] force constants, is given by Eq. (5) and, in terms of the longitudinal [111] ones as

$$\zeta=\frac{1}{2}+\left[\sum_{\text{odd}n} nk_n\right]\left[\sum_{\text{odd}n} k_n\right]^{-1} \tag{6}$$

(see Ref. 22). The pseudopotentials used in this work are probably too simple to conclude anything more than their convergence ($\zeta=0.786,0.649,0.600$ for $n=1,3,5$ in [100] and $\zeta=0.619$ and 0.603 for $n=1,3$ in [111]). Our calculated value $\zeta=0.601\pm0.002$ is somewhat smaller than the experiment[20] $\zeta=0.640\pm0.004$, but compares not as well with the older ones[21] $\zeta=0.71$. It seems to confirm the general trend emerging recently:[30] All values of $\zeta$ calculated *ab initio* by different methods[22,30,31] and on different materials lead systematically to a lower value than experiment, sometimes by as much as 20%.

## V. VIBRATIONS AND FORCES

The interplanar force constants defined by Eq. (1) and determined *ab initio* are summarized in Table I. As explained in Sec. III care was taken to remove from them the anharmonicity of the lowest order allowed by symmetry; the values quoted in parentheses were not used for calculation of phonon dispersion. Translational invariance of the supercell implies that the restoring force $-k_0$ on the displaced plane 0 is given by

$$-k_0=\sum_{n\,(\neq 0)} k_n\ , \tag{7}$$

which allows one to check error margins and internal consistency of each column in Table I: the discrepancies are, respectively, $+0.002\times10^5$, $-0.013\times10^5$, $-0.002\times10^5$, and $-0.001\times10^5$ dyn/cm. On the other hand, the sum

$$S\equiv\sum_{\text{odd}n} k_n \tag{8}$$

is required to be invariant for all four columns given in Table I—because it is proportional to the degenerate LTO($\Gamma$) frequency (squared)—independent in Ge of both propagation and polarization directions. Our values of $S$, respectively $-2.112$, $-2.057$, $-2.091$, and $-2.068$ (2.7% spread), allow one to judge the *overall consistency* of the numerical procedures. Furthermore, the value of $\zeta$ displayed in Fig. 5(c) shows that calculations using two different supercell geometries lead to the same result within 0.5%.

The complete eigensolutions, $\omega(\mathbf{k})$ and the normalized eigenvectors $w(\mathbf{k})$, are shown in Figs. 3 and 7. Internal consistency of the calculations [appearing already through the invariance of the expression (8)] is verified by the fact that four sets of force parameters, which were provided by four independent and completely different calculations, give the LO and TO branches converging to the *same*

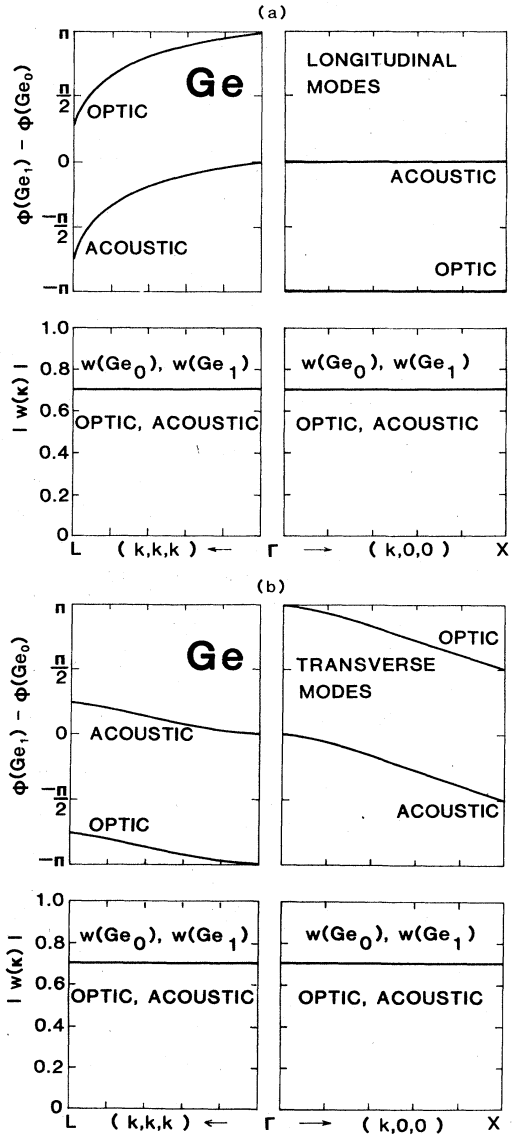


FIG. 7. Dispersion of amplitudes of eigenmodes in Ge. The complex quantities are translated into real amplitudes $|w(\kappa)|$ and phase factors $\phi(\kappa)$; the actual displacements of a plane $(l,\kappa)$ in a mode $(\mathbf{k},j)$ are given by Eq. (9). $\phi(\mathrm{Ge}_1)$ and $\phi(\mathrm{Ge}_0)$ are the $\phi(\kappa)$ of the two basis planes in Eq. (9); the numbering $\mathrm{Ge}_1$ and $\mathrm{Ge}_0$ refers to numbering of planes in Figs. 1 and 2.

LTO(Γ) frequency degenerate to within 1.3%. Also, the energy of the TO(Γ) mode agrees with our prediction using the frozen-phonon approach (i.e., proceeding via total energies) to within 0.3%, which illustrates the physical equivalence of both approaches. There is in general a very good agreement with experiment, except in the transverse acoustic branch [0.48 THz at point $X$ (−19%), and 0.80 THz at point $L$ (−42%)] which is due to the low quality of the ionic potentials used (local pseudopotentials) and, possibly, to the Slater $X\alpha$ form for the exchange; at the $L$ point, part of the problem comes from the insufficient range of forces considered. The same difficulty, and roughly the same disagreement, has already been encountered in GaAs, both in the frozen-phonon context[8] and in the force-constant approach;[2] of course, this particular phonon is the most difficult to reproduce by *any ab initio* method, cancellations of different contributions to its energy making it particularly sensitive to all approximations and roundoff errors. Finally, the imperfect agreement between the TA($X$) frozen-phonon calculation (1.61 THz) and the endpoint of the transverse branch (1.93 THz) suggests that even the real-space convergence may not yet be achieved perfectly with forces up to the fifth neighbors included (see Sec. IV.)

Figure 7 shows the second part of the eigensolutions, the normalized (complex) eigenvectors $w(\kappa\,|\,\mathbf{k},j)$, translated into (real) amplitudes $|\,w(\kappa\,|\,\mathbf{k},j)\,|$ and phases; the actual displacement of an atom $(l\kappa)$ in the mode $(\mathbf{k}j)$ is

$$u(l,\kappa\,|\,\mathbf{k},j)=[M(\kappa)]^{-1/2}\,|\,w(\kappa\,|\,\mathbf{k},j)\,| \times\exp\{i\phi(\kappa\,|\,\mathbf{k},j)+i\mathbf{k}\cdot\mathbf{x}(l,\kappa)-i\omega t\}\ . \quad (9)$$

The form of Eq. (9) [factor $\mathbf{x}(l,\kappa)$ rather than $\mathbf{x}(l)$] reflects the choice of phase factors in the dynamical matrix: The one used in the present work corresponds to the "$C$-type" matrix [Eq. (2.1.58) of Ref. 15] and the eigenvectors $w$ in Fig. 7 are those of Eq. (2.1.60) in Ref. 15. We note that the endpoints of the eigenvector dispersion in Ge are fully determined by symmetry plus normalization conditions, but not necessarily the variation between them. Closer inspection reveals that the *form* of the variation is determined (in nontrivial cases) essentially by the first-neighbor force constants and depends little on interactions with more distant planes.

Figure 8 displays graphically the longitudinal forces (negative of the planar force constants) resulting from the displacement of a (100) plane: The "restoring force" $-k_0$, acting on the displaced plane, aims at restoring the undistorted structure; the forces at the first and further neighbors have the same orientation as the displacement, and fall off rapidly. All longitudinal forces originate from cancellation between the Coulomb forces (ion-ion interactions between the unscreened $+4\,|\,e\,|$ cores) and the electronic forces (electron-ion interactions); $k_0$ and $k_2$ have their signs determined by ion-ion interactions, while the sign of $k_{\pm1}$ is given by the electronic forces. The "right-left" symmetry ($k_n=k_{-n}$) results from the crystal symmetry of the (longitudinally distorted) structure.

Quite a different symmetry is met in the structure with a transverse [100] displacement (Fig. 9): here the bonds at the left of the displaced plane are mainly bent, while those

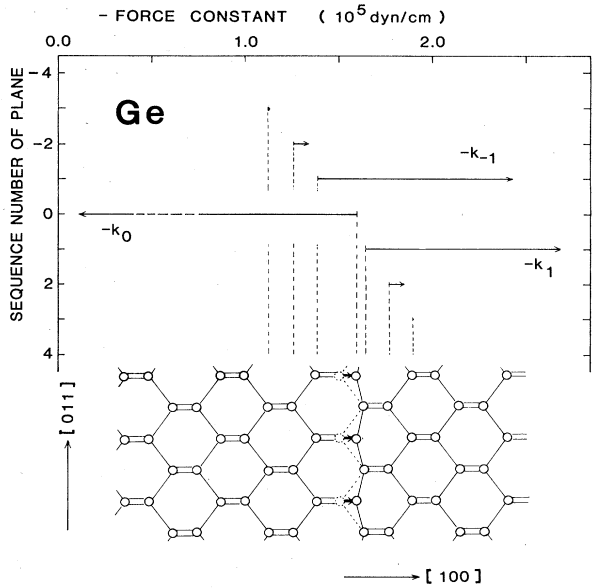


FIG. 8. Longitudinal forces in Ge for the [100] direction. The restoring force $-k_0$ is a sum of all other forces. The interactions are negligible at distances $\geq 3a/4$ (third neighbors).

at the right are mainly stretched. The lack of symmetry between bond-stretching ($k_1$) and bond-bending ($k_{-1}$) force constants is the first conspicuous feature of the planar forces for *transverse* vibrations in [100] (Fig. 9). Although in absolute value the forces fall off with distance fairly quickly, we note that $k_{-3}$ and $k_{-5}$ are still respectively 46% and 11% of $k_{-1}$; these "medium range" forces are those responsible for the flat TA($X$) branches—one of the characteristic features of covalent compounds already mentioned.

The most interesting feature of the forces in Fig. 9 is the regular alternation of their signs. This alternation, which was responsible for the peculiar convergence properties of $c_{44}$ in Sec. IV, can be explained by *angular* interactions,[32] which are another typical feature of covalent compounds (see Ref. 33). The connection can be seen more clearly if we adopt for a while the language of phenomenological theory, viz. a description in terms of Valence-Force-Field (VFF) potentials (see, e.g., Ref. 24). Figure 10 shows a chain of atoms, along the [100] direction, with each atom number $n$ in the $n$th plane (100); atom 0 is given a displacement $\mathbf{u}$, as in Fig. 9. As there is a central interaction between atoms 0 and 1, the (bond-bending or bond-stretching) force $\mathbf{F}_1$ follows the direction of $\mathbf{u}$. The force on atom 2 would equally follow the direction $\mathbf{u}$ if the 0—2 interaction were central, $E_A=\varphi(r)$. On the contrary, if it is angular—e.g., the one governed by a three-center potential $E_B=\frac{1}{2}k\theta_1^2$—the force $\mathbf{F}_2$ will have exactly the opposite sign: As $\mathbf{u}_0$ "opens" the angle $\theta_1$, it increases the potential energy $E_B$ and the force $\mathbf{F}_{2B}$ will thus tend to "close" $\theta_1$, in order to restore the equilibrium.

The *ab initio*-determined force constants in Tab. I or Fig. 9 leave no doubt as to which of the two potentials mediates the 0—2 interaction: They clearly support the idea of angular forces.

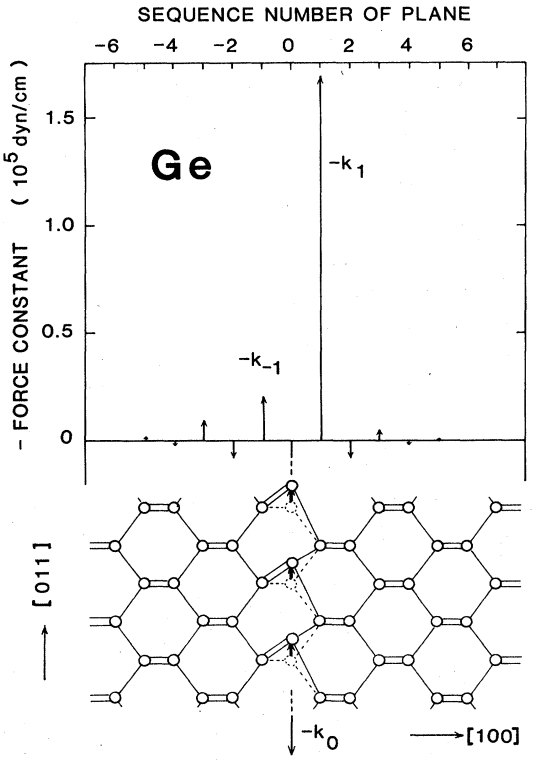


FIG. 9. Transverse forces in Ge for the [100] direction. The restoring force $-k_0$ is a sum of all other forces. The fifth-neighbor force $k_{-5}$ is still $\approx 10\%$ of the first-neighbor one $k_{-1}$; accounting for forces extending to distant neighbors is essential (see Fig. 6) for reproducing the flat TA branches of phonon dispersion. The force constant $k_{+1}$ is due essentially to bond stretching, the $k_{-1}$ to bond bending. The alternating signs of the forces reflect the presence of noncentral (angular) interactions (see Fig. 10).

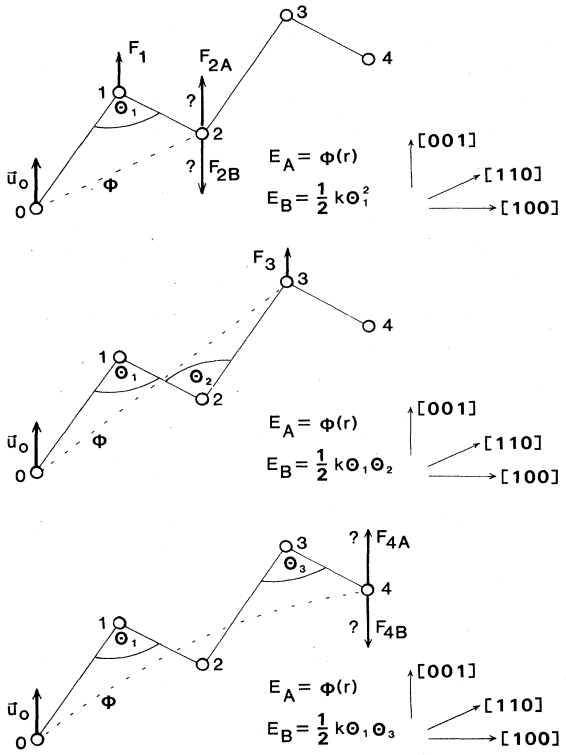


FIG. 10. Valence-force-field potentials which can explain the alternating signs of the transverse [100] forces in Fig. 9 (see text). Presence of noncentral (angular) interactions is typical of covalent materials.

The argument applies to more distant neighbors as well. For the third neighbors [Fig. 10(b)] and fifth neighbors (not shown), both central and angular mechanisms lead to the same direction of $\mathbf{F}_3$ or $\mathbf{F}_5$, a direction which agrees with that shown in Fig. 9. For the fourth neighbors, however [Fig. 10(c)], the dilemma central versus angular is, again, resolved by Table I, viz. in favor of the angular force $\mathbf{F}_{4B}$.

The above argument and the values of transverse force constants give a great deal of justification to the physical realism of the VFF descriptions of covalent crystals despite the disagreement on the actual range of interactions discussed in Sec. IV.

The transverse [111] forces show a similar behavior to the transverse [100] ones: In particular, the alternation of signs further supports the idea of angular forces; we do not plot them because the present picture, stopping at the fourth neighbors, would necessarily be incomplete (see Sec. IV).

Finally in Fig. 11 we have represented the transverse [100] forces of Fig. 9 as a sum of the ion-ion and electronic terms; in order to visualize also the barely visible distant terms, all forces are weighted by $n^2$. Two features are worth noting at Fig. 11: (1) The unscreened core-core interactions vanish beyond the fourth neighbors, and their contribution to $k_{\pm 4}$ is rather small. (2) The force $k_{+1}$ shows the "composition" typical of bond-stretching forces, $k_{-1}$ that of bond-bending ones: a strong ion-ion interaction, respectively, positive and negative, is opposed by a strong electronic contribution. Whereas in $k_{+1}$ the electrostatic interactions are only weakened (screened), they are "over-screened" in $k_{-1}$.

Configurations similar to those of bond-stretching and bond-bending forces are found in the analogous energy diagrams (Fig. 12), which similarly reconstruct the energies of the TO($\Gamma$) and TA($X$) frozen phonons. Here the ion-ion force respectively stabilizes and destabilizes[34] the crystal structure, whereas the electronic contributions provide compensation, allowing a stable structure to be achieved in both cases: The crystal's total energy increases when atoms are displaced. The force $k_{+3}$ in Fig. 11 behaves similar to $k_{-1}$, and the other ones show various intermediate compositions.

## VI. CONCLUSION

The lattice dynamics of germanium have been formulated in terms of planar force constants determined from first principles by using the local-density-functional theory. Two methodical questions of this approach have been examined: (1) dealing with anharmonicity and (2) spatial extent of forces present. We have demonstrated

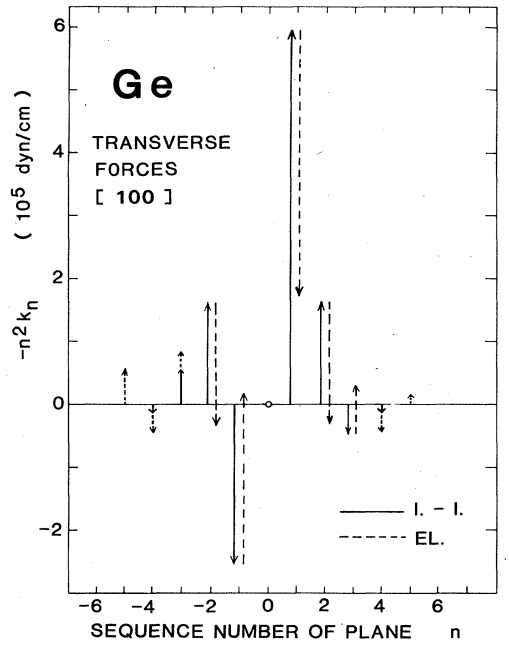


FIG. 11. Screening of ion-ion interactions in Ge by the electronic terms. The transverse [100] forces $k_n$ of Fig. 9 (weighted by $n^2$) are shown as the result of competition between the Coulomb forces (ion-ion interactions between the unscreened $+4|e|$ cores) and the "electronic" forces (electron-ion, Hartree, and exchange-correlation terms). The electrostatic contributions vanish at distances $\geq a$ (fourth neighbors), the forces at distant neighbors are then of purely electronic origin. Compare the "composition" of the bond-stretching force $k_{+1}$ and bond-bending one $k_{-1}$ with the "reconstruction" of the TO(Γ) and TA($X$) frozen phonon energies given in Fig. 12.

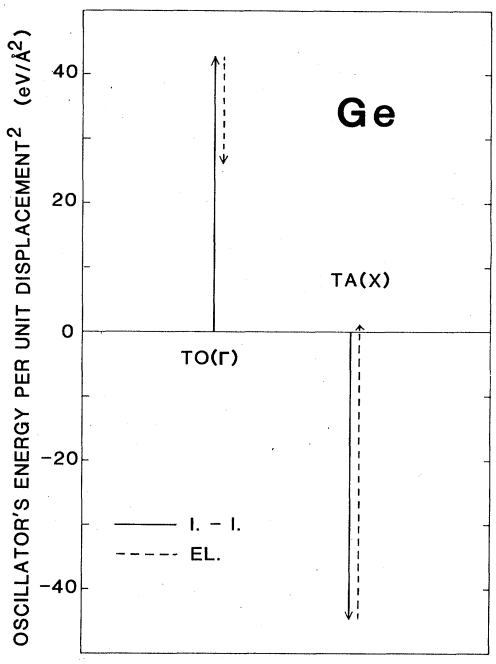


FIG. 12. Composition of the phonon energies in Ge from the ion-ion energy and "electronic" energy. [The ion-ion contribution corresponds to the energy of positive core charges in a uniform negative background ($\gamma^{\text{Ewald}}$), the electronic term is the sum of all contributions involving electrons: electron-ion energy, kinetic energy of electrons, Hartree- and exchange-correlation terms.] In TO(Γ) the ion-ion energy increases with displacement, i.e., the structure is "stabilized" by the ion-ion interactions, which are merely weakened by the electronic terms; with respect to the TA($X$) distortion, the structure is "destabilized" by the electrostatic interactions and stabilized by the electronic ones. This behavior of TA($X$) is typical of covalent crystals (cf. Ref. 34).

how the first problem is to be treated, and have found the anharmonic interactions to be the strongest in the $\mathbf{k}||[111]$ vibrations, particularly in the transverse ones. The spatial extent of interactions turns out to be fairly limited in longitudinal modes (second- to third-neighbor planes), in contrast to transverse vibrations where forces extending to the *fifth*-neighbor plane were found to be still significant, for both [111] and [100] phonons. As rather simple pseudopotentials have been employed, some uncertainty of the latter conclusion persists, however, and an error margin $\pm 2$ (neighbor planes) cannot be made smaller until determinations based on more elaborate pseudopotentials become feasible.

A surprising convergence property found for quantities controlled by transverse force constants is that accounting for one more interaction does not cause any improvement of the physical results; two have to be included. Thus, for achieving a fast convergence, the terms have to be grouped in pairs, with cutoff after an *odd*-neighbor interaction. It is shown how this behavior relates to the presence of angular forces (three- and more-center interactions), whose occurrence is characteristic of covalent substances.

Besides determining *ab initio* the complete phonon dispersion (eigenfrequencies and eigenvectors) along the [100] and [111] directions, we also studied the mechanisms building up the planar forces, which arise through screening or "over-screening" of the electrostatic core-core interactions by electronic terms, similar to the way frozen phonon energies arise from cancellation of ionic and electronic contributions.

## ACKNOWLEDGMENTS

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[10]The local potentials we are using have been conceived in Ref. 11 under the assumption of the Slater's $X\alpha$ exchange, $\alpha=0.8$. This simple form is, generally speaking, less accurate than any of the more modern expressions (Hedin-Lundqvist, Ceperley-Alder, etc); nevertheless it is important to apply the potential with exactly the same exchange as has been used for its generation. Our tests on GaAs have shown, indeed, that using the local potentials of Ref. 11 with, e.g., the Wigner's exchange, leads to lattice constant and bulk modulus, respectively, $+4\%$ and $+53\%$ off the experimental values, in contrast to $+1\%$ and $+22\%$ with the Slater's $X\alpha$.

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[14]The equilibrium lattice constant, calculated with the same cutoffs and using the Murnaghan equation of state, turns out to be $a=5.57$ Å ($-1.6\%$ error), bulk modulus $B=0.977$ Mbar ($+29\%$ error), (its pressure derivative $B'=4.17$), direct band gap 0.5 eV ($-50\%$ error), indirect $\Gamma$-$L$ 0.15 eV ($-80\%$ error).

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[27]It can be speculated that, e.g., a "correctly" predicted (i.e., slightly higher) frozen-phonon frequency would lead to a less severe "breaking" of the initial course of TA, which might then produce a flat branch without requiring forces on very distant neighbors.

[28]Unlike the case of GaAs, where the endpoint at point $X$ is not uniquely defined by symmetry and depends sensitively on forces.

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