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Harmonic lattice dynamics of germanium

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The phonon dispersion relations of the Δ, Λ, and Σ directions of germanium at 80 K are analyzed in terms of current harmonic-lattice-dynamical models. On the basis of this experience, a new model is proposed which gives a unified account of the strong points of the previous models. The principal elements of the presented theory are quasiparticle bond charges combined with a valence force field.

I. INTRODUCTION

Extensive experimental data on phonon dispersion relations in germanium at 80 K have been published elsewhere.[1,2] At this temperature the influence of anharmonicity may be completely neglected.[3] In Sec. II of the present paper, predictions by current harmonic-lattice-dynamical models are compared to the data of the Δ, Λ, and Σ directions and, when possible, also to the experimental values of the dielectric and the elastic constants. The models considered have been fitted to a maximum of about 140 phonon frequencies by the method of least squares. Our primary concern has not been to obtain as good fits as possible but to show how many parameters a model needs in order to produce a reasonable fit and what physical significance the parameters might be attributed. It is found that quite different and, perhaps, also seemingly mutually contradicting models may give rise to equally good fits. One of the purposes of the present work has therefore been to establish a unified account. We do also present such a model in Sec. III.

II. CURRENT MODELS

A. Deformation-dipole model

The earliest model of lattice dynamics, the Born–von Kârmân model[4] (BKM), needs a very large number of parameters in order to give a good account of the phonon dispersion in germanium. Herman[5] showed that a good fit of BKM to the data of Brockhouse and Iyengar[6] requires as much as 15 parameters. Then interactions out to the fifth-nearest-neighbor atoms are included. This long range of the force field has been considered as an evidence for the necessity to take the electronic polarization into the account. Attempts in this direction, e.g., on sodium chloride, by assuming *induced* dipole moments, which depend only on and are proportional to the local electric field, led to substantial improvements but also clearly showed that this was not sufficient.[7] In order to give a more proper account and to allow for polarization of atoms by *distortions* of their electron configurations due to short-range interactions with adjacent atoms must also be considered. Tolpygo[8] took a quantum-mechanical approach using a perturbation expansion based on tight-binding electron wave functions in the Hartree-Fock approximation. The mean electronic Hamiltonian so established allows for creation of dipoles by deformations of the valence electron clouds. This is the deformation-dipole model (DDM). In order to give a reasonable account of the dispersion relations, it must include short-range interactions out to second-nearest-neighbor atoms.[9,10] The model then contains eight free parameters besides the polarizability A_1. The solid lines in Fig. 1(a) represent the results of a fit to our germanium data. The parameters obtained are listed in Table I and the derived macroscopic constants in Table II. The fit to the branches of the Δ and Λ directions is very good, while that to the Σ branches is less satisfactory. For instance, the highest optic branches, $\Sigma_1(0)$ and $\Sigma_2(0)$, are poorly described, and the characteristic dip of $\Sigma_3(0)$ is hardly accounted for. As expected, if only Δ and Λ modes are included in the fit the result will be excellent for these branches while the Σ branches increase their disagreement with experiment [dashed lines in Fig. 1(a)]. Even the macroscopic constants, except C_{44}, improve their values remarkably. The approximations underlying DDM require the perturbations of the atoms to be small. This imposes the following conditions for some of the parameters[9]:

$$G \gg g \gg \mathcal{G}, \quad |H| \gg |h| \gg |\mathcal{H}| . \tag{1}$$

As can be seen from Table I, these relations are not strongly satisfied in either of the cases.

B. Shell-dipole model

Many of the consequences of the numerous approximations in the derivation of DDM are difficult to understand in detail. It is often instructive and of considerable value to represent quantum-me-

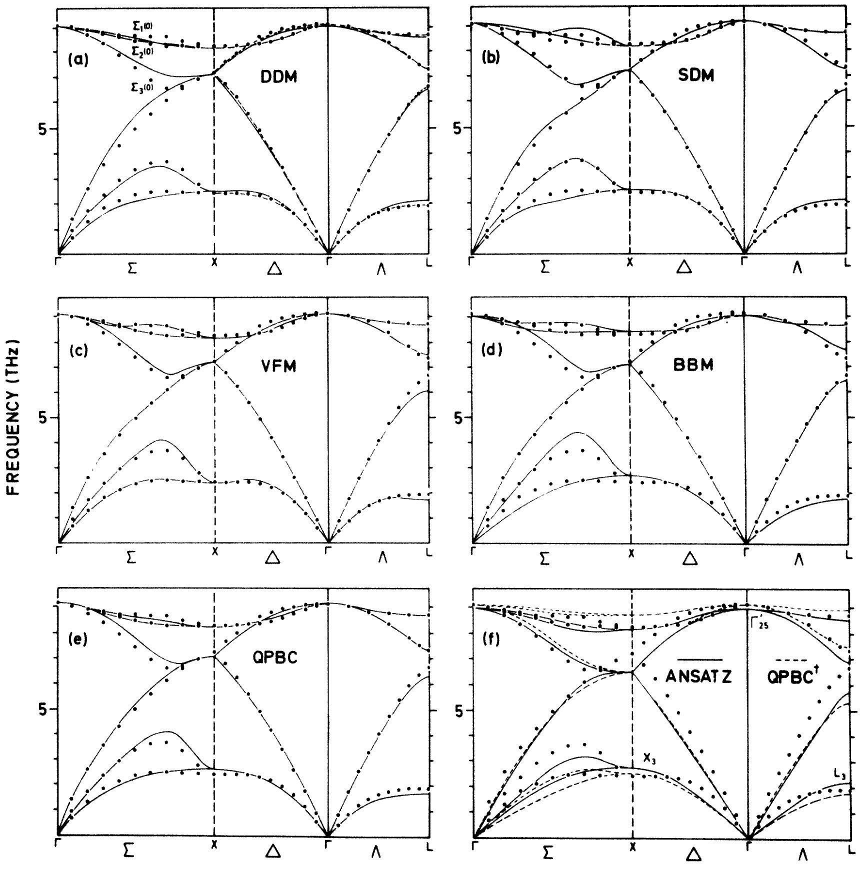

FIG. 1. Various model fits to the measured dispersion relations for germanium at 80 K:[1] (a) Nine-parameter DDM fitted to all the displayed data (solid lines) and to only those of the Δ and Λ directions (dashed lines), (b) 11-parameter SDM, (c) five-parameter VFM, (d) four-parameter BBM, (e) six-parameter QPBC, and (f) one-parameter Ansatz (solid lines) and two-parameter QPBC (dashed lines). For details the reader is referred to the text.

chanical concepts by a phenomenological model, particularly if this can be done prior to calculations from first principles. Dick and Overhauser[11] gave a plausible quantum-mechanical basis for a phenomenological model of an atom with a closed electron configuration. The atom in this model is made up of a point core, representing the nucleus and the inner electrons, surrounded by a massless spherical shell, representing the outer electrons, both entities being electrically charged. In a crystal, it is assumed that short-range forces act between core-shell, core-core, and shell-shell and that dipole moments are created by relative displacements between cores and shells. This is the shell-dipole model (SDM) which, when applied to germanium, leads to equations of motion formally identical with those of DDM.[12] The nine-parameter version of DDM, considered in Sec. II A, utilized only central forces between second-nearest neighbors. A fit of an 11-parameter version[13,14] of SDM including noncentral second-neighbor forces is presented in Fig. 1(b). Compared to the results in Fig. 1(a), the fit is improved but the basic difficulties in accounting for the Σ branches remain. Moreover, the excellent fit to the Δ and Λ directions, obtained for DDM, is no longer possible (results presented only in Tables I and II). Finally, the parameter values are in several cases obviously unreasonable, particularly for the second-neighbor forces (with lower suffix 4).

C. Penn's dielectric model

Intuitively, it is somewhat surprising that models like DDM and SDM, which assume an isotropic valence charge distribution, work at all on germanium. Moreover, it has been demonstrated, with the aid of dielectric screening theory, by Penn[15] and others that the valence electrons in germanium are nearly-free electron like. The tight-binding picture, where the valence electron charges are associated with individual atoms, is hardly compatible with this fact. Great effort has in the past been devoted to improvements of SDM by, for instance, allowing for deformations and, in order to account for the compressibility of the valence electron gas, "breathing" of the shells.[16] In the case of germanium, however, improvements along this and similar lines do not remove any of the objections raised above. As was remarked in Secs. II A and II B, the values of the parameters obtained for DDM and SDM were not satisfactory, particularly not for the latter model. Several of them are certainly to be considered rather as mathematical interpolation parameters than as physical constants. However, DDM and SDM must be regarded as great improvements in comparison with BKM.

D. Valence-force model

Although it predates quantum mechanics, the idea of valence forces is based on first-principle concepts. The electrons binding a group of atoms (molecule) are represented by wave functions possessing the group symmetry. The symmetry elements are lengths of bonds and directions of bonds or angles defined by any two bonds with a terminus atom in common. During a perturbation (vibration) of the group, forces act which tend to restore the equilibrium configuration. It is then natural to associate a restoring force with each of the symmetry elements defining this configuration. This is the valence-force model (VFM), which has proven to be very effective for molecular vibrational spectra.[17] A convenient formalism for its application to crystals with covalent bonds has been worked out by McMurry *et al.*[18]

The basic parameters of VFM, in the case of germanium, are the bond-stretching F_r and the angle-bending F_φ force constants. These are, however, not sufficient. When a disturbed bond or an angle rehybridizes its associated wave functions, interactions with neighboring symmetry elements must occur. This leads to the presence of off-diagonal elements in the force-field matrix. These parameters have to be chosen intuitively, but we may be guided by the experience from analysis of molecular spectra, as has been demonstrated by the VFM calculations on diamond[18] and silicon.[19,20] The results of a five-constant fit to the germanium data is presented in Fig. 1(c) and in Tables I and II. The force f_{rr} interacts between adjacent bonds, $f_{r\varphi}$ between bonds and angles where bond is leg of angle, and $f_{\varphi\varphi}$ between angles consecutive in a Σ plane and with one leg in common [Fig. 2(a)].

The overall fit in Fig. 1(c) is really good, and VFM must in this respect be considered as superior to DDM and SDM, particularly with regard to the small number of parameters employed. A more proper account of the nature of the covalent forces seems to be of greater importance than an inclusion of the electronic polarization. But to state that the polarization is negligible would certainly be wrong, the dielectric constant of germanium being as large as 16. The force field of VFM, listed in Table I, probably includes a partial simulation of the polarization effects. It is to be noted, for instance, that the off-diagonal constants $f_{r\varphi}$ and $f_{\varphi\varphi}$ are larger than F_φ—a situation not expected on an in-

TABLE I. Parameter values of the various models discussed in the text as obtained by least-squares fits to the data of the Δ, Λ, and Σ directions of germanium at 80 K. The asterisk indicates that the Σ data were excluded. The case QPBC† was not fitted but obtained as described in the text.

DDM	G	g	$\mathcal{G}$	H	h	$\mathcal{H}$	F	E	A_1		
(no. dim.)	21.44	3.424	1.960	−2.812	−1.202	−0.824	−0.021	0.225	0.127		
DDM*	G	g	$\mathcal{G}$	H	h	$\mathcal{H}$	F	E	A_1		
(no. dim.)	20.91	2.804	2.418	−2.757	−1.231	−1.019	0.097	0.159	0.135		
SDM	α_R	π	d	α_s/α_R	γ_R	γ_T	γ_S	μ_4	λ_4	ν_4	δ_4
(e^2/v_c)	23.33	0.0391	1.300	1.276	0.242	0.093	−0.180	−4.357	−9.103	1.898	7.008
SDM*	α_R	π	d	α_s/α_R	γ_R	γ_T	γ_S	μ_4	λ_4	ν_4	
(e^2/v_c)	25.30	0.0368	1.360	1.257	0.216	0.074	−0.176	−5.750	−9.700	2.269	
VFM	F_r	F_φ	$f_{r\varphi}$	$f_{r\varphi}$	$f_{\varphi\varphi}$						
(mdyn/Å)	1.3368	0.0222	0.0383	0.0290	0.0230						
BBM	α	β	γ	g(no dim.)							
(mdyn/Å)	11.705	1.414	0.566	0.645							
QPBC	F_R	F_θ	f_{RR}	$f_{R\theta}$	$f_{\theta\theta}$	Z (units of e)					
(mdyn/Å)	2.9163	0.1052	0.2407	0.0987	0.0584	0.2241					
Ansatz	r_G										
(Å)	1.5										
QPBC†	F_R	Z (units of e)									
(mdyn/Å)	2.9700	0.3000									

TABLE II. Elastic constants in units of 10^{12} dyn cm^{-2} and the dielectric constant as derived from the parameter sets in Table I and as described in the text.

	Expt	DDM	DDM*	SDM	SDM*	VFM	BBM	QPBC	*Ansatz*	QPBC†
C_{11}	1.32[a]	1.26	1.32	1.32	1.25	1.41	1.26	1.48	···	0.89
C_{12}	0.49[a]	0.59	0.48	0.47	0.51	0.68	0.81	0.75	···	0.64
C_{44}	0.68[a]	0.58	0.57	0.70	0.71	0.58	0.50	0.61	···	0.25
ϵ	15.8 ± 0.2[b]	8.3	16.5	12.9	14.7	···	···	13.7	12.0	5.2

[a] H. J. McSkimin, J. Appl. Phys. 24, 988 (1953).

[b] W. C. Dunlap, Jr., and R. L. Watters, Phys. Rev. 92, 1396 (1953); A. C. Baynham, A. F. Gibson, and J. W. Granville, Proc. Phys. Soc. Lond. 75, 306 (1960).

tuitive basis.

The success of VFM demonstrates the reason for the failure of BKM. This is because the former may be treated as a special case of the latter.[21] The force constants of BKM are so general that, when a particular crystal is considered, they allow for nonpresent interactions in addition to those of significance. Thus, in order to screen out insignificant contributions to the force field, further and irrelevant parameters have to be included. (The short-range interactions of SDM are also expressed by means of BKM matrices.) For example, Keating[22] has shown that in an insulator, i.e., a crystal where the lattice potential is only a function of the nuclear displacements, symmetry requirements forbid the existence of noncentral nearest-neighbor two-body forces. This type of force constant is the second one in every BKM calculation. The use of only symmetry-defining elements in VFM as bond lengths and angles between bonds, leads to an automatic satisfaction of all symmetry requirements.

Finally, it is worthy of notice that Herman[5] in his work on BKM noticed that the fit to the experimental data of germanium was improved only quantitatively when interactions with third- and fourth-nearest-neighbors were included. A qualitative improvement was obtained first when fifth-neighbor forces were also considered. The force field of VFM listed in Table I accounts for interactions with first-, second-, and fifth-nearest neighbors. Third- and fourth-neighbor interactions are not present. This we consider as a support to our belief that the set of force constants worked out is the best set possible for VFM. Moreover, all members of this set represent forces operative along a chain of bonds in a Σ plane, where the valence electron orbitals are expected to wend. The angle-angle parameter representing interactions between angles with one leg and the apex atom in common tended towards zero in a six-constant fitting procedure. The force-constant sets obtained for diamond[18] and silicon[19,20] reveal a similar situation there.

E. Broken-band model

Besides the BKM force type, frequent use has been made of the de Launay force type[23] which consists of radial and tangential two-body force con-

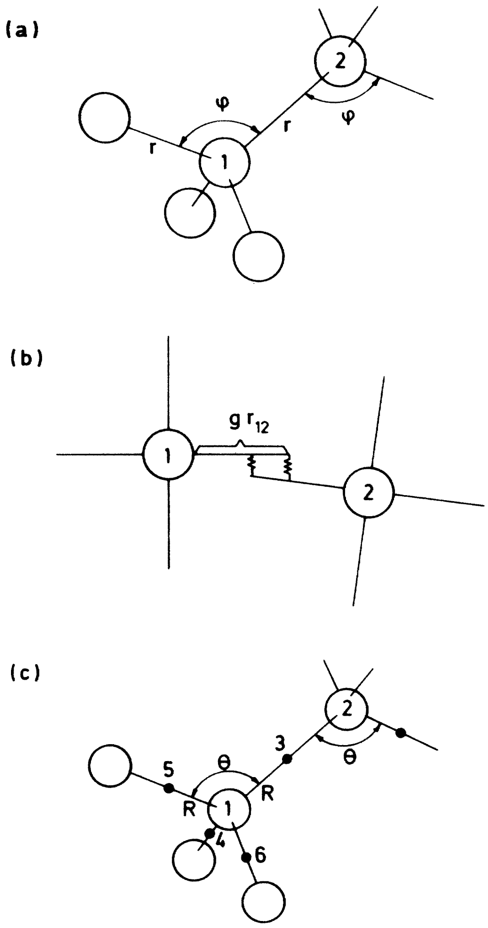

FIG. 2. Schematic illustrations of the idealized lattice of (a) VFM, (b) BBM, and (c) QPBC. R denotes the distance from a core to one of its nearest-neighbor quasiparticles. The charge numbers read as follows: $Z_i = 2Z_B$ for $i = 1, 2$ and $Z_i = -Z_B$ for $i = 3, \ldots, 6$.

stants. However, these forces violate the requirement of rotational invariance. Moizhes[24] pointed out that these conditions will, on the other hand, be satisfied if it is assumed that rotation of an atom results in a force acting on the nearest-neighbor atoms with a magnitude half that of the corresponding tangential force. One may raise objections against a method where symmetry violations are compensated by introduction of "counteracting" forces. As was pointed out in Sec. II D, noncentral first-neighbor two-body interactions are forbidden in an insulator. Moreover, distinguishable rotations of an atom are generally not in agreement with quantum theory concepts. However, for a covalently bonded solid like germanium, the directed valence orbitals do in fact define a reference system on every atom. This makes it, in principle, possible to define an atomic orientation-dependent contribution to the lattice potential, e.g., by Moizhes's rotational compensation force.

A model by Vasil'ev *et al.*[25] based on Moizhes's concepts, is illustrated schematically in Fig. 2(b). Each nucleus is represented by a point mass. The directional wave functions (or valence electrons) are represented by four stiff antennae of which the tips are linked together with the antennae of the adjacent atoms by springs. The interaction parameters are the radial α, and the tangential β, first-neighbor constants, the length of an antenna g, expressed as a fraction of the nearest-neighbor distance, the "symmetry-saving" rotational (spring) constant $\frac{1}{2}\beta$, and the second-neighbor radial constant γ. This leaves four independent parameters free for a least-squares fit. The model assumes that the angles between the bonds of a given atom do not change during vibration, i.e., only the overlap energy with the wave functions of adjacent atoms changes; the energy of the system being increased when the bonds are rotated in either direction.

The results of a fit to the germanium data are presented in Fig. 1(d) and in Tables I and II. The fit is good and much better than might have been expected. The success of this model, we believe, is a consequence of somewhat different reasons, however, than those discussed above. It is a fact that the bonds are treated as if they were broken [which is the reason for our name, the broken-bond model (BBM)]. Furthermore, the successful use of stiff antennae might be considered as an evidence for the pressure of strong forces acting between the bonds of an atom during rehybridization. In Sec. III we find support for these points of view.

F. Phillips's bond-charge model

According to Penn[15] (Sec. II C), the valence electrons in germanium are nearly free but not quite free. In fact, by means of a dielectric screening model, which assumed a free-electron dielectric function including the Hubbard-Sham exchange correction and a modified Heine-Abarenkov model potential, Martin[26] has shown that the free-electron picture leads to a lattice not stable under shear. These calculations were carried out for silicon, but they should also apply to the nearly homologous germanium.[27] In order to stabilize the lattice, i.e., to introduce off-diagonal elements in the dielectric function, at least some effects of the covalent bonding must be taken into the account. Employing linear screening with the Penn dielectric function, Phillips[28,29] pointed out that the characteristic dimensions of the bonding charge density are much smaller than those of the atomic charge density. (This result is primarily a consequence of Bragg interference between electron waves scattered off neighboring ions.) Thus, the covalent nature of the valence electron gas not only gives rise to an excess of negative charge in the bonds but also to a strong localization at the midpoints of them. According to Martin,[26] covalency is therefore to be represented by point bond charges attached to pairs of ions and responding so as to remain midway between the ions even when these are displaced. This arrangement gives the off-diagonal elements required in order to stabilize the lattice. The dispersion relations so obtained are of a quality comparable to that exhibited by the curves in Fig. 1(f).

Prior to Martin and in an attempt to improve the second-nearest-neighbor BKM for diamond, Warren[30] made a similar bond-charge approach which, however, utilized incorrectly defined Coulomb matrices.[26] Solbrig[31] combined the bond-charge matrices of Martin with VFM in an unsuccessful application to silicon. This caused Solbrig to initialize the development of a new version of VFM.[31] In this theory, the ionic cores are electrically charged and polarizable by induction from the local field, the bond charges are subject to the same constraints as in the Warren-Martin treatment with the dipole moments collected at the ionic positions, the short-range forces act between the ions, and linear charge exchange between the atoms is also allowed for. Applied to germanium this model would include three new parameters in addition to the ordinary valence force field. Trials to combine bond charges with the "breathing" SDM are reported by Kress,[16] who claims the results to be satisfactory. However, the results and arguments actually presented do not carry conviction.

No successful report of any bond-charge model is known to us. The reasons for this, we believe, is not that Phillips's theory is basically wrong. It is a fact that none of the models cited in the preceeding paragraph allows for electronic polarization caused by a direct coupling between the distortions of the bond-charge configurations and the short-range forces. The Warren-Martin constraints may well be invalidated by a refined microscopic theory. The results of Sec. III will give support to these statements.

G. *Ansatz*

Sinha[32,33] has developed a microscopic theory of lattice dynamics from which, in principle, all phenomenological dipole models may be derived. The model divides the perturbed valence electron density into a part which moves rigidly with the core and a deformation part. The latter, which has to satisfy a self-consistency equation, is assumed to define a dipole field. The dipoles are not restricted to be situated at the cores and they are assigned a finite spatial extension described by a form factor. The second basic approximation is a general *Ansatz* which allows for an explicit inversion of the dielectric function in terms of a generalized polarizability tensor, the dipole form factors, and the electron-electron interaction potential. This is very convenient in the case of an insulator where off-diagonal elements have to be considered (Sec. II F). Loosely speaking, the *Ansatz* may be regarded as a parametrized combination of the free-electron and the tight-binding pictures. The model has been applied to our germanium data by Sinha *et al.*[34] The dipole form factor used represents a real space extension characterized by being constant within a radius r_G and zero otherwise. Isotropic polarizability was also assumed. r_G was the only free parameter in the self-consistency fitting procedure; the results of which are presented in Fig. 1(f) and in Tables I and II. The dipoles were assumed to be positioned at the cores. When they were attached to the bond sites instead, however, poor agreement with experimental data was obtained, probably owing to the oversimplified form factor and polarizability. On the other hand, the results must be considered promising, and future attempts to account for bond-charge polarization will probably do much better.

III. NEW MODEL

Let the germanium lattice be described as follows. The nucleus of an atom and its surrounding inner electrons, i.e., the closed or localized part of the electronic configuration, is considered as a spherical ionic core. It may thus be represented by an electrically charged mass point. Assume that the electronic polarizability of the tightly bound core can be neglected compared to that of the nearly-free valence electron gas. The core will then behave like a rigid ion. The valence electron gas is treated according to Phillips's bond-charge theory, i.e., point charges are to be attached at the midpoints of the bonds. (This point representation is also supported by nonlinear screening theory. According to Heine and Jones,[35] the bond charge is indeed well localized, although it is not quite a point charge.) The remaining parts of the valence electron gas are then attributed a much lower charge density. These charge clouds keep the bond charges and the ionic cores apart with directed valence in an sp^3 or, perhaps better, an O_h^7 crystal hybridization.[29,36] They should be responsible for the short-range interactions, which, moreover, ought to be described in terms of a valence-force field. Quantum mechanically, electronic polarizability is represented by a nonlocal (integral) operator. Assume, however, that the bond-charge pileup is so strong that the contributions to a bond-polarization center will fall off rapidly enough with distance to justify a neglecting of integration overlap effects. (The actual magnitude of a bond charge will be discussed below.) The electronic polarization may in that case be considered as a local property attributed to the bond charges. If we, moreover, prescribe it to be directly affected by the short-range forces, a particle treatment of the bond charges will be required that makes them free to move in the same manner as the ionic cores without any explicit constraints. The short-range forces will thus act between the ions via the interjacent quasiparticles. The number of particles per primitive cell is now six [Fig. 2(c)]. The adiabatic approximation will be satisfied by setting the eigenvalues of the quasiparticles identical to zero in the equations of motion. It is hoped that a future refinement of the first-principle bond-charge theory will give a firmer justification of our quasiparticle-bond-charge model (QPBC). The formal elements of the present theory are given in the Appendix.

We first worked with the hypothesis that the short-range forces are operative only within the considered atom (origin atom), i.e., not beyond the four first-nearest-neighbor quasiparticles. This conjecture was, however, not successful. A good agreement with experimental data was obtained first when it was assumed that the short-range field not only links first-nearest-neighbor atoms together but is also operative exclusively in a Σ plane. The final set of force constants was found to be a direct analog to the five-constant set obtained for VFM. The results of a fit with this six-parameter version of QPBC are exhibited in Fig. 1(e) and in Tables I and II. The fit is, quantitatively, found to be approximately the same as for VFM but it differs in a qualitative sense, particularly for "transverse" acoustic modes. The values of the force constants obtained are, however, now arranged in an order which may be expected on an intuitive basis, i.e., $F_R > f_{RR} > F_\theta$

$>f_{R\theta}>f_{\theta\theta}$. The results of QPBC are also in agreement with the formalism of BBM: The broken-bond picture is compatible with the present model, and four of the five short-range force constants are operative within the origin atom, thus exhibiting strong rehybridization forces and supporting the stiff antennae approach. Concerning the derived values of the macroscopic constants listed in Table II, we notice that fair agreement with experiment is obtained in all cases except for C_{12}. This discrepancy is present also for the corresponding values of VFM and BBM.

Phillips[29] estimated the magnitude of the bond charge to be

$$Z_B = 2/\epsilon , \tag{2}$$

expressed in units of e. Equation (2), which gives $Z_B \sim 0.1$ for germanium, is obtained if contributions to Z_B arise only from the incomplete screening of the ionic cores. However, if the overlap of the spherical part of the atomic form factors is also taken into the account the magnitude of Z_B will increase. Levine[37] gave for a completely covalently bonded crystal the formula

$$Z_B = 2/\epsilon + k , \tag{3}$$

where k is a constant. Levine estimated from Eq. (3) with the help of the electrical susceptibility the bond charge in germanium to $\sim 0.6\, e$. Our value of the effective bond charge is $\sim 0.22\, e$, which, when multiplied by the square root of the experimental value of the dielectric constant, gives a bare charge of $\sim 0.88\, e$. Although lacking a more accurate check of our value, we may anyhow state that it is of a reasonable order and that the value derived for the dielectric constant (Table II) is good. Moreover, the strong bond charge obtained and expected from screening theory may be taken as a support of the above treatment of the electronic polarizability as a local property.

It is known that the sum

$$S = \sum_{i=1}^{6} \nu_i^2(\vec{q}) \tag{4}$$

is almost independent of $\vec{q}$ for germanium; the maximum deviation being not larger than 3% for the Δ, Λ, and Σ modes.[27] According to Rosenstock,[38] this implies for a nonmetallic crystal that, if the long-range forces in germanium obey the Laplace's equation, the short-range forces should act, practically, only between first-nearest-neighbor atoms. The QPBC force field obtained satisfies this rule. This is, however, not the case for either BKM, DDM, SDM, VFM, or BBM, which models include short-range interactions out to the fifth-, second-, second- fifth-, and second-nearest-neighbor atoms, respectively.

We have treated the bond charges as being fixed in magnitude. However, charge redistributions certainly occur between adjacent bonds during vibrations. The force constant f_{RR} has been interpreted in terms of such effects by means of quantum-mechanical resonance theory.[39,17] The contributions to the phonon spectrum by this constant are less important than for anyone of the other QPBC constants. In fact, if f_{RR} is dropped and its value subtracted from that of F_R the only notable effect on the dispersion relations is a gradual decrease of "longitudinal" mode frequencies when the zone boundaries are approached. The actual figures are about -0.3 THz on the average at the points X and L. The exchange charges should, intuitively, be smaller, if not even much smaller, than both the ionic and the bond charges, and so their contributions to the spectrum should also be. One might thus expect an approach in this direction to be fruitful. However, the actual form of the mathematical description of a phenomenological charge exchange, we feel, does need some separate investigation, which, preferably, also should include efforts to substitute other off-diagonal force constants as well by explicit phenomenological representations of other first-principle concepts.

QPBC leads to a stable lattice provided the bond-stretching (F_R) and the Coulombic (Z_B) fields are incorporated. The dashed lines of QPBC† in Fig. 1(f) show the results obtained if F_R is determined by the Raman frequency, Γ'_{25} (Z_B does not contribute) and if Z_B is chosen so that the fit to the frequencies of X_3 and L_3 is optimized (F_R contributes practically nothing). The similarities with the *Ansatz* spectrum are obvious, but it is less clear for the moment how this should be interpreted. When the remaining short-range parameters are included, it is found that the "longitudinal" acoustic modes are dominated by R-dependent forces while contributions from other than θ- and Z_B-dependent forces are entirely negligible for the "transverse" acoustic modes. This is in accord with the results of a previous paper,[27] where it was found that the "longitudinal" acoustic branches mainly reflect the bulk properties (compressibility) of the electron gas while "transverse" acoustic branches are sensitive to the details of the charge distribution. This sensitivity, we believe, is the main reason for the difficulties encountered in the various approaches to account for the electronic polarizability in germanium. The point-dipole bond-charge approximation assumed here works well while, for instance, the corresponding finite-dipole approach used in the *Ansatz* failed. A systematic investigation of various quasiparticle bond-charge dipole form factors (and the polarizability tensor as well) with the *Ansatz* should be fruitful and give further insight into the properties of the valence-charge distribution.

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APPENDIX

Let $\underline{\mathrm{q}}(l) = \|\vec{\mathrm{u}}_i(l)\|$, where $\vec{\mathrm{u}}_i(l)$ represents the displacement of the ith particle in the lth cell, denote the column vector obtained when i runs from 1–6. The kinetic energy of the infinite crystal is then given by

$$2T = \sum_l \dot{\underline{\mathrm{q}}}^\dagger(l) \hat{M} \dot{\underline{\mathrm{q}}}(l) , \tag{A1}$$

where $\hat{M}$ is the diagonal mass tensor defined by $M_{ii} = M$ for $i = 1, 2$ and $M_{ii} = 0$ for $i = 3, \ldots, 6$; M being the germanium atomic mass. Let $\vec{\mathrm{S}}_{nmi}(l)$ denote the Wilson S vector[17] for the action on the nth valence coordinate of the lth cell, $h_n(l)$, by a displacement of the ith particle in the mth cell. Define the column vector of the valence coordinates of the lth cell, $\underline{\mathrm{H}}(l) = \|h_n(l)\|$, by the relation[17,18]

$$\underline{\mathrm{H}}(l) = \sum_m \hat{D}_{lm} \underline{\mathrm{q}}(m) ,$$

where $\hat{D}_{lm} = \|\vec{\mathrm{S}}_{nmi}(l)\|$; the row index $n = 1, \ldots, n_{\max}$ and the column index $i = 1, \ldots, 6$. The potential energy due to the short-range interactions are then given in the harmonic approximation[4] by

$$2V_s = \sum_{lm} \underline{\mathrm{H}}^\dagger(l) \hat{F}_{lm} \underline{\mathrm{H}}(m) , \tag{A2}$$

where $\hat{F}_{lm} = \|f_{li;mj}\|$ and $f_{li;mj}$ is the interaction force constant between the valence coordinates $h_i(l)$ and $h_j(m)$. The quadratic term of the Coulombic interaction energy may be written

$$2V_c = (Z_B e)^2 \sum_{lm}{}' \underline{\mathrm{q}}^\dagger(l) \hat{C}_{lm} \underline{\mathrm{q}}(m) , \tag{A3}$$

where

$$\hat{C}_{lm} = \|\hat{\underline{\mathrm{C}}}_{li;mj}\| , \quad \hat{\underline{\mathrm{C}}}_{li;mj} = \|C_{lix}^{mjy}\|$$
$$\equiv \left\| Z_i Z_j \left[\frac{\partial^2}{\partial u_i^x(l)\, \partial u_j^y(m)} \left(\frac{1}{|\vec{\mathrm{R}}_{li;mj}|} \right) \right]_0 \right\| .$$

Z_i is the charge number of particle i, $\vec{\mathrm{R}}_{li;mj}$ is the instantaneous vector from (mj) to (li), x and y are the cartesian indices, and (ix) are the row and (jy) the column indices of $\hat{\underline{\mathrm{C}}}_{li;mj}$. The index 0 indicates that the differentiation is to be carried out at the equilibrium configuration, and the prime after Σ indicates that the case $\vec{\mathrm{R}}_{li;mj} = 0$ is excluded from the summation. In accord with the periodic boundary conditions,[4] write

$$\underline{\mathrm{q}}(l) = \sum_k \underline{\mathrm{Q}}(\vec{\mathrm{k}})\, e^{-i\vec{\mathrm{k}}\cdot\vec{\mathrm{l}}} , \tag{A4}$$

where $\vec{\mathrm{k}}$ is a reciprocal-lattice vector. After substitution of Eq. (A4) into Eqs. (A1)–(A3) and application of the usual procedures (Ref. 4, p. 297), we obtain

$$\begin{aligned} 2T &= N \sum_k \dot{\underline{\mathrm{Q}}}^\dagger(\vec{\mathrm{k}}) \hat{M} \dot{\underline{\mathrm{Q}}}(\vec{\mathrm{k}}) , \\ 2V_s &= N \sum_k \underline{\mathrm{Q}}^\dagger(\vec{\mathrm{k}})\, \hat{\mathfrak{s}}(\vec{\mathrm{k}}) \underline{\mathrm{Q}}(\vec{\mathrm{k}}) , \\ 2V_c &= N \sum_k \underline{\mathrm{Q}}^\dagger(\vec{\mathrm{k}}) \hat{\mathfrak{C}}(\vec{\mathrm{k}}) \underline{\mathrm{Q}}(\vec{\mathrm{k}}) , \end{aligned} \tag{A5}$$

where N is the number of cells in the crystal and

$$\begin{aligned} \hat{\mathfrak{s}}(\vec{\mathrm{k}}) &= \hat{\mathfrak{D}}^\dagger(\vec{\mathrm{k}}) \hat{\mathfrak{F}}(\vec{\mathrm{k}}) \hat{\mathfrak{D}}(\vec{\mathrm{k}}) , \\ \hat{\mathfrak{D}}(\vec{\mathrm{k}}) &= \sum_l \hat{D}_{0l}\, e^{-i\vec{\mathrm{k}}\cdot\vec{\mathrm{l}}} , \\ \hat{\mathfrak{F}}(\vec{\mathrm{k}}) &= \sum_l \hat{F}_{0l}\, e^{-i\vec{\mathrm{k}}\cdot\vec{\mathrm{l}}} , \\ \hat{\mathfrak{C}}(\vec{\mathrm{k}}) &= (Z_B e)^2 \sum_l \hat{C}'_{0l} , \\ \hat{C}'_{0l} &= \left\| C_{0ix}^{ljy} e^{-i\mathrm{k}\cdot\mathrm{l}} - \delta_{ij} \sum_{j'} C_{0ix}^{lj'y} \right\| . \end{aligned} \tag{A6}$$

The Lagrangian procedure,[4] applied to Eq. (A5), then yields the secular equation

$$|\hat{M} \underline{\mathrm{E}} - [\hat{\mathfrak{s}}(\vec{\mathrm{k}}) + \hat{\mathfrak{C}}(\vec{\mathrm{k}})]| = 0 ,$$

where $\underline{\mathrm{E}} = \| E_\lambda \|$ is the eigenvalue column vector and $E_\lambda = 4\pi^2 \nu^2$ for $\lambda = 1, \ldots, 6$ and $E_\lambda = 0$ for $\lambda = 7, \ldots, 18$ (in order to satisfy the adiabatic approximation[4]); ν being the phonon frequency. The matrix $\hat{\mathfrak{C}}(\vec{\mathrm{k}})$ in Eq. (A6) is evaluated numerically after application of the Ewald transformation[4]:

$$\hat{\mathfrak{C}}(\vec{\mathrm{k}}) = (Z_B e)^2 / v_c \left\| Z_i Z_j \Delta_{xy}^{ij}(\vec{\mathrm{k}}) - \delta_{ij} Z_i \sum_{j'} Z_{j'} \Delta_{xy}^{ij'}(0) \right\| ,$$

where

$$\begin{aligned} \Delta_{xy}^{ij}(\vec{\mathrm{k}}) = 4\pi \sum_g \frac{G_x G_y}{G^2} \exp[-i(\vec{\mathrm{G}}\vec{\mathrm{r}}_{ij} + G^2/4\pi\eta^2)] \\ - v_c \sum_l \left(\frac{L_x L_y}{L^2} [3\phi(L) + 2\eta^3 \operatorname{erf}'(\eta L)] \right. \\ \left. - \delta_{xy} \phi(L) \right) e^{-i\vec{\mathrm{k}}\vec{\mathrm{l}}} , \end{aligned}$$

$$\phi(L) = \frac{\operatorname{erfc}(\eta L)}{L^3} + \frac{\operatorname{erf}'(\eta L)}{L^2} ,$$

$$G = |(G_1, G_2, G_3)| = |\vec{\mathrm{g}} - \vec{\mathrm{k}}| ,$$

$$L = |(L_1, L_2, L_3)| = |\vec{l}+\vec{k}| \ .$$

v_c is the primitive cell volume, $\vec{g}$ is a reciprocal-lattice vector, $\vec{r}_{ij}$ is the vector from the ith to the jth particle in the origin cell, η is the Ewald parameter, and $\mathrm{erf}' = (d/dx)\,\mathrm{erf}(x)$. In the case of $\vec{r}_{ij} = 0$ the summation over the ordinary lattice is carried out for $\vec{l} \neq 0$ but with the addition

$$-\tfrac{4}{3}(v_c \eta^3/\sqrt{\pi}\,)\,\delta_{ij}\,\delta_{xy} \ .$$

The macroscopic constants of the long-wavelength limit are obtained with the method of long waves,[4] which has to be slightly but trivially modified. After series expansion of $\hat{S}(\vec{k})$ and $\hat{C}(\vec{k})$ for small $|\vec{k}|$ and separation of the macroscopic field from $\hat{C}(\vec{k})$, comparison is made between the condition of solubility for the equations of the second-order coefficients and the macroscopic equations of elasticity and dielectric polarization. The procedure is lengthy but fairly straightforward, and no formulas will be given here. The macroscopic constants and the matrices $\hat{C}(\vec{k})$ together with their derivatives were calculated by means of a computer.

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