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Adiabatic bond charge model for the phonons in diamond, Si, Ge, and α-Sn

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An adiabatic bond charge model (BCM) for the lattice dynamics of diamond-type crystals is developed. Our BCM unites elements of earlier models by Phillips and Martin, Keating, and Cochran. Four types of interactions are used: (a) central ion-ion forces, (b) Coulomb interactions of the ions and bond charges (BC's), (c) central ion-BC forces, and (d) bond-bending forces. These interactions represent the metal-like (a) and covalent (b)–(d) part of the crystal bonding. The phonon dispersion curves for Si, Ge, and α-Sn are calculated using only four disposable parameters; for diamond, five parameters are employed. For all crystals, very good agreement with experiment is obtained. In particular, the typical flattening of the transverse acoustic phonons in the semiconducting materials is understood as a consequence of the adiabatic motion of the BC's, when the effective ion-BC coupling (b) + (c) is weak compared to the bond-bending forces (d). In an alternative representation of the BCM, the interactions (b) and (c) are replaced by central and noncentral ion-BC-ion potentials along one bond. The remaining long-range part of the Coulomb forces is unimportant; therefore, all essential interactions of the BCM are of very short range. Furthermore, the interaction parameters follow clear trends from diamond to α-Sn: type (a) increases, whereas types (b)–(d) decrease, especially the ion-BC coupling tends to vanish toward α-Sn.

I. INTRODUCTION

In a previous Letter,[1] hereafter referred to as I, a new bond charge model (BCM) for the phonons in diamond-type semiconductors was presented. It was demonstrated that the flattening of the transverse-acoustic (TA) phonons in these substances can be understood by interactions involving the bond charges (BC's) when these move adiabatically. Calculations for the phonon dispersion curves of Ge show very good agreement with neutron data, using only four parameters. In this paper the model is presented in detail. It is illustrated that the BCM incorporates and unites elements of various important earlier models. It is also shown that the BCM can be applied equally well for the phonons in Si and α-Sn, and—with a minor modification—for diamond. The model thereby elucidates the changes in the bonding character from diamond to α-Sn. Extensions of the BCM for the lattice dynamics of III-V compounds and for the interpretation of infrared and Raman spectra of group-IV elements have been reported elsewhere.[2-4]

This paper is organized as follows. In the rest of Sec. I various models for the phonons in semiconductors are surveyed. In Sec. II the adiabatic BCM is developed and results of calculations for Si, Ge, and α-Sn are shown. The BCM for diamond is dealt with in Sec. III. An alternative representation of the BCM is derived in Sec. IV. In Sec. V our results are discussed and compared to other work in the literature. Final conclusions are given in Sec. VI. In the Appendix we present, respectively, some details of the BCM dynamical matrix, give expressions for the elastic constants and the susceptibility, and derive the condition of stable equilibrium.

We now briefly discuss those earlier models which are of significance for the development of the adiabatic BCM. Our survey is far from complete; for comprehensive reviews of phonons in semiconductors the reader is referred to articles by Cochran,[5] Sinha,[6] and Sham,[7] which include critical surveys of model theories and of *ab initio* calculations.

The lattice-dynamical theories of diamond-type crystals start with a classic paper by Born.[8] He proposed a model with nearest-neighbor central and noncentral force constants A' and B', respectively. The elastic constants are then given by

$$c_{11}+2c_{12}=2r_0(A'-2B'),\qquad c_{11}-c_{12}=2r_0B',$$

$$c_{44}=2r_0B'(A'+\tfrac{1}{4}B')/(A'+B'),$$

with r_0 being the lattice constant. Note that positive shear moduli, i.e., the stability of the diamond lattice against shear waves, are provided only by the noncentral force constant B'. The elastic constants are linearly dependent, and the so-called Born identity

$$I_B=4c_{11}(c_{11}-c_{44})/(c_{11}+c_{12})^2=1$$

was found later to be very well fulfilled experimentally for Si(1.09) and Ge(1.02), not, however, for diamond (1.49). This agreement was considered to be a strong support of the model. However, the inelastic-neutron-scattering experiments of Brockhouse and Iyengar[9] for the phonons in Ge seemed to discard Born's model completely, as severe deviations from the Born model were found at short wavelengths. In particular, the TA phonons have very low frequency and are very flat away from zone center. Since the shear moduli have rather high values, this flattening requires long-range interatomic force constants in a Born–von Kármán model, extending up to sixth-nearest neighbors.[10] The flattening of TA phonons also occurs in Si, and is even more pronounced in α-Sn (see Fig. 1). Indeed it was found that low-lying TA phonons are a common feature of the dispersion curves of zinc-blende materials, too.[5,6] Diamond, however, does not exhibit this lowering; there, the zone-boundary TA modes have very high energy (see Fig. 1).

As early as 1959, it was suggested by Cochran[11] that the long-range interatomic forces required to describe the flat TA branches are caused by mainly short-range ion-electron and electron-electron interaction. In Cochran's shell model (SM), which is based on earlier work by Dick and Overhauser,[12] the ion cores are coupled by a finite force constant to its shell of valence electrons, which, in turn, interacts with neighbor shells. When an atom is displaced, all shells adjust instantaneously to this motion, thereby transmitting forces to higher-neighbor ions, although only nearest-neighbor shells are coupled. Cochran presented a five-parameter SM calculation, with the short-range forces limited within nearest neighbors (nn).[11] He obtained very good agreement with the neutron data of Brockhouse and Iyengar,[9] and, moreover, in the long-wavelength limit, his model turned into Born's model, and thus fulfilled the Born identity for the elastic constants.

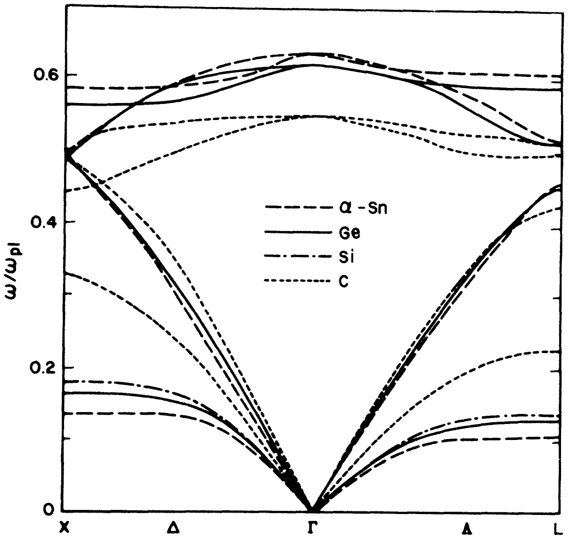

FIG. 1. Phonon dispersions relations for diamond, Si, Ge, and α-Sn along the Δ and Λ directions. The phonon energies are scaled by the respective ion plasma frequencies. (The numbers on the ordinate axis should be divided by $\sqrt{2}$.) The Si and Ge curves are almost identical; thus the Si curves are shown only where they deviate perceptibly from Ge.

Phillips[13] has criticized the application of the SM for covalent materials because it is unphysical to divide the electrons in a bond between two atoms, when they are shared between the two. Also, Cochran's model could not be generalized to zinc-blende crystals without introducing many new parameters, although the phonon dispersion curves are very similar.[6] Furthermore, the agreement with experiment especially the splitting of the TA branches in the then not measured $(\zeta,\zeta,0)$ direction is unsatisfactory, it is much too small (see, e.g., Fig. 2 in I). This deficiency can be improved only by 2nn force constants or by a "breathing" shell model.[14]

Another disadvantage of the model was later seen to be the use of the noncentral two-body forces, taken over from the Born model. A derivation of these forces from a crystal potential, e.g., a sum of two-body potentials, would require that they are zero, or compensated by higher-neighbor noncentral forces when the condition of stable equilibrium is fulfilled. Yet higher-neighbor forces also would influence the phonon dispersion. Further, it has been suspected that the noncentral two-body forces violate the rotational invariance condition. However, this could not be proved for an infinite crystal (see, e.g., Ref. 6, p. 277).

To avoid the problem of the noncentral two-body forces, which in Born's model are crucial for the shear stability of the diamond structure, Keating[15] has introduced invariants of the crystal from which he constructs the crystal potential. In particular, he has chosen the bond-stretching potential

$$V_{\mathrm{bs}}=\tfrac{1}{2}\,\alpha(x_{0i}^2-r_{0i}^2)^2/r_{0i}^2, \tag{1}$$

and the bond-bending term

$$V_{\mathrm{bb}}=\tfrac{1}{2}\,\beta(\vec{\mathrm{x}}_{0i}\,\vec{\mathrm{x}}_{0j}+a^2)^2/4a^2\ . \tag{2}$$

Here x_{0i} is the instantaneous distance vector between two atoms $0, i$ of a bond, and $\vec{\mathrm{r}}_{0i}$ is the vector for the equilibrium distance. Further

$$a^2=-\vec{\mathrm{r}}_{0i}\,\vec{\mathrm{r}}_{0j}\ .$$

As only two parameters α and β are introduced in Keating's model, an identity follows

$$I_K=2c_{44}(c_{11}+c_{12})/(c_{11}-c_{12})(c_{11}+3c_{12})=1\ .$$

Experimentally, this relation is even better fulfilled than Born's identity: 0.99 for C and Si; 1.07

for Ge.

Keating's model has been widely used to study elastic and static properties of covalent semiconductors.[15-17] Calculations of the phonon dispersion with this model show good agreement with experiment, except for the TA branches which, again, lie at too high frequencies. It should be pointed out that the potential functions proposed by Keating are closely related to the valence-force-field potentials, commonly applied in the theory of molecular vibrations,[18] and also used for the lattice dynamics of group-IV elemental crystals.[19-22]

A different approach to the lattice dynamics of semiconductors is the dielectric screening model of Martin,[23] which is based on the bond charge model of Phillips.[24] As the band structure of Si and Ge is nearly-free-electron- (NFE) like, the bare ion-ion forces are expected to be screened in a NFE-like manner, i.e., by the diagonal elements of the inverse dielectric function $\epsilon^{-1}(\vec{q}+\vec{G}, \vec{q}+\vec{G}')$. Yet because of the finite gap between valence and conduction bands, the screening is incomplete and there remains a residual Coulomb potential $4/\epsilon_\infty r$ at each ion. In order to achieve complete screening, Phillips introduced charges of magnitude $-2/\epsilon_\infty$ at the bond sites. These bond charges (BC's) represent the effect of the off-diagonal elements of ϵ^{-1}. Martin showed that the diagonal or metal-like screening leads to short-range two-body forces, essentially between nearest-neighbor (1nn) ions only. He also demonstrated that the interactions involving the BC's yield effective noncentral forces between the ions, and thus produce the stability of the diamond lattice against shear. The bond charge interactions therefore represent the covalent character of the bonding.

Martin[23] proposed a simple BC model, employing only two parameters, the 1nn central or bond-stretching force constant and the magnitude of the BC. He assumed that the BC's were always fixed midway between the instantaneous positions of the ions. With this assumption the problem that the BC position is unstable with respect to pure Coulomb interactions was avoided. Fair agreement with experimental phonon curves was achieved, althrough the TA flattening could not be obtained.

II. ADIABATIC BOND CHARGE MODEL FOR Si, Ge, AND α-Sn

The starting point of this model is the bond charge model of Phillips and Martin.[23,24] Just as in their model, the two types of bonding—metal-like and covalent bonding—are represented by short-range central forces between the ions and by interactions involving the BC's, respectively. The latter, however, are treated differently. The constraint that the BC's are fixed on the midway position between the atoms is removed. Instead, they are allowed to move adiabatically like the electronic shells in a SM. But now the problem arises that the Coulomb forces do not provide a position of stable equilibrium for charges at the bond sites: when the BC is displaced along the bond, it is attracted by the nearest ion. Only when the BC is elongated perpendicular to the bond direction, it experiences a restoring force. In order to stabilize the BC's on their sites, we introduce short-range ion BC forces. Furthermore, we take a coupling between neighbor bonds into account.

The four types of interactions are sketched in Fig. 2. The nearest-neighbor central potential ϕ_{i-i} (a) and the Coulomb interactions (b) are the same as in Martin's model.[23] We have added an ion-BC central potential (c) and a bond-bond interaction (d) of Keating type [Eq. (2)]; the subscripts i and j in Eq. (2) now denote BC's, not ions. The dynamical matrix of this model is given in some detail in the Appendix.

Our adiabatic BCM employs the four disposable parameters ϕ''_{i-i}, z^2/ϵ, $\phi''_{i-\mathrm{bc}}$, and β. The value of ϕ'_{i-i} is determined by the equilibrium condition (see Appendix), as we have put $\phi'_{i-\mathrm{bc}}=0$. A physical interpretation of this assumption is given in Sec. IV. In our calculation for Si, Ge, and α-Sn, the values of the parameters have been obtained from a least-squares fit to experimental elastic constants and to the neutron data of Dolling,[25] Nilsson and Nelin,[26-28] and of Price *et al.*[29] It should be noted that for the fit we had to include information of phonons at short wavelengths—in practice we fitted the frequencies at X, L and (0.6, 0.6, 0). It is not possible to determine the four parameters from the elastic constants c_{11}, c_{12}, c_{44} and the zone-center mode ω_R, because

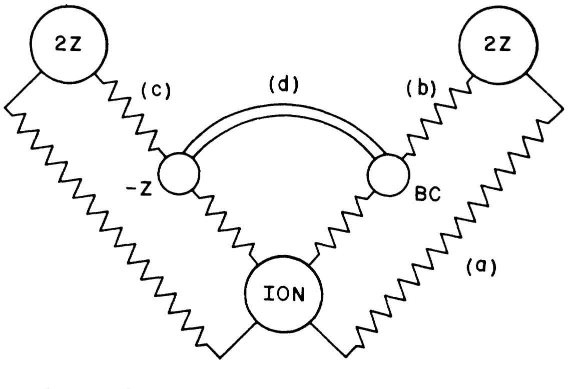

FIG. 2. Schematic presentation of the bond charge model. The four types of interactions (a)–(d) are discussed in detail in Sec. II.

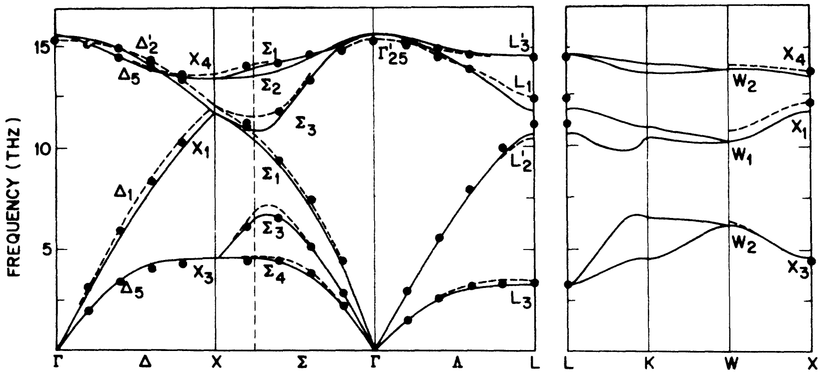

FIG. 3. Phonon dispersion curves for Si. Solid lines show the BCM results. The experimental values (solid circles) are from Refs. 25 and 28. Dashed lines represent the VFF calculations of Ref. 22.

ϕ''_{i-i} and $\phi''_{i-\mathrm{bc}}$ enter the expressions for the c_{ij} and ω_R in the same linear combination [see Eqs. (A2) and (A3)].

In Figs. 3–5, respectively, the calculated phonons curves for Ge, Si, and α-Sn are compared with the neutron data. The values of the model parameters are given in Table I, the calculated elastic constants are listed in Table II. For convenience, the values of the short-range force constants, as derived from the parameters of Table I, are given in Table IV.

The theoretical dispersion curves agree very well with experiment, the average deviation from the measured phonon energies is only about 2%, with some frequencies off by up to 5%. For Ge the agreement along the symmetry lines $L \rightarrow K \rightarrow W \rightarrow X$ which have not been fitted is of similar quality. In Si and α-Sn, phonons in these directions have not been measured yet. The elastic constants also compare very well with experiment, especially the shear moduli. In Figs. 3 and 5 we also show the calculations of Tubino *et al.*,[22] who use a six-parameter valence-force-field model; in Fig. 4 the results of Nelin's[30] BCM for Ge are displayed. For discussion of these models see Sec. V.

In the following, we discuss the influence of the various interaction terms on the dispersion curves. The direct ion-ion central force constant (FC) ϕ''_{i-i} dominates the optic phonons and the longitudinal-acoustic branches; the contributions from the BC interactions to these modes are less important. In principle, ϕ''_{i-i} also influences the TA branches, except at the X and L points (see, e.g., Ref. 10, Appendix). The importance of ϕ''_{i-i} depends, however, on the magnitude of the other interactions. In our case we find that—apart from the long-wavelength limit—a variation of ϕ''_{i-i} shifts the TA frequencies only very little. We conclude therefore that no stretching of bonds takes place in the TA modes; instead, the atoms move perpendicular to the bond directions. In contrast, the noncentral ion-ion FC ϕ'_{i-i}/r does influence the TA phonons. ϕ'_{i-i} balances the Coulomb forces in the equilibrium condition [Eq. (A9)]. However, ϕ'_{i-i} is quite small and negative, so that it actually destabilizes the TA phonons. It is of no interest in the following discussion.

The TA phonons are then determined only by the BC interactions (b)–(d) of Fig. 2. The most sensitive parameters for the shape and position of TA dispersion curves turned out to be the effective central and noncentral ion-BC FC's. They consist of the sum of the short-range term (c) and the nearest-neighbor part of the Coulomb interaction (b). The central FC is, in units e^2/v_a,

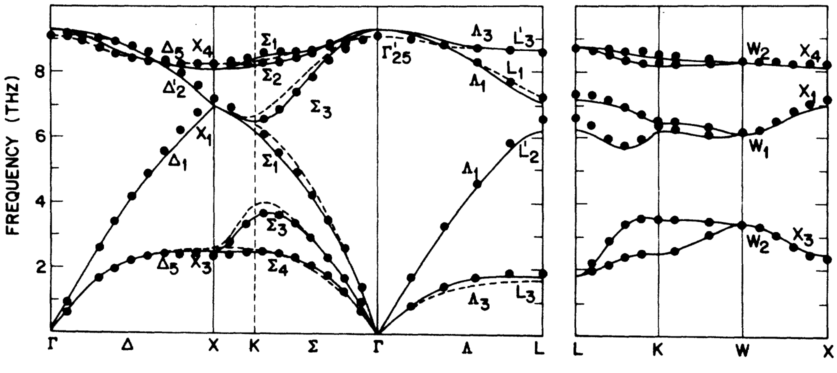

FIG. 4. Phonon dispersion curves for Ge. Solid lines show our BCM calculations. Experimental values are from Refs. 26 and 27. Dashed lines depict results of the BCM of Ref. 30.

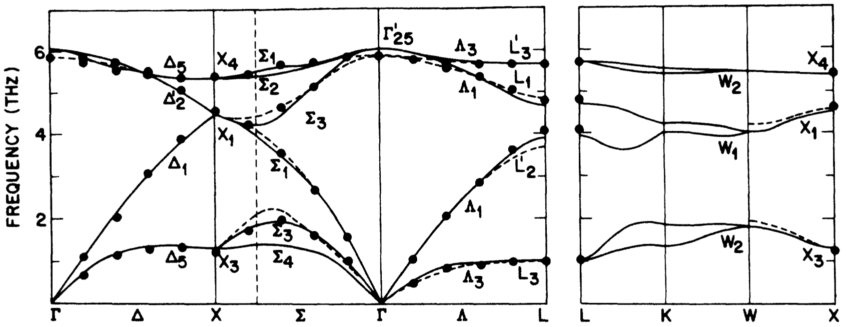

FIG. 5. Phonon dispersion curves for α-Sn. Solid and dashed lines, respectively, represent our BCM results and the VFF calculations of Ref. 22. Experimental values are from Ref. 29.

$$A_{\text{eff}}=\tfrac{1}{3}\phi''_{i\text{-bc}}-(512/9\sqrt{3})(z^2/\epsilon)\ . \qquad (3)$$

A_{eff} is very small, as (b) and (c) almost cancel each other. The noncentral FC is purely Coulombic

$$B_{\text{eff}}=(256/9\sqrt{3})(z^2/\epsilon)\ . \qquad (4)$$

The values of A_{eff} and B_{eff} are also given in Table I.

The flattening of the TA branches away from zone center is obtained when the effective ion-BC coupling constants are small compared to the bond-bond interaction (d). As the BC's adjust their instantaneous positions in order to avoid an increase of energy, they move in such a way that the potentials of type (d) are kept almost constant. As a consequence, hardly any forces are transmitted between the ions. This mechanism is illustrated in I by a one-dimensional model. It is shown that, in the case (d) ≫ (c), the ions vibrate like local modes or Einstein oscillators in an almost rigid BC lattice. The frequency of the dispersionless branch is determined by the weak ion-BC coupling. In one dimension, the ions and BC's move along the chain, i.e., all modes are longitudinal. [For this illustration, the direct ion-ion term (a) has been omitted.] The bond-bond interaction potentials (d) remain constant when the BC-BC distances do not change. This leads to the picture of isolated ions vibrating in "cages" of BC's. In one dimension, (d) is equivalent to a two-body BC-BC force. In the three-dimensional case, the atoms move perpendicular to the bond directions for the TA modes, and the term (a) is not involved, as was discussed above. The BC's may, however, move either along the bond or perpendicular to it, in order to keep the bond-bending energies (d) very small. Indeed, various possibilities for equipotential motions of the BC's around an ion exist. Closest to the "cage" picture comes the set of rigid rotations of the entire BC tetrahedron. Another set is best described as graphitelike displacement: One BC moves along the trigonal axis and the other three BC's move toward a planar configuration with respect to the ion.

The average frequency ω_{TA} of the TA phonons in the flat regions approximately obey the relation

$$\omega^2_{\text{TA}}\propto(A^{-1}_{\text{eff}}+B^{-1}_{\text{eff}})^{-1}\ ,$$

provided that at least one of the effective ion-BC

TABLE I. BCM parameters for diamond, Si, Ge, and α-Sn. All force constants are given in units e^2/v_a. Also listed are the effective central and noncentral ion-BC force constants A_{eff} and B_{eff}, as defined by Eqs. (3) and (4). The BCM for diamond has one additional parameter $a'^2=0.51r_0^2/16$ [see Eq. (5)].

	C	Si	Ge	α-Sn
$\frac{1}{3}\phi''_{i\text{-}i}$	−10.0	6.21	6.61	7.43
z^2/ϵ	0.885	0.180	0.162	0.163
$\frac{1}{3}\phi''_{i\text{-bc}}$	50.0	6.47	5.71	5.59
β	12.56	8.60	8.40	7.80
A_{eff}	20.91	0.56	0.40	0.21
B_{eff}	14.53	2.79	2.65	2.68

TABLE II. Theoretical and experimental values for the elastic constants, in units of 10^{12} dyn/cm^2. The c_{ij}^{exp} are taken from Ref. 15. For Ge, the theoretical values in brackets are those obtained by Ref. 30. Further listed are the BC susceptibilities [Eq. (A5)], and, for comparison, the dielectric constants ϵ [from J. A. Van Vechten, Phys. Rev. 183, 891 (1969)]. Also given are values of the internal strain parameter ζ [Eq. (A4)], the values in brackets are calculated with Keating's model (given in Ref. 37), the ζ^{exp} are from Ref. 43.

		C	Si	Ge	α-Sn
r_0 (Å)		1.78	2.715	2.825	3.23
c_{11}	Theor.	10.90	1.56	1.33(1.48)	0.79
	Expt.	10.76	1.66	1.29	
c_{44}	Theor.	5.53	0.78	0.65(0.61)	0.37
	Expt.	5.76	0.79	0.67	
$c_{11}-c_{12}$	Theor.	8.91	0.98	0.81(0.73)	0.44
	Expt.	9.51	1.02	0.81	
$4\pi\chi_{\text{bc}}$		0.50	1.40	1.70	3.46
ϵ		5.7	12	16	24
ζ	Theor.	0.12(0.21)	0.50(0.56)	0.52(0.55)	0.57
	Expt.	···	0.62 ± 0.04	0.64 ± 0.04	···

force constants is small compared to the bond-bond coupling constant β. If both $A_{\text{eff}} \ll \beta$ and $\beta_{\text{eff}} \ll \beta$, then all TA modes have almost the same, very small frequency. Yet the splitting of the TA branches away from $(\zeta, 0, 0)$ and (ζ, ζ, ζ) directions; e.g., along $(\zeta, \zeta, 0)$ depends sensitively on the ratio $A_{\text{eff}}/B_{\text{eff}}$. This is also true for the ratio $\omega_{\text{TA}}(X)/\omega_{\text{TA}}(L)$. In our least-squares fits for Si, Ge, and α-Sn, we used special weights to reproduce these features correctly, thereby spoiling slightly the agreement in the optic branches. When we omitted the special emphasis on the TA phonons, we could find a variety of parameter sets which, at first glance, give equally good results. Indeed we investigated even a three-parameter model, with ϕ''_{i-i} being completely replaced by $\phi''_{i-\text{bc}}$, so that $A_{\text{eff}} > \beta$, but $B_{\text{eff}} \ll \beta$. This model showed—apart from very good agreement in the optic and LA branches—reasonably flat curves for the purely transverse branches Δ_5, Δ_3 and Σ_4 along the $(\zeta, 0, 0)$, (ζ, ζ, ζ), and $(\zeta, \zeta, 0)$ directions, respectively. However, the ratio $\omega_{\text{TA}}(X)/\omega_{\text{TA}}(L)$ was not given correctly. Moreover, the Σ_3 branch along $(\zeta, \zeta, 0)$ had much too high a frequency and a strong longitudinal component.

In the long-wavelength limit, the BC's move in phase with the ions. Then they are situated on the midway position between the atoms, just as in Martin's model. In this limit, the strong bond-bond coupling β contributes fully to the dynamics of the atoms and produces the high values of the shear moduli. This property of the BCM is also illustrated in I for the one-dimensional case. It can further be shown that, in the elastic limit, our model is equivalent to Keating's model (see Sec. V).

Although for Si, Ge, and α-Sn, the agreement of our four-parameter model with experiment is very good, we investigated whether some remaining minor discrepancies could be removed by introducing additional interaction parameters. The main deviations from experiment occur near LA (L) and in the optic branches which have somewhat too large a bandwidth. A 2nn ion-ion coupling has been added, also various additional BC-ion-BC interactions, in particular in the form of valence-force-field potentials.[18,19] However, none of these terms gave a significant improvement over the original model, nor did—for the semiconductors—a linear term in the potential V_{bb}.

III. BCM FOR DIAMOND

The dispersion curves for diamond look quite different from those of the other group-IV elements (see Fig. 1). The TA branches do not show any flattening away from zone center: This is indicated by the ratio $\omega^2_{\text{TO}}(X)/\omega^2_{\text{TA}}(X) \approx 2$ compared to 12 in Ge. On the other hand, the LO branch along the $(\zeta, 0, 0)$ direction exhibits only little curvature; one finds $\omega^2_R(\Gamma)/\omega^2_{\text{LO}}(X) = 1.3$ (1.6 in Ge). Further, when normalized with the ion plasma frequency, the optic modes near Γ lie well below those of the semiconductors. Also in contrast to the other materials, the $X_1(\text{LA}, \text{LO})$ mode lies *above* the $X_4(\text{TO})$ mode. As a consequence of this inverse order, the Σ_3 branches in $(\zeta, \zeta, 0)$ direction have little separation in energy, especially near $\zeta = 0.7$.

Because of these substantial differences between diamond and the other materials, we also may expect qualitative changes in our model. It is obvious that the stiffening of the TA phonons leads to values of the ion-BC coupling constants A_{eff} and B_{eff} much larger than in Si or Ge. Moreover there occur new features in the optic branches, which we could not describe very well within the original model. Thus we modified the BCM by allowing for a linear term in the potential [Eq. (2)],

$$V_{\text{bb}} = \tfrac{1}{2}\beta(\vec{X}_{0i}\vec{X}_{0j} + a'^2)^2/4a^2 , \tag{5}$$

i.e., we now assume that $a'^2 \neq -r_{0i}r_{0j}$. This linear term is included in the equilibrium condition [Eq. (A9)] and is balanced by a linear term in $\phi_{i-\text{bc}}$. (The latter assumption is not essential for the results, equally well we could have used ϕ'_{i-i}.) The model has five disposable parameters, which were determined by fitting to the experimental phonon frequencies[31] at X, L, and $(0.7, 0.7, 0)$, and to the elastic constants. Further, the theoretical value of $\omega_R(\Gamma)$ was fixed to the experimental Raman frequency. The values of the parameters are given in Tables I and IV. In Fig. 6 the calculated dispersion curves are compared to the neutron data of Ref. 31. On the average, they deviate only by 1% from experiment, that is even better than the 2% average accuracy for the semiconductors. Our five-parameter model is of the same quality as the 11-parameter SM presented in Ref. 31, and the six-parameter valence-force-field (VFF) model of Tubino *et al.*[22] The differences between our theory and the other models are so small that they could not be displayed in Fig. 6. Maximum deviations of some frequencies are of order 3%, with $c_{11} - c_{12}$ (proportionate to ω^2) being off by 7%. We believe that it is possible to improve the agreement in $c_{11} - c_{12}$ by slightly changing the parameters, but we have not pursued this point any further.

The linear term in V_{bb} was found to be important for the optic branches, it helped to establish the inverse order of TO and LO at X. As mentioned above, this parameter did not improve the phonon dispersion curves for the semiconductors. The

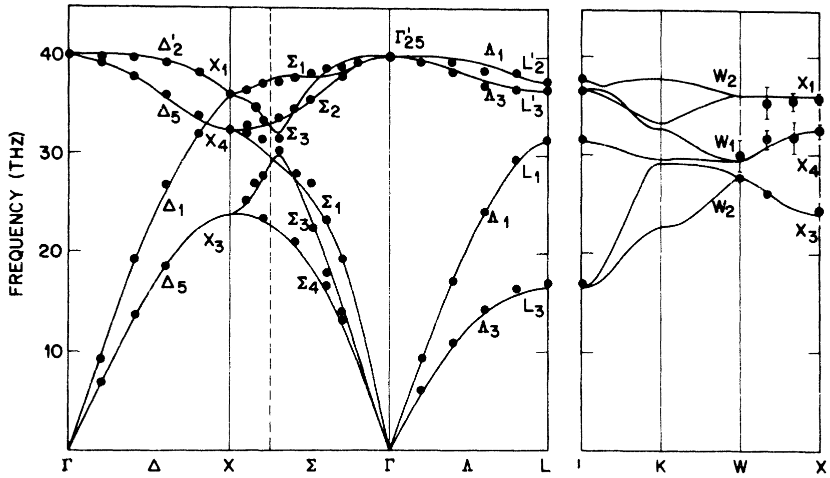

FIG. 6. Phonon dispersion curves for diamond. Solid lines represent the five-parameter BCM calculations. Experimental values are from Ref. 31.

term ϕ_{i-i}'' turns out to be negative, which looks like an unphysical result. However, in a different representation of the BCM, this shortcoming will be removed (see Sec. V).

We want to comment on a specific feature of the diamond dispersion curves. Between $0<\zeta<0.5$, the LO $(\zeta, 0, 0)$ branch shows very little dispersion, if any at all. It might even exhibit some overbending, so that the maximum phonon frequency need not be ω_R at Γ, as it is the case for the semiconductors, but some place along the $(\zeta, 0, 0)$ direction. The neutron data are inconclusive about this effect. Raman scattering studies[32] show, however, a small peak lying about 0.2% above $2\omega_R$. This peak has been interpreted either as a two-phonon bound state[33] or as an additional peak in the two-phonon density of states due to probable overbending of the LO$(\zeta, 0, 0)$ branch.[34] Our model does not exhibit the overbending even when the parameters are somewhat away from the best-fit values. Only when we include a very small 2nn ion-ion central force constant, we obtain the overbending. However, with this additional parameter, we do not improve the agreement with experiment at other q values. A BCM with small 2nn ion-ion FC's was taken as a basis for the calculation of the two-phonon Raman scattering by Go *et al.*[3] Using a bond polarizability model, they found very good agreement for the relative intensities of the main peaks. Owing to the overbending, they also obtained a peak in the Γ_1 spectrum for diamond near $2\omega_R$. Because of matrix element effects, this peak was much more enhanced over the pure two-phonon density of states than the other structures. This result was interpreted as a strong support of the overbending hypothesis.[3] Recently, it was argued that a careful calculation of the one-phonon dispersion in diamond, using the VFF model of Ref. 22, revealed an overbending of the LO branch.[35] Our model yields as good an overall agreement with experiment as that of Ref. 22, i.e., ≈1% average deviation but does not show the overbending. Since the effect at issue is of order 0.2%, we believe that model theories are inconclusive about this point.

IV. ALTERNATIVE REPRESENTATION OF THE BCM

The essential parameters for the TA phonons at short waves are the effective ion-BC coupling constants A_{eff} and B_{eff}. But they do not have a direct physical meaning because they are the sum of a short-range and a Coulomb part. We now define interaction potentials, which yield A_{eff} and B_{eff} as their coupling constants, thus allowing a better physical interpretation. These potentials incorporate the interaction of the BC with the *two* adjacent ions, in the spirit that the charge in a bond is shared between two ions.[13] The simplest central and noncentral potentials we can find are

$$V_{\text{c}}=\tfrac{1}{2}A(r_{0i}-r_{0j})^2 , \tag{6}$$

$$V_{\text{nc}}=\tfrac{1}{2}Br_{0i}\,r_{0j}(\Delta\theta_{i0j})^2 . \tag{7}$$

Here r_{0i} is the distance between BC 0 and ion i, and $\theta_{i0j}=\pi$ is the angle formed by the ions i and j and the BC 0. V_{c} and V_{nc} describe the resistance against a displacement of the BC away from the midway position, either parallel or perpendicular to the bond direction. The force constants derived from V_{c} and V_{nc} are given in Eq. (A8). We thus can identify

$$A=\tfrac{3}{2}A_{\text{eff}}=\tfrac{1}{2}\,\phi_{i-\text{bc}}''-(256/3\sqrt{3}\,)(z^2/\epsilon) , \tag{8}$$

$$B=\tfrac{3}{2}B_{\text{eff}}=(128/3\sqrt{3}\,)(z^2/\epsilon) . \tag{9}$$

V_{c} and V_{nc} also give rise to ion-ion force constants. These are $-\frac{1}{2}$ the value of the respective ion-BC FC [see Eq. (A8)]. As a consequence V_c and V_{nc} do *not* contribute to the elastic constants, *nor* to ω_R. Because of the ion-ion FC in V_c and V_{nc}, the ion-ion interaction has to be rearranged also. There we include the Coulomb forces between the ions so that all electrostatic forces along a bond are comprised in the short-range terms. The new central ion-ion FC A' is then given by

$$A' = \tfrac{1}{3}\phi''_{i-i} + (128/9\sqrt{3})(z^2/\epsilon) + \tfrac{1}{3}A \ . \qquad (10)$$

The noncentral ion-ion force constant has two contributions, both of Coulombic origin. One is the direct term, the other arises from the equilibrium condition. With the rearrangement of the Coulomb forces, the Madelung sum also changes to $\alpha_M^r = \alpha_M - 4 = 0.453$. Then, the term

$$\Delta\phi'_{i-i}/\tau = (16/9\sqrt{3})(\alpha_M - \alpha_M^r)(z^2/\epsilon)$$

and the equally large direct Coulomb term add up to $-\tfrac{1}{3}B$ and are absorbed in V_{nc}. The remaining noncentral FC

$$B' = (16/9\sqrt{3})\alpha_M^r z^2/\epsilon$$

is very small and has practically no effect on the dispersion curves. We note that with the assumption $\phi'_{i-bc} = 0$ in the old representation we have implicitly chosen the potential V_{nc}.

So far, the new representation is completely equivalent to the old one; the phonon dispersion curves have not been changed, as only the force constants have been rearranged. There are still four disposable parameters in the model, as the value of B is linked to the value of z^2/ϵ. For Ge we have also studied a model with five parameters by lifting the connection of B and z^2/ϵ. However, no real improvement over the original model was found; the effect of the residual Coulomb interaction is small for any reasonable value of z^2/ϵ, which may be expected from the small α_M^r. On the other hand, a purely short-range model with $z^2/\epsilon = 0$, gives very satisfactory results. This can be seen from Fig. 7. There we compare the full BCM for Ge with its short-range part, i.e., with the residual Coulomb interactions being switched off. The curves agree very well, only for the LA and LO branches near X and L, there are some differences. We thus conclude that all essential interactions in our model are of very short range, limited within nearest-neighbor distance.

V. DISCUSSION

The changes in the phonon dispersion curves of the four elements are reflected in their phonon densities of states (see Fig. 8). Again Si, Ge, and α-Sn have very similar density curves. There appear two large peaks at the high- and the low-frequency end of the spectra, arising from the TO and TA phonons, respectively. Between these peaks are two smaller ones, associated with the LA and LO phonons. When going toward α-Sn, the TA peak shifts toward zero, whereas the TO peak moves toward the ion plasma frequency. Also both peaks become narrower. The LO, LA peaks remain more or less the same. In contrast, the phonon density of states for diamond looks very different from those of the other elements. The pronounced TA peak has disappeared, instead, the TA phonons are distributed rather uniformly over a broad energy range. Also, the LO peak has been submerged in the TO peak, so that only one big peak is left arising from all the optic phonons. When scaled with the ion plasma frequency, this peak lies well below the center of the optic peaks in Si. On the other hand, the TA phonons are found at much higher energy in diamond than elsewhere. Only the LA peak lies at about the same position in all four elements.

The trends in the phonon spectra show up in the changes of the model parameters. This is seen from Table III, where the redefined parameters are listed for all four elements. The following trends are observed:

(i) The ion-ion central force constant A', representing the metal-like bonding, increases continuously from diamond to α-Sn. Because of the rearrangement of the Coulomb forces, the negative sign of ϕ''_{i-i} for diamond has disappeared, and the value of A' lies close to those of the other elements. A' essentially determines the frequency of the zone-center optic mode ω_R, which increases from C to α-Sn, when scaled with the ion plasma frequency (see Fig. 1). The increase of A' and ω_R may indicate the growing importance of the

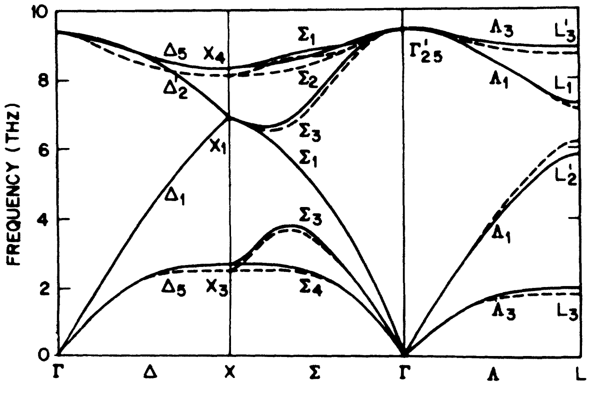

FIG. 7. Phonon dispersion curves for Ge as calculated from the short-range part of the BCM (solid lines). For comparison, the curves of the full model are given by dashed lines.

metallic bonding.

(ii) The parameters β, A, and B decrease toward α-Sn, with a big step between C on the one side and Si, Ge, and α-Sn on the other. These parameters represent the interactions involving the bond charge and reflect the strength of the covalent bonding. The bond-bending term β, which is the dominant contribution to the shear moduli c_{44} and $c_{11} - c_{12}$, changes by a factor 1.5 from C to Si. Even larger, by an order of magnitude, is the decrease in the ion-BC-ion terms A and B between C and Si. A and B determine the TA phonon frequencies at shorter wavelengths; their decrease causes the flattening of the TA branches in our model. The vanishing ion-BC coupling also indicates the impending instability of the diamond structure for the higher group-IV elements. In particular, the central force constant A would be nearly zero, when extrapolated to Pb.

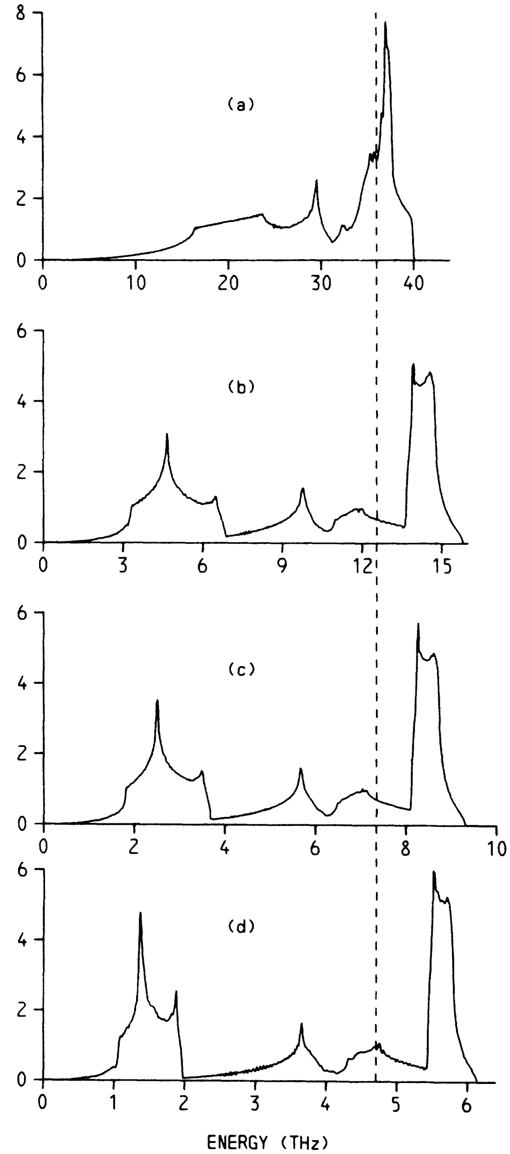

FIG. 8. Phonon densities of states, as calculated with the BCM, for (a) diamond, (b) Si, (c) Ge, and (d) α-Sn. The energy axes are normalized with the respective ion plasma frequencies. The vertical dashed line represents $\omega_{\text{pl}}/\sqrt{8}$. The areas of the density curves are also normalized.

A and B do *not* contribute to the long-wavelength phonons. There A' and β are the only important parameters, as the residual Coulomb forces are very small. Since in the elastic continuum limit the BC's move in phase with the ions, β can be written as an ion-ion term, as was mentioned earlier. Consequently, our BCM turns into Keating's model[15] at long wavelengths, and we can identify A' and $\frac{1}{4}\beta$ with Keating's bond-stretching and bond-bending terms α and β (see Table III). The values of A' and $\frac{1}{4}\beta$ are very close to those of Ref. 15, except for diamond, where the residual Coulomb forces are larger, and the linear term in V_{bb} [Eq. (5)] is included.

For all four elements, the value of the BC is close to $z = 2$, as used by Phillips and Martin. It would always be possible to choose $z \equiv 2$ and treat B as an independent parameter, without spoiling the fits to the phonon dispersion curves, because of the minor importance of the residual Coulomb interaction.

As the BC's move adiabatically, they contribute to the electronic susceptibility χ or the dielectric constant ϵ, which is defined as

$$\epsilon = \lim_{\vec{q}\to 0} \frac{1}{\epsilon^{-1}(q+G, q+G)} \bigg|_{G=0} .$$

This is different from $\lim \epsilon(q)$ as $\vec{q} \to 0$ because the inversion of the dielectric function $\epsilon_{GG'}$, leads to some contribution of the off-diagonal elements $\epsilon_{GG'}$, to the diagonal elements ϵ^{-1}_{GG}. Phillips and Martin assumed, however, that this difference is small for the semiconductors.[23,24] The quantity $4\pi\chi_{\text{bc}}$ [Eq. (A5)] represents the off-diagonal con-

TABLE III. BCM parameters in the new representation. For comparison, the force constants α_K and β_K of Keating's model (Ref. 15) are also listed. All FC's in units e^2/v_a.

	C	Si	Ge	α-Sn
A	31.36	0.84	0.60	0.32
B	21.8	4.43	3.98	4.03
A'	7.72	7.97	8.14	8.88
$\frac{1}{4}\beta$	3.14	2.15	2.10	1.95
α_K	6.31	8.42	7.56	...
β_K	4.14	2.39	2.35	...

tribution to ϵ, and, indeed, the values of $4\pi\chi_{\text{bc}}$ are small compared to ϵ. It has also been found by direct calculations of $\epsilon(q)$ from the band structure of Si and Ge, that the difference $\epsilon - \lim \epsilon(q)$ as $\vec{q} \to 0$ is small.[36]

Similar to Keating's model are the valence force field (VFF) models.[18-22] McMurray *et al.*[19] have presented a VFF model for diamond, and Solbrig[20] and Kress[21] have used similar models for Si and Ge. A complete study of all four elements was published by Tubino *et al.*[22] It is of interest to compare these results with ours. The two models yield phonon dispersion curves which agree equally well with experiment. For Si and α-Sn, the BCM is somewhat superior in the TA branches, the VFF model is slightly better in the optic branches (see Figs. 3 and 5). The Ge results should not be compared, as the VFF model was fitted to the old data of Ref. 9. For diamond, practically no difference exists between the two models, except of course, in the overbending issue (see Sec. III). The Tubino *et al.* model, the same as used in Ref. 19, employs six VFF potentials. Five of them, a 1nn bond-stretching term k_R, an angle-bending potential k_θ, and three correlation terms $k_{RR'}$, $k_{R\theta}$, and $k_{\theta\theta'}$ are limited within 2nn range. This means that all five independent 1nn and 2nn force constants [see Eq. (A10)] have been used. A sixth term $k_{\theta\bar{\theta}}$, correlating angles θ and $\bar{\theta}$ in the (110) plane which have one leg in common, extends up to 5nn. For these parameters the following trends are observed:

(i) k_R, by far the largest parameter, increases when scaled by e^2/v_a, from C to α-Sn, in a very similar way as A'.

(ii) The other important short-range terms k_θ and $k_{R\theta}$ decrease, relative to k_R, by about a factor of 2 between C and (Si, Ge, α-Sn). This is roughly the same change as observed for the Keating-type term β in our model. It should be noted that β can be expressed as a linear combination of k_θ, $k_{R\theta}$, and $k_{RR'}$.[37] The resulting ratio $k_\theta : k_{R\theta} : k_{RR'}$ is similar (but not equal) to those obtained in Ref. 22.

(iii) Relative to k_R, the term $k_{\theta\bar{\theta}}$ increases between C and α-Sn, with a big step from C to Si. $k_{\theta\bar{\theta}}$ includes the long-range interatomic forces required for the flattening of the TA phonons. In our model, however, these long-range forces are transmitted via the adiabatically moving BC's. The weaker the ion-BC coupling becomes, the stronger are the forces transmitted to higher neighbors and the longer their range.

An adiabatic bond charge model similar to ours has been proposed by Nelin.[30] However, in this model, the short-range interactions are treated very differently. The Phillips-Martin idea of the NFE-like screening has not been realized. Thus, no direct ion-ion forces are used; instead, all forces between the ions act via the BC's. Consequently χ_{bc} is fitted to χ_{exp}. For the ion-BC coupling, Nelin uses the VFF terms k_R, k_θ, $k_{R\theta}$, $k_{RR'}$, and $k_{\theta\bar{\theta}}$, in analogy to those of Refs. 19 and 22. The sixth parameter is the bond charge z. k_R and $(k_\theta, k_{RR'}, k_{R\theta})$ are similar to $\phi''_{i-\text{bc}}$ and β. However, $k_{\theta\bar{\theta}}$ is not limited within 1nn BC's, it couples directly to further distant BC's. We think that $k_{\theta\bar{\theta}}$ is not in the spirit of the model, as the long-range forces should arise from the adiabatic motion of the BC's, but not from direct coupling terms. Our four-parameter model is superior to Nelin's six-parameter fit, especially in the TA branches and in the elastic constants, which are off by about 10% in his model (see Fig. 4 and Table II). Moreover, the mechanism of TA flattening is not recognized.

We should note that in Ref. 30 it is incorrectly stated that the adiabatic BCM fulfills the so-called Rosenstock-Brout sum rule; i.e., the sum

$$S(q) = \sum_{i=1}^{6} \omega_i^2(q)$$

is q independent. Only Martin's BCM[23] fulfills this sum rule because there the BC's are fixed midway between the atoms. When the BC's are allowed to move from their equilibrium position, a sum rule

$$S' = \sum_{i=1}^{18} \omega_i^2(q) \neq S'(q)$$

holds for all 18 degrees of freedom; i.e., including the BC vibrations. Yet the partial sum over the six phonon modes may indeed show a q dependence. This result is not changed when the adiabatic approximation is applied. In our model we have calculated $S(\vec{q})$ and find a maximum variation for $S(q)$ of $\approx 4\%$ for Si, Ge, and α-Sn, and $\approx 20\%$ for diamond, very close to what is observed by experiment.[28]

Also discussed in Ref. 30 is a model by Vasil'ev *et al.*,[38] the so-called "broken-bond" model. This model is also quoted in Ref. 7. For the broken-bond model, very good agreement with experiment is reported, using only four parameters. However, we have been informed that it is *not* possible[39] to recalculate the dispersion curves given in Ref. 38. Moreover, attempts to find similar dispersion curves by refitting the model parameters failed.[40] It is suspected[39] that a basic numerical error led to these erroneous results of Ref. 38.

Another adiabatic bond charge model has been put forward by Johnson and Moore.[41] These authors consider only electrostatic interactions between various charge densities, which are centered both at the ion and the bond sites. The ion charge densities consist of a core and a "valence" contribution and follow rigidly any motions of the nuclei; however, the bond charge densities move adiabatically. The spherically symmetric charge densities, approximated by sums of Gaussians, have considerable overlap in order to avoid the Coulomb instability which would occur for non- or weakly overlapping densities. The charge distribution is adjusted to yield the phonon frequencies. The number of disposable parameters seems to be five or more, the results for diamond and Si are by far not as good as ours. We think that it is unphysical to simulate the quantum-mechanical forces which lead to the covalent bond by purely electrostatic interactions.

Very recently, Sokel and Harrison[42] have interpreted the long-range interatomic forces in Ge as arising from an exponentially decaying two-body type interaction with a decay length of $\hbar[2(m_1+m_2)E_g]^{-1/2}$, where m_1 and m_2 are the valence-band and conduction-band effective masses and E_g is the minimum energy gap. To obtain this result, these authors have studied the shift in energy caused by a displacement of a pair of atoms, to second order in the perturbation. They then concentrate on the phase space around the smallest gap using an effective-mass approximation for both the valence and conduction bands. We note that, in their calculation, a consideration of all bands throughout the Brillouin zone should result in an ion-ion interaction very similar to the NFE-like screening term of Martin.[23] Sokel and Harrison further argue that similar exponentially decaying forces are obtained when expanding the dynamical matrix of our BCM in terms of Born and von Kármán force constants for which only two-body interactions between atoms need to be considered. This result is derived from the linear chain BCM discussed in I, where it was used to illustrate the flattening mechanism. As the bond-bond interaction V_{bb} [Eq. (2)] happens to be a two-body term in one dimension, a Born and von Kármán expansion with two-body interatomic foces is indeed possible. In three dimensions, however, the bond-bending term β is a noncentral potential involving not two but *three* particles. A Born and von Kármán expansion of the BCM in three dimensions may also yield exponentially decaying interactions, but now involving noncentral; i.e., three-body and higher-order interactions, terms similar to $k_{\theta\theta'}$ discussed above. As we have mentioned in I and have shown in detail in Sec. II, the two-body ion-ion interactions are *not* involved in the TA flattening. We therefore cannot accept the interpretation given in Ref. 42 for the TA flattening as arising from exponentially decaying two-body interactions and equating these terms with the long-range forces in the BCM. We should also note that the effective-mass approximation for the conduction band is valid only in a very small phase space around the minimum gap. We thus estimate that the exponentially decaying term is very small compared to the total term.

In the BCM as presented here, it is assumed that the bond charge is a constant, and does not change under the motion of the atoms constituting the bond. What would be the effects of a model with a variable BC? We expect that the strongest change of the BC is induced when the bond length is varied and that changes due to bond bending are of secondary importance. Then, to first order, the variable BC does not influence the TA phonons, as in these modes the bond length does not vary (see Sec. II). Consequently, the mechanism for the TA flattening is not affected. However, there will be a first-order effect on all other phonons. We recall that the agreement for LA, LO, and TO branches—though still very satisfactory—is somewhat inferior to the results for the TA phonons. As mentioned in Sec. II we have not been able to remove these minor discrepancies by replacing β with the VFF potentials k_θ, $k_{RR'}$, and $k_{R\theta}$ or by 2nn ion-ion central forces. This may be an indication that the variable BC as a new feature in the model is needed to refine results for the non-TA phonons.

The improvement in the phonons cannot be dramatic however. We expect, though, that the result for the internal strain parameter ζ [Eq. (A4)] will be improved considerably. For Si and Ge, ζ deviates by $\approx 20\%$ from experiment (see Table II). The internal strain parameter ζ defines the sublattice shift under uniaxial pressure; e.g., along the [111] direction. In this case ζ describes the change in the bond lengths which exceed the dilation part.[43] Thus ζ indicates how "unequal" the [111] and, e.g., the $[1\bar{1}\bar{1}]$ bonds become under the uniaxial pressure. In the variable BCM, inequivalent bond lengths lead to different values of the BC's at the two bonds, or in other words, to a charge flow from one bond to the other. Its magnitude will in turn influence the value of ζ. It should be noted that ζ has only been measured for Si and Ge,[43] but not for diamond, where one might expect a particularly strong correction of a variable BC on ζ.

VI. CONCLUSION

In this paper we have given a detailed presentation of the adiabatic bond charge model for the phonons in group-IV elemental crystals with diamond structure. Our model is based on the bond charge model of Phillips and Martin. It describes the effect of the nearly-free-electron-like or metallic bonding by nearest-neighbor ion-ion forces (a) and represents the covalent bonding by interactions involving the BC's, part of which are the long-range Coulomb forces (b). In contrast to the Phillips-Martin model, where the BC's are always constrained on the midway position between the atoms, we allow that the BC's move adiabatically like the electronic shells in the shell model. As a consequence, we have to introduce short-range ion-BC central forces (c) in order to stabilize the BC's on their sites. In addition, we take into account bond-bending interactions of Keating type (d) between neighbor bonds (BC-ion-BC).

With this four-parameter model we obtain very good agreement with the experimental phonon dispersion curves of Si, Ge, and α-Sn. The average deviations are only $\approx 2\%$, even along symmetry lines not included in the fit. This agreement is of the same quality as that of six-parameter valence-force-field models and ten and more parameter shell models.

In particular, we show that with the adiabatic motion of the BC's, the typical flattening of the TA phonons away from zone center is achieved when the effective ion-BC coupling (b) + (c) is weak compared to the bond-bond interaction (d). In this limit, the frequencies of the TA phonons at short waves depend only on the effective central and noncentral ion-BC force constants A_{eff} and B_{eff}, obtained from (b) + (c). This leads to the picture of atoms vibrating like Einstein oscillators in a BC lattice. In the long-wavelength limit, however, the strong bond-bending term (d) dominates and yields the high values of the shear moduli. All other phonons are mainly influenced by the central ion-ion forces (a).

For diamond, a five-parameter BCM gives very good agreement with experiment (average deviation 1%), again of the same quality as a six-parameter valence-force-field model or a 12-parameter shell model. The dispersion curves of diamond do not exhibit the TA flattening, typical for the semiconductor materials. We thus find strong ion-BC coupling constants. The additional parameter, a linear term in the bond-bending potential (d), is necessary for a good fit of the optic branches, which exhibit some features not found in the dispersion curves of the semiconductors.

Further, the BC interactions are represented in an alternative way, guided by the idea that the charge in a bond is shared between the two constituting atoms. Central and noncentral ion-BC-ion interactions are defined with FC's A and B, directly equivalent to A_{eff} and B_{eff}. In this alternative representation the Coulomb FC's along a bond are combined with the short range FC's. This rearrangement also affects to some extent the ion-ion term (FC A'), especially for diamond, but not the bond-bond interaction (d) (FC β). It is found that the residual long-range part of the Coulomb forces is small and influences the phonon dispersion curves only little. Thus, all important interactions in our model are of very short range, none exceeding the nearest-neighbor ion-ion distance. All other models presented so far employ forces of much longer range. Furthermore, in the elastic continuum limit, (A) and (B) do not contribute, but only (A') and (β). Therefore, at long wavelengths, our model is equivalent to Keating's model.

The terms A', A, B, and β obey clear trends when going from diamond to α-Sn. A', which represents the strength of the metallic bonding, increases continuously toward α-Sn. A, B, and β decrease toward α-Sn, with a big step between diamond and Si. β is reduced least, by only a factor 1.5, yet A and B decrease by an order of magnitude reflecting the flattening of the TA phonons. In particular A tends toward zero when extrapolated toward Pb. This trend shows the weakening of the covalent bonding, which eventually limits the stability of the diamond structure for the higher group-IV elements.

Note added in proof. Concerning the problem of the two-body noncentral forces in the Born model (Sec. I), Professor H. Bilz has informed me that it can be proven that these forces do not violate the rotational invariance condition.

ACKNOWLEDGMENTS

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APPENDIX

The matrices $\phi_{xy}(l\kappa, l'\kappa')$ of the 1nn ion-BC and BC-BC FC's are

$$\phi_{xy}(l1, l3) = \begin{pmatrix} \alpha & \beta & \beta \\ \beta & \alpha & \beta \\ \beta & \beta & \alpha \end{pmatrix}, \quad \text{etc.},$$

$$\phi_{xy}(l3, l6) = \begin{pmatrix} \mu & \nu & \delta \\ \nu & \mu & \delta \\ \bar{\delta} & \bar{\delta} & \lambda \end{pmatrix}, \quad \text{etc.}$$

Here, the ions ($\kappa = 1, 2$) and BC's ($\kappa = 3, 6$) in a primitive unit cell are labeled according to Fig. 9. These matrices have the same form as the

1nn and 2nn ion-ion FC matrices.[10] We thus denote the latter ones by a prime.

The short-range part $\underline{D}_{\mathrm{SR}}$ of the dynamical matrix D for the BCM is obtained in the usual way.[44] $\underline{D}_{\mathrm{SR}}$ is conveniently divided into the respective ion-ion, ion-BC, BC-ion, and BC-BC matrices, $\underline{R}$, $\underline{T}$, $\underline{T}^{+}$, and $\underline{S}$. The Coulomb part $\underline{D}_C$ of D reads as

$$\underline{D}_C=\frac{e^2}{v_a}\frac{z^2}{\epsilon}\begin{pmatrix}4\underline{C}_R & -2\underline{C}_T\\ -2\underline{C}_T^{+} & \underline{C}_S\end{pmatrix}.$$

Here $v_a=2r_0^3$ is the volume of the primitive unit cell. $\underline{D}_C$ can be calculated using the Ewald transformation. The translational invariance condition leads to nonzero elements in the block diagonals of $\underline{S}$ and C_S, e.g.,

$$S_{xy}(3,3)=(2\alpha+4\mu+4\lambda)\delta_{xy}+(2\beta+4\nu)(1-\delta_{xy}),$$
$$(C_S)_{xy}(3,3)=83.9977(1-\delta_{xy}).$$

Using the adiabatic approximation, we can eliminate the 12 BC degrees of freedom. Then we obtain the equation of motion

$$\underline{m}\omega^2\underline{u}=\{\underline{R}+4(z^2/\epsilon)\underline{C}_R-[\underline{T}-2(z^2/\epsilon)\underline{C}_T]\times[\underline{S}+(z^2/\epsilon)\underline{C}_S]^{-1}[\underline{T}^{+}-2(z^2/\epsilon)\underline{C}_T^{+}]\}\underline{u},\tag{A1}$$

with $\underline{u}$ being the hypervector of the atomic displacements.

To obtain expressions for the elastic constants, we use the fact that the BC sites are centers of inversion. Thus, at long waves, the BC's have to move in phase with the atoms. We find

$$\begin{aligned}fc_{11}&=\tfrac{1}{2}\alpha+\alpha'+2\mu+8\mu'+2.22z^2/\epsilon,\\ fc_{12}&=\beta+2\beta'-\tfrac{1}{2}\alpha-\alpha'+2\nu+8\nu'\\ &\quad-\mu-4\mu'-\lambda-4\lambda'-28.54z^2/\epsilon,\\ fc_{44}&=\tfrac{1}{2}\alpha+\alpha'+\mu+4\mu'+\lambda+4\lambda'-1.11z^2/\epsilon\\ &\quad-(\tfrac{1}{2}\beta+\beta'-17.65z^2/\epsilon)^2/(\tfrac{1}{2}\alpha+\alpha'),\end{aligned}\tag{A2}$$

with

$$f=4r_0^4/e^2,$$

and the FC's given in units e^2/v_a.

For the zone-center optic mode, we get

$$m\omega_R^2=4\alpha+8\alpha',\tag{A3}$$

and for the internal strain parameter[37,43]

$$\xi=(\tfrac{1}{2}\beta+\beta'-17.65z^2/\epsilon)/(\tfrac{1}{2}\alpha+\alpha').\tag{A4}$$

As the BC's move adiabatically, they also contribute to the dielectric constant ϵ,

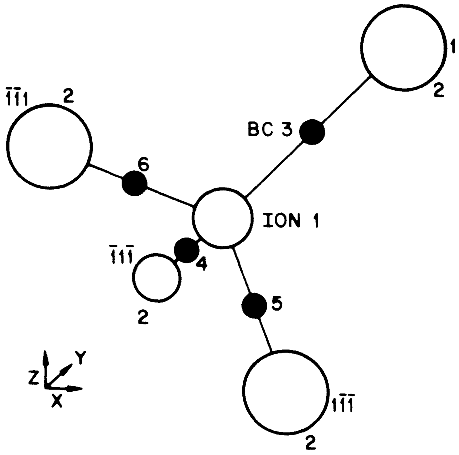

FIG. 9. Unit cell of the diamond structure with ions 1 and 2 (open circles) and BC's 3–6 (solid circles). The coordinates of the ions 2 with respect to the center ion 1 are indicated by 111, etc.

$$\begin{aligned}\epsilon_{\alpha\beta}^{bc}&=\epsilon^{bc}\delta_{\alpha\beta}\\ &=1+4\pi\chi^{bc}\\ &=\delta_{\alpha\beta}+4\pi\frac{z^2}{\epsilon}\lim_{\vec{q}\to 0}\sum_{\kappa\kappa'}\left(\underline{S}(\kappa\kappa')+\frac{z^2}{\epsilon}\underline{\tilde{C}}_S(\kappa\kappa')\right)^{-1}.\end{aligned}\tag{A5}$$

$\underline{\tilde{C}}_S$ is the regular part of $\underline{C}_S$, i.e., without the macroscopic electric field, ϵ is the NFE part of the dielectric constant.

We now give some force-constant matrices of the potentials which we used. A 1nn ion-BC central potential $\phi(r)$ leads to

$$\phi_{xy}(l1,l3)=\tfrac{1}{3}\phi''\begin{pmatrix}1&1&1\\1&1&1\\1&1&1\end{pmatrix}+\frac{1}{3}\frac{\phi'}{r}\begin{pmatrix}2&\bar{1}&\bar{1}\\ \bar{1}&2&\bar{1}\\ \bar{1}&\bar{1}&2\end{pmatrix}.\tag{A6}$$

The potential V_{bb} [Eq. (5)] yields

$$\begin{aligned}\phi_{xy}(l1,l3)&=\tfrac{1}{4}\beta\begin{pmatrix}2&\bar{2}&\bar{2}\\ \bar{2}&2&\bar{2}\\ \bar{2}&\bar{2}&2\end{pmatrix}-\tfrac{3}{4}\beta\left(1-\frac{a'^2}{a^2}\right)\delta_{xy},\\ \phi_{xy}(l3,l6)&=\tfrac{1}{4}\beta\begin{pmatrix}1&1&1\\1&1&1\\ \bar{1}&\bar{1}&\bar{1}\end{pmatrix}+\tfrac{1}{4}\beta\left(1-\frac{a'^2}{a^2}\right)\delta_{xy}.\end{aligned}\tag{A7}$$

For V_{c} and V_{nc} [Eqs. (6) and (7)] we obtain

$$\phi_{xy}(l1,l3)=\tfrac{2}{3}A\begin{pmatrix}1&1&1\\1&1&1\\1&1&1\end{pmatrix}+\tfrac{2}{3}B\begin{pmatrix}2&\bar{1}&\bar{1}\\\bar{1}&2&\bar{1}\\\bar{1}&\bar{1}&2\end{pmatrix},$$

$$\phi_{xy}(l1,l2)=-\tfrac{1}{3}A\begin{pmatrix}1&1&1\\1&1&1\\1&1&1\end{pmatrix}-\tfrac{1}{3}B\begin{pmatrix}2&\bar{1}&\bar{1}\\\bar{1}&2&\bar{1}\\\bar{1}&\bar{1}&2\end{pmatrix}. \tag{A8}$$

It is easy to see that neither V_c nor V_{nc} contribute to the elastic constants or to ω_R. In Table IV we give the values of the 1nn ion-BC, BC-BC, and ion-ion FC as obtained from the best-fit model parameters of Table I.

The energy per atom $E(\tau)$ as a function of the nearest-neighbor distance τ is[23]

$$E(\tau)=\sum_n m_n\phi_n(\tau)-\tfrac{1}{2}\alpha_M\frac{4z^2}{\epsilon}\frac{e^2}{\tau},$$

where the $\phi_n(\tau)$ are short-range two-body, etc., potentials and m_n are appropriate prefactors. The Madelung constant is $\alpha_M=4.453$. For the short-range potentials we will consider the ion-ion and ion-BC central potentials ϕ_{i-i} and $\phi_{i-\mathrm{bc}}$, and the bond-bond interaction V_{bb} [Eq. (5)]. The value of the BC is assumed to be independent of the bond length τ. Then the equilibrium condition reads as

$$\left.\frac{\partial E}{\partial\tau}=0\right|_{\tau=\tau_0}$$

$$=2\phi'_{i-\mathrm{bc}}(\tfrac{1}{2}\tau_0)+2\phi'_{i-i}(\tau_0)+\tau_0V'_{\mathrm{bb}}(-\tfrac{1}{12}\tau_0^2)+\tfrac{1}{2}\alpha_M(4z^2/\epsilon)(e^2/\tau_0^2).$$

TABLE IV. BCM force constants for diamond, Si, Ge, and α-Sn, as derived from the parameters of Table I (in units e^2/v_a).

	C	Si	Ge	Sn
α	51.68	10.77	9.91	9.49
β	45.26	2.17	1.51	1.69
μ	4.67	2.15	2.10	1.95
ν	3.14	2.15	2.10	1.95
λ	−1.61	−2.15	−2.10	−1.95
δ	3.14	2.15	2.10	1.95
α'	−18.16	4.57	5.14	5.94
β'	−6.10	7.03	7.35	8.18

This equation relates the first derivatives of the short-range potentials to the Madelung constant α_M. On the other hand, these quantities also contribute to the FC's [see Eqs. (A6)–(A8)]. We thus obtain a relation between the short-range FC's and the Madelung energy. We have generalized this relation to hold not only for the models discussed above but also for models which include other potentials ranging up to 1nn BC-BC or 2nn ion-ion distances. We have found

$$(\alpha-\beta)+2(\alpha'-\beta')+2(\mu+\lambda-\nu-\delta)+8(\mu'+\lambda'-\nu'-\delta')+27.42(z^2/\epsilon)=0\,. \tag{A9}$$

In particular, any VFF model with interactions up to 2nn ions obeys the relation

$$(\alpha'-\beta')+4(\mu'+\lambda'-\nu'-\delta')=0\,. \tag{A10}$$

i.e., there exist only five indepenent 1nn and 2nn FC's.

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