tude increase (for the $n=2$ excited state) over the ground state ($n=1$) calculation may be related to the nearly degenerate $2s$ and $2p$ exciton energy levels $E(2s)$ and $E(2p)$. In fact $[E(2p)-E(1s)]/[E(2p)-E(2s)] \simeq -17$ [R. Dinges, D. Fröhlich, B. Staginnus, and W. Staude, Phys. Rev. Lett. 25, 922 (1970).

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New Bond-Charge Model for the Lattice Dynamics of Diamond-Type Semiconductors

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A new bond-charge model for phonons in semiconductors of diamond structure is presented. I show that the flattening of the transverse acoustic phonon branches in these materials can be understood by interactions involving the bond charges, when these move adiabatically. The phonon spectrum of Ge is calculated using only four parameters, all of which are physically meaningful, and very good agreement with experimental values is obtained.

The phonon dispersion relations of all semiconductors with diamond or sphalerite structure[1] exhibit one characteristic feature, from which only diamond itself is excepted: The transverse acoustic (TA) phonon branches have very low frequencies and are very flat away from the zone center, although the corresponding shear moduli have rather high values. In the following, I show that this can be understood by interactions involving the bond charges (BC's), if these are allowed to move adiabatically. My model also enables us to elucidate the differences in the nature of the binding forces in the group IV materials.

Based on Phillips's bond-charge model[2] for covalent crystals, Martin[3] has used a dielectric screening model to calculate the phonon spectrum of Si. He assumed that the bare-ion-core potentials are screened in a nearly free-electron-like manner; i.e., by the diagonal elements of the inverse dielectric function $\epsilon^{-1}(\vec{q}+\vec{G}, \vec{q}+\vec{G}')$. This metallike binding gives rise to short-range central forces between the ions, which die out rapidly beyond nearest neighbors. The effect of the off-diagonal elements of ϵ^{-1} is described by Coulombic interactions involving the BC's. These forces represent the covalent character of the binding; they lead to effective noncentral forces between the ions, which produce the stability of the diamond structure against shear. The specific assumption was made that the BC's were fixed midway between the ions, even when the latter are displaced. Martin obtained fair agreement with experimental dispersion curves, except that the flattening of the TA phonons could not be reproduced.

In 1959, Cochran[4] pointed out that this flattening of TA branches, which in a Born and von Kármán model requires very long-range force constants,[5] is in fact due to mainly short-range ion-electron and electron-electron interactions. Cochran's shell model (SM), however, has many drawbacks. The noncentral two-body forces, which are crucial for the stability against shear, are not adequately understood.[6] Further, the electrons in a bond are shared by two atoms and it is unphysical to divide them between the two.[7] Finally, it turned out to be impossible to extend the SM to III-V compounds without introducing many new parameters, although the phonon spectra are very similar.[1]

The starting point of my work is the bond-charge model; i.e., I describe the effect of the metallike binding by central forces between nearest-neighbor ions; the covalent binding shows up in interactions involving the BC's. However, I relax the constraint that the BC's are fixed midway between the ions. Instead, I allow that the BC's move adiabatically like the electronic shells in a SM. As a consequence, I have to introduce short-range ion-BC forces in order to stabilize the BC's on their sites. I also take into account interactions between neighboring bonds.

The dynamical matrix in my model is derived in the usual way[8] by treating the BC's as independent lattice particles. In the harmonic and adiabatic approximations, the Fourier-transformed equations of motion for diamond-structure crystals may then be written as

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

$$\underline{\sigma} = [\underline{T}^+ - (2z^2/\epsilon)\underline{C}_T{}^+]\underline{u} + [\underline{S} + (z^2/\epsilon)\underline{C}_S]\underline{s}. \qquad (2)$$

Here m, z, and ϵ are the ion mass, the value of the BC, and the dielectric constant, respectively. The hypervectors $\underline{u}$ and $\underline{s}$ denote the displacements of the (two) ions and (four) BC's. $\underline{R}$, $\underline{T}$, and $\underline{S}$ are the respective Fourier-transformed force-constant matrices of the short-range ion-ion, ion-BC, and BC-BC interactions. $\underline{C}_R$, $\underline{C}_T$, and $\underline{C}_S$ denote the corresponding Coulomb matrices. The adiabatic approximation is expressed by having put the mass of the BC's equal to zero on the left-hand side of Eq. (2). Thus, we are able to eliminate the BC degrees of freedom $\underline{s}$ in Eq. (1).

We have limited the short-range ion-BC and BC-BC interactions to nearest neighbors. The corresponding force-constant matrices are of the same form as those between nearest and next-nearest neighbor ions, respectively.[9] Moreover, one can show that they enter the expressions for the elastic constants in the same manner as those ion-ion force constants, although divided by a factor of 2 or 4, respectively. This comes from the fact that, in the long-wavelength limit, the BC's move in phase with the ions, as if they were fixed midway between them, just as in the Phillips-Martin model. At shorter wavelengths, however, the BC's move adiabatically under the influence of net forces acting on them.

This is a crucial point for the understanding of the dispersion of TA phonons. To illustrate this, let us consider a monoatomic linear chain with BC's midway between the ions. We assume a short-range ion-BC force constant f, and for the sake of simplicity we neglect the Coulomb forces. The interactions between two neighboring bonds are described by a potential as first used by Keating:

$$V = (\beta/a^2)(\vec{x}_{0i}\cdot\vec{x}_{0j} + a^2/4)^2. \qquad (3)$$

Here $\vec{x}_{0i} = \vec{r}_{0i} + \vec{u}_0 - \vec{u}_i$ is the distance vector between atom 0 and BC i, with $\vec{r}_{0i}$ being the equilibrium value; further $a^2/4 = -\vec{r}_{0i}\cdot\vec{r}_{0j}$. In the linear case, V yields only a force constant $f' = \beta/2$ between neighboring BC's. Proceeding then along the lines sketched above, one finds the dispersion equation

$$m\omega^2 = 2f\frac{(f+2f')\sin^2(\frac{1}{2}qa)}{f+2f'\sin^2(\frac{1}{2}qa)}. \qquad (4)$$

The Phillips-Martin constraint leads to

$$m\omega^2 = 2f\sin^2(\tfrac{1}{2}qa) + f'\sin^2(qa). \qquad (5)$$

In Fig. 1, various dispersion curves are shown for the two approaches. The elastic constant $\propto f + 2f'$ is kept fixed for all curves, while the ratio f'/f is varied. If $f'/f \gg 1$, Eq. (4) depicts the typical flattening of the dispersion curve away from $q \approx 0$. In this case, the ions are coupled only weakly to the BC's, which form an almost rigid lattice. The ions vibrate like Einstein oscillators in this lattice, and their frequency is given by the weak ion-BC force constant f. Only in the long-wavelength limit, where the BC's move in phase with the atoms, does the strong bond-bond interaction contribute to the dynamics of the atoms, thus producing the high value of the

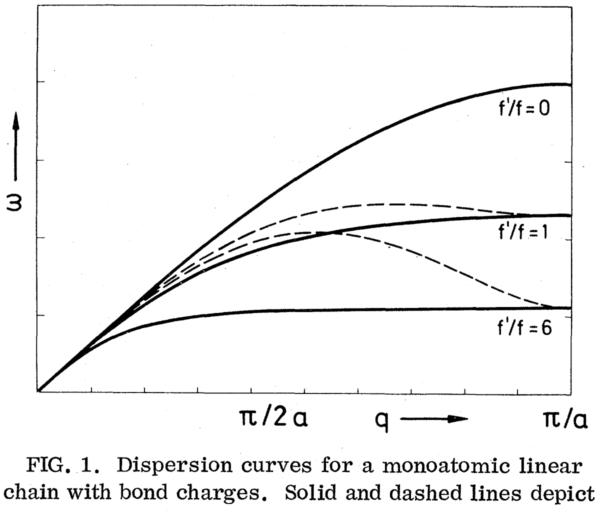

FIG. 1. Dispersion curves for a monoatomic linear chain with bond charges. Solid and dashed lines depict, respectively, the curves according to Eq. (4) (adiabatically moving bond charges) and Eq. (5) (Phillips-Martin constraint). The elastic constant is kept fixed for all curves.

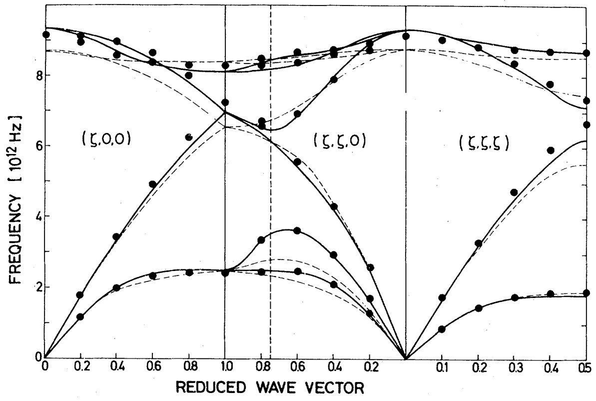

FIG. 2. Phonon dispersion curves for Ge. Solid circles represent the experimental values of Ref. 11. Solid lines show the results of my four-parameter bond-charge model. Dashed lines depict the results from the shell model of Ref. 4. The unpublished curves in the $(\zeta,\zeta,0)$ direction were kindly provided by W. Kress and K. Kunc.

elastic constant.

In our calculation for Ge we have used four types of interactions: (a) a central potential $\varphi_{i-i}(\tau)$ between nearest-neighbor ions; (b) Coulombic interactions of point charges at the sites of the ions and the bonds; (c) a central potential $\varphi_{i-\mathrm{BC}}(\tau)$ between nearest-neighbor ions and BC's; and (d) the interactions between two adjacent bonds described by Keating's potential as given in Eq. (3). The condition of stable equilibrium relates the first derivatives of the short-range potentials with the Madelung energy of the system (see Ref. 3).

The phonon dispersion curves of Ge, as calculated with this model, are shown in Fig. 2. They are compared to Cochran's five-parameter SM,[4] which also has the merit of limiting the short-range force constants within nearest neighbors.[10] In our model four parameters are used; their values have been found by a least-squares fit from the neutron data of Nilsson and Nelin.[11] Assuming $\varphi_{i-\mathrm{BC}}'=0$, we have obtained $\varphi_{i-i}''(\tau_0)=10.15$, $\varphi_{i-\mathrm{BC}}''(\tau_0/2)=8.76$, $\beta=4.3$ (all in units 10^4 dyn/cm); $z^2/\epsilon=0.1616$. The equilibrium condition leads to $\varphi_{i-i}'/\tau_0=-1.13$. The average deviation from experimental values of Ref. 11 is about 2%, while the maximum error at some frequencies is 5%. We may also compare the elastic constants (in units 10^{12} dyn/cm^2): $c_{11}=1.326$ (1.29), $c_{11}-c_{12}=0.825$ (0.81), $c_{44}=0.65$ (0.67); the experimental values as quoted in Ref. 6 are given in parentheses.

The direct ion-ion force constant φ_{i-i}'' dominates in all phonon branches except in the TA modes, which are independent of it. Thus, the TA phonons depend only on the interactions involving the BC's. Just as for the linear chain model, we obtain the peculiar shape of the TA branches if the interactions between neighboring bonds are rather strong as compared to the ion-BC coupling. The latter consists both of the short-range and the Coulomb part, which cancel each other partially, so that the effective ion-BC force constants are small: $\varphi_{\mathrm{eff}}''=0.61$ and $\varphi_{\mathrm{eff}}'/\tau_0=2.03$. The Coulomb interaction between more distant neighbors turns out to be less important; one can show that a short-range model with effective ion-BC force constants, but without a Coulomb term, yields very similar dispersion curves. The contribution of φ_{i-i}' due to the equilibrium condition also turns out to be small and, moreover, destabilizing. Furthermore, in the short-wave TA modes, the BC's approximately move on surfaces where the potentials of Eq. (3) remain constant. Therefore, in these modes, only very small forces are transmitted between the ions. Thus the ions vibrate like Einstein oscillators, and their frequencies are given by the magnitude of the effective ion-bond coupling.

In the long-wavelength limit, the strong bond-bond coupling yields the high values of the shear moduli. As was indicated above, in this limit the interactions involving the BC's can be written as effective interactions between the atoms. Apart from some Coulombic term, we obtain the bond-stretching and bond-bending force constants $\alpha_{i-i}=4.84$ (3.8), $\beta_{i-i}=1.07$ (1.3). These values are quite similar to those of Keating,[6] which are given in parentheses. Moreover, concerning more elaborate valence force field models,[12] the transmission of forces due to the adiabatic motion of the BC's provides a physical understanding of terms which correlate bond lengths and bond angles of adjacent tetrahedra.

Furthermore, the BC has the value of $z\simeq 1.6$, which is comparable to $z=2$ used by Phillips and Martin. However, in my model the BC's do contribute to the electronic susceptibility $\chi=(\epsilon-1)/4\pi$. I have obtained $4\pi\chi_{\mathrm{BC}}=1.7$. This number, which represents the off-diagonal contribution to ϵ, is small compared to $4\pi\chi_{\mathrm{exp}}=15$ in Ge. Thus, my result confirms the assumption of Phillips and Martin that the dominant part of ϵ comes from the diagonal or metallike screening. This is also corroborated by band-structure calculations.[13]

Detailed calculations for all diamond-type crystals will be presented elsewhere; here we summarize the most important results. When scaled with the ion plasma frequency, Si and α-Sn are very similar to Ge. In diamond, the ion-BC coupling is much stronger than in the other materials; the bond-bond interaction increases to a lesser extent. According to the above discussion, this can be seen from the variation both of the TA zone boundary frequencies and of the shear moduli. Furthermore, the direct ion-ion forces due to the metallike binding show up only in semiconductors; in diamond, however, all forces between the ions act via the bonds. Altogether, we find that, with the increase of the metallike binding, the sublattices of the ions and the BC's tend to decouple from each other.

I have presented a new bond-charge model for the phonons in tetrahedrally coordinated semiconductors. For Ge, I have obtained very good agreement with experimental phonon curves, using a four-parameter theory. The parameters describe the two types of binding in Ge. The metallike binding shows up in central forces between nearest-neighbor ions. These forces influence dominantly the longitudinal acoustic and the optic modes. The covalent binding is represented by interactions involving the BC's, only these forces determine the dispersion of TA phonons; they are essential for the stability of the diamond structure against shear. When the BC's are allowed to move adiabatically, the typical flattening of TA branches away from the zone center is obtained, if the ion-BC coupling is weak compared to the interactions between neighboring bonds. Thus, in the short-wave TA modes, the atoms vibrate like Einstein oscillators; at long waves, however, the strong bond-bond coupling contributes to the dynamics of the atoms, thus producing the high values of the shear moduli.

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Observation of Covalency Effects in K_2CuF_4 by Critical Scattering of Neutrons

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Direct evidence of covalency effects on spin densities of the $Cu^{2+} - F^-$ antibonding orbital in ferromagnetic K_2CuF_4 has been observed by means of critical scattering of neutrons. The form factor observed was in good agreement with the one calculated based on linear combination of atomic orbital wave functions using covalency parameters determined by NMR.

According to Hubbard and Marshall,[1] the form factor of a magnetic ion surrounded by ligand ions is modified by the covalency, and such effect should be observed directly by neutron scattering. This effect should produce on the form factor a forward peak at small scattering angles less than