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First- and Second-Order Dipole Moments of Homopolar Crystals*

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The first- and second-order electric moments of crystals having the homopolar structures of the diamond, zinc blende, and wurtzite types are treated on the basis of formal results obtained previously. This formal analysis is first reformulated in terms of localized functions closely related to Wannier functions so that (a) the electrons in a crystal may be treated more realistically and (b) the existing theoretical work for unperturbed lattices may be more readily applied. The magnitude of the second-order moments of one-dimensional analogs of germanium and silicon is shown to be smaller than those previously calculated for ionic crystals if the same anharmonicity is present. The corresponding moments of diamond itself are comparable with those of ionic crystals. The first-order moment calculation for the zinc blende and wurtzite cases demonstrates how the valence electrons tend to follow the anionic nucleus rather than the cation. Because of the lack of inversion symmetry present in these compound crystals, the second-order moment coefficients are different from those of the diamond-like crystals and are appreciably greater in magnitude than those in ionic crystals. From the magnitude of the second-order moments in diamond-like crystals, a crude estimate of the perfection necessary for the intrinsic second-order moment to make the dominant contribution to infrared absorption is made. This agrees well with existing experimental results. The results for the second-order moments of the zinc blende and wurtzite structures show that, in contrast with the results for the alkali halides, the second-order moment contribution to two-phonon absorption is comparable with the direct anharmonic contribution.

I. INTRODUCTION

In an earlier article,[1] hereafter referred to as I, it was shown, by means of a calculation based on a one-dimensional analog, that the second-order dipole moment of the alkali-halide type of crystal is relatively small and thus that the second-order moment contribution to two-phonon infrared absorption is small compared with the direct anharmonic contribution. It is the purpose of the present article to report calculations of the first- and second-order moments of the other important class of simple nonmetallic crystals, those with the predominately homopolar diamond, zinc blende, and wurtzite structures.

The magnitude of the second-order moments in these crystals is of considerable interest, mainly because it determines the relative contributions of second-order moment and anharmonicity mechanisms to the broadening of the fundamental lattice absorption line in the zinc blende and wurtzite structures[2,3] and to two-phonon absorption, generally. In the case of crystals with the diamond structure, the inversion symmetry present causes the first-order moment to vanish[2] and thus it becomes necessary to estimate how perfect such a crystal must be before the intrinsic second-order moment contribution to absorption dominates that due to the extrinsic first-order moment induced by strains, impurities, and other defects which remove the inversion symmetry locally. In the previous article, I, it was shown that the second-order moments of general crystals arise from anharmonicity (cubic anharmonicity, in particular). This purely formal result is sufficient to show that arguments regarding the relative contributions to two-phonon absorption in homopolar compound crystals which are based on estimates of the anharmonicity present[3] are invalid. In actual fact, it was tentatively suggested on the basis of the alkali halide results in I that the anharmonic and second-order moment effects are probably comparable in the more covalent solids. This suggestion was necessarily tentative since the model chosen for the alkali halides involved the shell-model approximation to the ions. While this is a fairly reasonable first approximation to the ions in very ionic solids, it is likely to be too crude for predominately covalent crystals where valence-electrons exchange effects are of considerable importance. It is necessary to treat the valence electrons of these crystals in a more realistic manner from the outset.

In the next section of this article, we review and recast the formal results obtained in I in terms of localized one-electron functions so that the electrons may be treated in greater detail. The third section is devoted to the discussion and calculation of the second-order moments of diamond-like crystals, which form a distinctly different class of solid, owing to the inversion symmetry present. The fourth section consists of a calculations of the first- and second-order moments of crystals of the zinc blende and wurtzite type. Although the formulation of Sec. II is quite general, the actual calculations are based on one-dimensional analogs of the real three-dimensional crystals.

II. THE DIPOLE MOMENT FORMALISM IN TERMS OF LOCALIZED ONE-ELECTRON FUNCTIONS

The formalism developed in I is based on the Born-Oppenheimer approximation and defined in terms of a general many-electron function. It involves the use of

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[1] P. N. Keating and G. Rupprecht, Phys. Rev. 138, A866 (1965).

[2] M. Lax and E. Burstein, Phys. Rev. 97, 39 (1955).

[3] E. Burstein, *Phonons and Phonon Interactions*, edited by T. A. Bak (W. A. Benjamin, Inc., New York, 1964).

electron displacement variables, formally defined in I as

$$\mathbf{v}(j,l)=\int[\Phi^*(\mathbf{x},\mathbf{r})\mathbf{r}(j,l)\cdot\Phi(\mathbf{x},\mathbf{r})-\Phi^*(\mathbf{x}_0,\mathbf{r})\mathbf{r}(j,l)\cdot\Phi(\mathbf{x}_0,\mathbf{r})]d^3r\,,$$

where $\mathbf{r}(j,l)$ is the position vector of the jth electron in the lth unit cell, the $\mathbf{x}$ and $\mathbf{r}$ represent the nuclear and electronic position vectors, respectively, and $\Phi(\mathbf{x},\mathbf{r})$ is the many-electron state function for the electrons in the distorted crystal. The $\Phi(\mathbf{x}_0,\mathbf{r})$ is the many-electron-state function for the crystal in its undistorted, equilibrium condition. Thus $\mathbf{v}$ is the displacement of the average position of an electron in the distorted crystal from its average position when the lattice is in its equilibrium state.

This definition in terms of the many-electron wave function is inconvenient if the electrons are to be considered in detail since any use of existing theoretical results will inevitably involve functions of the one-electron approximation. Furthermore, the electron labeling system could be improved since it is more convenient to associate an occupied electron state in nonmetallic crystals with a particular nucleus. We obviously wish to redefine the problem in terms of one-electron functions. The eigenfunctions $\psi_s(\mathbf{k},\mathbf{r})$ of the one-electron Hamiltonian of the equilibrium crystal are periodic functions and not really suitable for the present problem, which involves localized perturbations due to atomic displacements. A more suitable set of functions belonging to the equilibrium lattice are the localized Wannier functions centered around the equilibrium nuclear positions:

$$a_s(\mathbf{r}-\mathbf{x}_{j0})=\frac{\Omega^{1/2}}{(2\pi)^{3/2}}\int_{\text{zone}}\psi_s(\mathbf{k},\mathbf{r})e^{-i\mathbf{k}\cdot\mathbf{x}_{j0}}d^3k\,,$$

where s is a band index, Ω is the unit cell volume, and $\mathbf{x}_{j0}$ is the position vector of the jth nucleus. The integration is over one Brillouin zone. We note that we now have a more convenient labeling of the electrons: The nuclei are labeled by j and the electrons by j and s. There is one electron per occupied Wannier state. We can now define the electronic displacement variables by

$$\mathbf{v}_{sj}=\int[\varphi_s^*(\mathbf{r}-\mathbf{x}_{j0})\cdot\mathbf{r}\cdot\varphi_s(\mathbf{r}-\mathbf{x}_{j0})-a_s^*(\mathbf{r}-\mathbf{x}_{j0})\cdot\mathbf{r}\cdot a_s(\mathbf{r}-\mathbf{x}_{j0})]d^3r\,,\quad(1)$$

where $\varphi_s(\mathbf{r}-\mathbf{x}_{j0})$ is the localized function, derived from the Wannier function $a_s(\mathbf{r}-\mathbf{x}_{j0})$, and perturbed by the nuclear displacements. The band index s is not a good quantum number for the distorted crystal but is retained as a label to demonstrate the Wannier function to which φ tends as the perturbation vanishes.

The first-order dipole moment coefficient is thus[1]

$$\mathfrak{M}_{\alpha\beta}{}^{(1)}(k)=eZ_k\cdot\delta_{\alpha\beta}-e\sum_{s,j}\left(\frac{\partial v_{sj\alpha}}{\partial u_{k\beta}}\right)_0,\qquad(2)$$

where α, β are Cartesian coordinate labels, $\mathbf{u}_k=\mathbf{x}_k-\mathbf{x}_{k0}$ (i.e., the nuclear displacement), Z_k is the atomic number of the kth nucleus. The sum over s is a sum over occupied states and the derivatives are evaluated at "0," the lattice equilibrium condition. The labeling tends to become inordinately clumsy if the coordinate label is retained. We therefore adopt the same convention used in I and include the coordinate label in the nuclear label. In this case

$$\mathfrak{M}^{(1)}(k)=eZ_k-e\sum_{s,j}a_{jk}{}^s\,,$$

where $a_{jk}{}^s=(\partial v_{sj}/\partial u_k)_0$ and the summation over j does not include a sum over the corresponding coordinate label. It was shown in I that, using the new notation,

$$a_{jk}{}^s=\sum_{i,t}e_{ji}{}^{st}p_{ik}{}^t\,,$$

where $p_{ik}{}^t=(\partial F_{ti}/\partial u_k)_0$ if F_{ti} is a component of the force on the (t,i) electron, defined in terms of the one-electron functions by

$$\mathbf{F}_{ti}=-\langle\boldsymbol{\nabla}V\rangle_{ti}=-\int\varphi_t^*(\mathbf{r}-\mathbf{x}_{i0})\cdot\boldsymbol{\nabla}V(\mathbf{r})\cdot\varphi_t(\mathbf{r}-\mathbf{x}_{i0})d^3r\,,$$

if $V(\mathbf{r})$ is the total potential energy, including exchange terms. The $e_{ji}{}^{st}$ are most conveniently considered as forming a matrix **E** which is the inverse of a matrix **B** which has components

$$-b_{ij}{}^{ts}=-(\partial F_{ti}/\partial v_{sj})_0\,.$$

The formal expression [Eq. (7) of I] for $\mathfrak{M}^{(2)}(k,l)$, the second-order coefficient, is now

$$\begin{aligned}\mathfrak{M}^{(2)}(k,l)&=-e\sum_{s,j}(\partial^2v_{sj}/\partial u_k\partial u_l)_0\\&=-e\sum_{i,j,m,n;\,s,t,v,w}e_{ji}{}^{st}\cdot[q_{ikl}{}^t+r_{ikm}{}^{tv}a_{ml}{}^v\\&\qquad+r_{ilm}{}^{tv}a_{mk}{}^v+c_{imn}{}^{tvw}a_{mk}{}^va_{nl}{}^w]\,,\end{aligned}\qquad(3)$$

where, again, the sum over j does not include the sum over the corresponding coordinate label; the coefficients are defined

$$q_{ikl}{}^t=(\partial^2F_{ti}/\partial u_k\partial u_l)_0\,,$$
$$r_{ikm}{}^{tv}=(\partial^2F_{ti}/\partial u_k\partial v_{vm})_0\,,$$
$$c_{imn}{}^{tvw}=(\partial^2F_{ti}/\partial v_{vm}\partial v_{wn})_0\,.$$

The s, t, v, w are band labels and i, j, m, n are nuclear labels.

It is convenient to simplify Eq. (3) slightly:

$$\mathfrak{M}^{(2)}(k,l)=\sum_{m,n;\,v,w}(Q_{kl}+R_{km}{}^va_{ml}{}^v+R_{lm}{}^va_{mk}{}^v+C_{mn}{}^{vw}a_{mk}{}^va_{nl}{}^w)\,,\qquad(4)$$

where

$$Q_{kl}=-e\sum_{i,j;\,s,t}e_{ji}{}^{st}q_{ikl}{}^t\,,\quad R_{km}{}^v=-e\sum_{i,j;\,s,t}e_{ji}{}^{st}r_{ikm}{}^{tv}\,,$$

$$C_{mn}{}^{vw}=-e\sum_{i,j;\,s,t}e_{ji}{}^{st}c_{imn}{}^{tvw}\,,$$

and the coordinate label is excluded from the sum over j.

We note that the q, r, c coefficients are not all independent, even if no symmetry is present. The requirement that the force on an electron be invariant under an arbitrary displacement of the whole lattice [i.e., $\mathbf{F}_{si}(\mathbf{u},\mathbf{v})=\mathbf{F}_{si}(\mathbf{u}+\mathbf{d},\mathbf{v}+\mathbf{d})$] gives rise to the conditions

$$\sum_{j,t}(c_{ijk}{}^{stv}+r_{ijk}{}^{sv})=0\,,$$

$$\sum_{k,v}(q_{ijk}{}^{s}+r_{ijk}{}^{sv})=0\,.$$

Furthermore, the $q_{ijk}{}^{s}$ and $c_{ijk}{}^{stv}$ are coefficients of a quadratic form and are thus symmetrical:

$$c_{ijk}{}^{stv}=c_{ikj}{}^{svt};\quad q_{ijk}{}^{s}=q_{ikj}{}^{s}\,.$$

These requirements give rise to the conditions

$$\sum_{j,t}(C_{jk}{}^{tv}+R_{jk}{}^{v})=0=\sum_{k,v}(Q_{jk}+R_{jk}{}^{v})$$

and

$$C_{jk}{}^{ts}=C_{kj}{}^{st};\quad Q_{jk}=Q_{kj}\,. \tag{5}$$

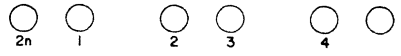
We also note that the requirement that the electron displacements also change by **d** if all the nuclei are shifted by this vector, gives rise to the useful sum rule

$$\sum_{i} a_{ji}{}^{s}=1\,. \tag{6}$$

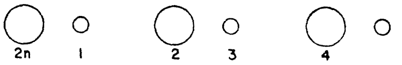
III. SECOND-ORDER MOMENTS OF CRYSTALS OF THE DIAMOND TYPE

The most important difference, from the point of view of the dipole moment, between diamond-like crystals and the alkali halides, and zinc blende and wurtzite crystals is the inversion symmetry present. The zinc blende and wurtzite crystal type has no inversion symmetry (see Fig. 1), of course, and that exhibited by the diamond structure is quite different from that present in the rock-salt type. In the latter case, an inversion operation couples atoms on the same sublattice (Fig. 1), but, in the diamond structure, atoms on the two different sublattices are coupled by inversion (Figs. 1 and 2). This difference gives rise to quite different conditions on the dipole moment coefficients, as Lax and Burstein have shown.[2] For example, in the diamond structure, the first-order coefficients vanish and $\mathfrak{M}^{(2)}(1,2)=0$, $\mathfrak{M}^{(2)}(1,1)=-\mathfrak{M}^{(2)}(2,2)$ where 1, 2 refer to atoms on the two different sublattices of a one-dimensional analog of the real crystal.[2] The remainder of the present work is also based on essentially one-dimensional models. The one-dimensional model of the diamond lattice on which the present calculations are based is shown in Fig. 2 together with a view of part of the three-dimensional model so that the relationship between them is apparent. We note that the points in the one-dimensional lattice correspond to planes in the three-dimensional system and that atoms labeled 1 and 3 are nonequivalent nearest neighbors of atom 2. The inversion symmetry present in the three-dimensional structure is plainly visible in the one-dimensional model.

(a) ROCKSALT STRUCTURE



(b) DIAMOND STRUCTURE



(c) ZINC BLENDE & WURTZITE STRUCTURES

FIG. 1. One-dimensional analogs of the three types of simple nonmetallic crystal, demonstrating their inversion symmetry.

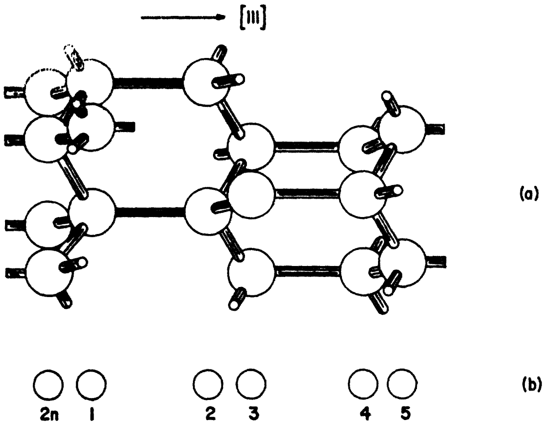


FIG. 2. Three- and one-dimensional models of the diamond type of crystal (a) view (approximately along ⟨11$\bar{2}$⟩ direction) of part of the three-dimensional model, (b) the corresponding one-dimensional analog.

Lax and Burstein have shown[2] that a combination of inversion symmetry requirements and the condition that the dipole moment is invariant under displacements of the whole lattice gives rise to the approximate relationship

$$\mathfrak{M}^{(2)}(1,1)=-2\mathfrak{M}^{(2)}(1,3)$$

if the coefficients $\mathfrak{M}^{(2)}(1,5)$, etc., are small. This result will be useful in computing the coefficient $\mathfrak{M}^{(2)}(1,1)$ since the direct calculation involves an appreciable number of canceling terms. However, we must first examine the validity of this approximation. The anharmonic coefficients C_{12}, C_{12N}, C_{11} will be comparable while C_{13} etc., will be very much smaller since changes in the second-nearest-neighbor interactions are largely dipolar in nature and thus much less anharmonic than the nearest-neighbor interactions, which involve large exchange and orthogonality effects. The largest term in $\mathfrak{M}^{(2)}(1,5)$ will thus be of order $C_{34}a_{31}a_{45}$ (i.e., of order $C_{12}a_{31}a_{23}$) since $a_{i,i+r}$ decreases as r increases. Similarly, the largest term in $\mathfrak{M}^{(2)}(1,3)$ is of order $C_{12}a_{11}a_{23}$ and thus the Lax and Burstein approximation rests on the inequality $a_{31} \ll a_{11}$. Now a_{31} is the electronic displacement induced on atom 3 by a displacement of nucleus 1. We can define harmonic coefficients k^{st}, k'^{st}, $k_1{}^s$ for the force constants between electrons on 1 and 2, between electrons on 2 and 3, and between an electron and its nucleus, respectively. Using similar reasoning to that used in I, we find that $a_{11} \approx 1$ and $a_{31} \approx kk'/k_1{}^2$ if $k_1 \gg k$, k'. The Lax and Burstein approximation is obviously valid when k, $k' \ll k_1$. Now k_1 can be related to the electronic polarizability, α_e, and k, k' to the elastic constants c_{11} and c_{12}. In the case of the alkali halides, it was shown in I that the c_{11} and α_e values were such that the approximation $k \ll k_1$ was a very good one. In the case of silicon and germanium, the refractive indices and c_{11}, c_{12} values are such that the approximation k, $k' \ll k_1$ is not unreasonble, although not as good as in the case of the ionic crystals in I. In diamond, however, the elastic constants are so large that k, k', k_1 are all comparable. Thus the Lax and Burstein approximation is valid for silicon and germanium but probably invalid for diamond itself. We shall therefore postpone consideration of the case of diamond until later. It is of interest to note in passing that these considerations show why the Born relation[4] between the elastic constants fails for diamond although it is very good for germanium and silicon. The Born relation is based on nearest-neighbor interactions only and obviously requires $a_{31} \ll 1$.

The inversion symmetry present in this type of crystal also imposes conditions on other coefficients. For example,

$$c_{111}{}^{rst} = -c_{222}{}^{rst} \quad \text{and} \quad c_{122}{}^{rst} = -c_{211}{}^{rst},$$

which leads to the condition

$$C_{11}{}^{st} = -C_{22}{}^{st}.$$

Similarly,

$$c_{112}{}^{rst} = c_{121}{}^{rts} = -c_{221}{}^{rst} \quad \text{so that} \quad C_{12}{}^{st} = -C_{21}{}^{st}.$$

Because of Eqs. (5), we have

$$C_{12}{}^{st} = -C_{21}{}^{st} = -C_{21}{}^{ts}.$$

In the same way, we can show that

$$R_{11}{}^{s} = -R_{22}{}^{s} \quad \text{and} \quad R_{12}{}^{s} = -R_{21}{}^{s}, \text{ etc.}$$

We can now proceed with the calculation of $\mathfrak{M}^{(2)}(1,3)$, which is

$$\mathfrak{M}^{(2)}(1,3) = \sum_{m,n;s,t} (Q_{13} + R_{1m}{}^{s}a_{m3}{}^{s} + R_{3m}{}^{s}a_{m1}{}^{s} + C_{mn}{}^{st}a_{m1}{}^{s}a_{n3}{}^{t}).$$

We note that Q_{13} involves second-nearest-neighbor anharmonicity which will be small, even in diamond, as we discussed previously. For the same reasons, coefficients such as R_{13} will also be negligible. Furthermore, C_{11} and C_{12} are likely to be comparable while a_{13} is appreciably smaller than a_{12} for silicon and germanium. Thus, to a fairly good approximation,

$$\begin{aligned}\mathfrak{M}^{(2)}(1,3) &\simeq \sum_{s,t} (R_{12}{}^{s}a_{23}{}^{s} + R_{32}{}^{s}a_{21}{}^{s} + C_{23}{}^{st}a_{21}{}^{s}a_{33}{}^{t} + C_{12}{}^{st}a_{11}{}^{s}a_{23}{}^{t}) \\ &= \sum_{s,t} (R_{12}{}^{s}a_{12N}{}^{s} + R_{12N}{}^{s}a_{12}{}^{s} + C_{2N1}{}^{st}a_{12}{}^{s}a_{11}{}^{t} + C_{12}{}^{st}a_{11}{}^{s}a_{12N}{}^{t}),\end{aligned}$$

where we have used the translational invariance properties of the lattice and the fact that $a_{12}{}^{s} = a_{21}{}^{s}$ because of inversion symmetry.

Now, for germanium and silicon, $a_{13}{}^{s} \ll a_{12}{}^{s} \ll 1$ so that, using the sum rule (6), we have $a_{11}{}^{s} \simeq 1$. Thus, we have the approximate results

$$\mathfrak{M}^{(2)}(1,3) \simeq \sum_{s,t} [(R_{12N}{}^{s} - C_{12N}{}^{st})a_{12}{}^{s} + (R_{12}{}^{s} - C_{12}{}^{st})a_{12N}{}^{s}] \quad (7)$$

and

$$\mathfrak{M}^{(2)}(1,1) = 2\sum_{s,t} [(C_{12N}{}^{st} - R_{12N}{}^{s})a_{12}{}^{s} + (C_{12}{}^{st} - R_{12}{}^{s})a_{12N}{}^{s}]. \quad (8)$$

IV. FIRST- AND SECOND-ORDER MOMENTS OF CRYSTALS OF THE ZINC BLENDE AND WURTZITE TYPES

The lack of inversion symmetry in this type of structure, which is partly ionic, means that there are no conditions which cause any of the moment coefficients to vanish. There are, however, a number of conditions imposed by general invariance requirements such as those given in Sec. II. The condition of the first-order moment coefficients

$$\mathfrak{M}^{(1)}(1) = -\mathfrak{M}^{(1)}(2)$$

is another general condition due to the invariance of the dipole moment under lattice displacements[2] (i.e., because of neutrality).

We shall assume that the core electrons are sufficiently well bound to their nucleus that their contribution to the dipole moment is just that due to their moving fully with the nucleus. We take "1" as referring to the cation sublattice and "2" to the anions. Thus,

$$\mathfrak{M}^{(1)}(1) = e[1 - \sum_{s,j} a_{j1}{}^{s}],$$

where $s = 1, 2, 3, 4$, ranging over the valence electrons. If we utilize the sum rule (6) and, initially, ignore terms of higher order than $a_{21}{}^{s}$ and $a_{12}{}^{s}$,

$$\mathfrak{M}^{(1)}(1) \simeq e[-1 + \sum_{s} (a_{12}{}^{s} - a_{21}{}^{s}) + (a_{12N}{}^{s} - a_{2N1}{}^{s})].$$

But the effective charge on the cation in these crystals is *positive* and thus we see that $a_{12}{}^{s} > \frac{1}{4}$. In other words, the electrons in the valence Wannier states centered

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[4] See, for example, H. B. Huntington, *Solid State Physics* (Academic Press Inc., 1958), Vol. 7, p. 299.

about the cations respond strongly to movements of the neighboring anion. This effect, quite different from the case of silicon and germanium, reflects the fact that the valence charge density is concentrated near the anion nuclei. Thus we see that the (harmonic) interaction between the cation nucleus and its Wannier valence electrons is roughly comparable with that between the Wannier states belonging to the neighboring nuclei; in other words, $k \sim k_1$. It is reasonable to assume that the interaction between the valence electrons of the anion and the anion nucleus is much larger. It is, indeed, necessary to make this assumption since otherwise the electronic polarizability and refractive index would be much larger than the experimental values. Thus we have k, $k' \sim k_1 \ll k_2$ and thus we expect $a_{21}{}^s \ll 1$. Because $a_{12}{}^s$ is relatively large, it is necessary to examine the magnitude of $a_{13}{}^s$; however, it is obvious that the condition $k_2 \gg k$, k' ensures that this term will be small. Thus, to a reasonable first approximation,

$$\mathfrak{M}^{(1)}(1) = e\Big[-1+\sum_s (a_{12}{}^s + a_{12N}{}^s)\Big] = -\mathfrak{M}^{(1)}(2)\,, \quad (9)$$

where the summation term is greater than unity.

We now proceed to the calculation of the second-order moments. The dominant coefficient $\mathfrak{M}^{(2)}(1,1)$ is given by

$$\mathfrak{M}^{(2)}(1,1) = \sum_{m,n;\, s,t} \big[Q_{11} + 2R_{1m}{}^s a_{m1}{}^s + C_{mn}{}^{st} a_{m1}{}^s a_{n1}{}^t\big]$$

$$\simeq \sum_{s,t} (Q_{11} + 2R_{11}{}^s + C_{11}{}^{st})\,, \quad (10)$$

since $a_{21}{}^s$, etc., are small compared with unity. The other dominant coefficient is

$$\mathfrak{M}^{(2)}(2,2) = \sum_{m,n;\, s,t} \big[Q_{22} + 2R_{2m}{}^s a_{m2}{}^s + C_{mn}{}^{st} a_{m2}{}^s a_{n2}{}^t\big]. \quad (11)$$

In this case, there are some off-diagonal contributions since $a_{12}{}^s > \frac{1}{4}$. The other coefficients can be calculated in the same way from Eq. (4).

It is interesting to see how the terms in expression (10) vanish when the inversion symmetry of the diamond structure is present. The dominant terms vanish because the general invariance requirements [Eqs. (5)] when coupled with the symmetry conditions, require

$$Q_{11} = \sum_{s,t} C_{11}{}^{st} = -\sum_s R_{11}{}^s, \quad Q_{12} = 0.$$

We are then left with the next largest terms such as $C_{12} a_{11} a_{12N}$ which occur in Eq. (8). No such cancellation occurs for the compounds, of course.

V. DISCUSSION

The very different results obtained in Secs. III and IV demonstrate the importance of the presence of inversion symmetry as far as the first- and second-order dipole moments are concerned. It is proposed to discuss these results in more detail at this point; this discussion is most conveniently carried out in separate subsections.

1. Discussion of the Results for Diamond-Like Crystals

It can be seen from expressions (7) and (8) that the second-order moments are again linearly dependent on the anharmonic nearest-neighbor coupling coefficients as in the ionic crystal case reported in I. It is instructive to compare the magnitudes of the second-order moment coefficients calculated here for diamond-like crystals and those determined in I for ionic crystals. In the rocksalt case the largest coefficient was found[1] to be of order eA/k_1 where A is an anharmonic coupling constant for the nearest-neighbor electron-electron interaction (other anharmonic interactions were neglected). If, for comparison pureposes, we include only the electron-electron terms, we note[1] that C_{12} is of order $eA/(k_1+k+k')$ and thus the largest coefficient in germanium and silicon is of order $eAk/k_1{}^2$, which is somewhat smaller than the dominant term in the alkali halides for the same degree of anharmonicity. The case of diamond itself can be discussed semiquantitatively by analogy with the germanium and silicon results. We conclude that the second-order moment of diamond will be comparable with that calculated for ionic crystals since the k_1 values are again not very different and $k \sim k_1$.

Because of the present lack of a reliable estimate of the magnitude of the dipole moment induced by imperfections, it is difficult to estimate the relative contributions of the intrinsic second-order moment and the extrinsic moment. We can, however, obtain a crude estimate by assuming that the relation of the extrinsic moment in the diamond-like crystal to the first-order moment of an ionic crystal is in proportion to the relative imperfection concentration. In other words, we get an order of magnitude estimate by taking the extrinsic moment as $c.\ \mathfrak{M}_{\text{ion}}$, where c is the imperfection concentration and $\mathfrak{M}_{\text{ion}}$ is the first-order moment of an alkali halide. As in I, we use Szigeti's treatment[5,6] of the different contributions to one- and two-phonon processes. For the intrinsic second-order moment contribution to two-phonon absorption to be comparable with the extrinsic first-order contribution to one-phonon absorption, we require, using Szigeti's notation,

$$c\alpha_0/\omega \sim (\hbar/\omega^3)^{1/2}\beta\,,$$

where ω is the optical phonon frequency, $\alpha_0 \sim \mathfrak{M}^{(1)}{}_{\text{ion}}/\mu^{1/2}$, $\beta \sim \mathfrak{M}^{(2)}/\mu$, and μ is the reduced mass of the ion pair.

Thus, we require

$$ce/\mu^{1/2} \sim (\hbar/\omega)^{1/2}(4eAk/\mu k_1{}^2)\,,$$

i.e.,

$$c \sim 4(\hbar/\mu\omega a_0{}^2)^{1/2}(k/k_1)^2\,,$$

if we take, as a crude estimate of the anharmonicity,

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[5] B. Szigeti, Proc. Roy. Soc. (London) **252**, A217 (1959).
[6] B. Szigeti, Proc. Roy. Soc. (London) **258**, A377 (1960).

$A \sim k/a_0$ where a_0 is the nearest-neighbor distance. Taking $k \simeq 0.15 k_1$ for silicon and germanium, as suggested by the elastic constant and refractive index data, we obtain a "critical" imperfection concentration in the order of 3.10^{-3}, corresponding to a density of around 10^{18} cm^{-3}.

The density will be somewhat higher in the case of diamond itself, of course. In view of the crude nature of this estimate, the agreement with the experimental results of Collins and Fan[7] is good.

It is of interest to note that the shell model fails in a very obvious way in the calculation of the second-order moments of diamond-like crystals. Using the shell model, the second-order moment is very much smaller than the results of Eqs. (7) and (8) because there is further cancellation. The coefficient $C_{12}^{ss}=0$ by virtue of the inversion symmetry present and thus $C_{12}=C_{12N}=0$ for the shell approximation. Furthermore, the general invariance requirements (5), with the inversion symmetry, then cause the R_{12} and R_{12N} to vanish and the calculated second-order moment is very much smaller.

2. Discussion of Results for Homopolar Compound Crystals

The calculation of the first-order moment is of primary interest because of the light it sheds on the nature of the harmonic interactions in these solids. The improvement of the Wannier function model of the electronic structure over the shell model is particularly striking in this case. For example, if we were to use the shell model we should have to assume an anionic charge of $+3$ electronic units and then that the deformability of the anion was much more extensive than that of the cation, to bring the effective charge to about $+\frac{1}{2}$. This is to be constrasted with the more realistic result that the valence electrons actually follow the anion to a larger extent than the cation. We note that, for most of the III-V and II-VI compounds having the zinc blende and wurtzite structures, we can expect $a_{13} \ll 1$ and thus the Born relation between the elastic constants to hold. However, in view of the behavior of diamond, we can expect that, for some of the large band-gap III-V compounds such as BN, the Born relations may again fail because k is no longer small compared with k_2.

The second-order moment of Eq. (10) is seen to be quite large. We expect C_{11}^{st} to be in the order of $eA/(k_1+k+k')$ and thus $\mathfrak{M}^{(2)}(1,1)$ is roughly the same (formally) as the largest second-order moment of the ionic crystals. Furthermore, the first-order moment is very similar to that in the alkali halides, as we can see by comparing values[3] of the Szigeti effective charge, which is closely related to the first-order coefficient. We follow the same arguments, based on Szigeti's work,[5,6] which were used in I to estimate the relative contributions to two-phonon absorption from second-order moment and anharmonicity mechanisms. The ratio of the two Hamiltonian terms is[1]

$$|H_A/H_M| \sim (Z_{\rm eff}/4k')(k_1+k+k'),$$

where $eZ_{\rm eff}$ is the Szigeti charge and the factor 4 arises from the number of valence electrons. Now $Z_{\rm eff} \simeq \frac{1}{2}$ for most of the III-V's, for example, and $k,k' \simeq k_1$. Thus, the direct anharmonic contribution is comparable with the contribution from the second-order mechanism. The conclusions of Geick,[8] based on experimental absorption data, are in agreement with this. This result is quite different from that obtained in I for very ionic crystals, the difference being due to the much increased deformability of the valence electron charge density. It is instructive to consider this difference further from a physical viewpoint.

The valence electrons in ionic crystals can sensibly be considered as belonging to the anion and are strongly coupled to the anionic nucelus; their interaction with electrons on the neighboring cations is small. Thus the deformability of the valence electrons is relatively small. In predominately covalent crystals, however, the charge density is not associated with any one ion (although it is concentrated around the anion) and Wannier valence states associated with neighboring sites interact relatively strongly via exchange. This electron-electron coupling is comparable with the coupling between the cationic Wannier states and the cation nucleus and thus the electronic deformability is appreciably greater than in the case of the very ionic solids.

Burstein's qualitative arguments[3] on this point agree with this part of the discussion and we note that the difference between his qualitative conclusion and the present quantitative result is due to the invalid argument concerning the magnitude of the anharmonicity present.

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