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# Lattice Vibrations of Zincblende Structure Crystals*

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In this article we present expressions, based on the shell model of lattice dynamics, for all important long-wavelength properties of the lattice vibration spectrum of a zincblende structure crystal, and for the vibration frequencies having wave vectors at the Brillouin zone boundary in the [100] direction. General first and second neighbor short-range force constants are used. The formulas are presented in the distortion dipole form of Mashkevich and Tolpygo, which uses one constant, $\alpha$, to describe the electronic polarizability of each atom, rather than the two redundant constants $Y$ and $k$, the shell charge and polarization spring, respectively, used in the shell model. Some of the force constants in our expressions are evaluated for GaAs, InSb, AlSb, and ZnS with the aid of available experimental data. We were unable to fit all of the data for any substance with only first neighbor force constants. When small, realistic values of second neighbor constants were used, a multitude of fits resulted. The absence of a criterion determining the "best" fit results in a spread of possible ionic charge values of about one electronic charge for the 3–5 compounds, and an inability to decide whether ZnS is very ionic or rather covalent. Our results point up the necessity of calculations of atomic force constants from fundamental quantum mechanics.

## I. INTRODUCTION

In recent years a great deal of effort has been expended by many workers in theoretical studies of the lattice vibration spectra of compounds which crystallize in the zincblende structure.[1–6] This work has been stimulated by the ever increasing availability of relevant experimental data on these compounds, by the need for accurate vibration spectra in connection with studies of properties involving electron-lattice interactions (e.g., electron transport properties and the absorption of electromagnetic radiation by crystals), and by recent work on the strong connection between the vibrational and electronic structures of crystals.[7–9]

The early theoretical work[1,2] was rather crude, being based on the traditional rigid ion model as summarized definitively by Born and Huang.[10] This model was not capable of correlating the large range of available experimental information, and any conclusions drawn at that time concerning interesting parameters such as the effective ionic charge, if correct, are only fortuitously so.

The shell model, originated by Dick and Overhauser,[11] and extensively developed by Cochran[12,13] and Cowley,[8] and the largely equivalent distortion dipole formulation by Tolpygo and his students[7,14] have led to more complex but much more realistic treatments of the vibration spectra of zincblende structure crystals. The most complete treatment to date, by Tolpygo,[6] attempts to correlate, with some success, a wide range of long-wavelength information. Since that time Demidenko, Kucher, and Tolpygo[15] (hereafter DKT) have made an extremely careful analysis of the vibration spectra of the similar diamond-structure compounds germanium and silicon, for which the experimental data are extremely refined, due particularly to the availability of dispersion curves in symmetry directions in the Brillouin zone as determined by inelastic neutron scattering experiments. This analysis shows that a model of germanium vibrations analogous to the one used by Tolpygo in his study of zincblende structure crystals is not adequate because it omits some first neighbor and all second neighbor short-range force constants.

In this article, we present expressions for various experimentally obtainable quantities for zincblende structure crystals based on a model of comparable generality to the successful model of DKT for germanium and silicon. The model includes all first neighbor short-range force constants, and all second neighbor short-range force constants that can influence the expressions that we have derived. Our expressions are given in a form similar to that used by Tolpygo and some of them are quite cumbersome. This form has the advantage that two redundant parameters which appear

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[15] Z. A. Demidenko, T. I. Kucher, and K. B. Tolpygo, Fiz. Tverd. Tela **3**, 2482 (1961); **4**, 104 (1962) [translation: Soviet Phys.—Solid State **3**, 1803 (1961); **4**, 73 (1962)].

in the shell model, which is merely a mechanical realization of a quantum-mechanical result, are eliminated. This has been pointed out by Cochran[12] and by Cowley.[8] However, the derivation of the formulas will be presented in shell-model terms. Fortunately, several of the expressions are simple enough so that it is possible to devise a procedure whereby various fits to the experimental data may be obtained. The data for each substance consist of the elastic constants, the piezoelectric constant, the low- and high-frequency dielectric constants, the reststrahl frequency and the four phonon frequencies at the Brillouin zone boundary in the [100] direction. (For two of the substances considered the piezoelectric constant had not been measured and we used a reasonable guess for this parameter.) This task has been carried out with the aid of an IBM 709 computer for ZnS, GaAs, InSb, and AlSb and the results will be discussed later. Two qualitative conclusions will be noted here: (1) It is not possible to arrive at a well-defined value for the effective ionic charge for any of the compounds studied; (2) for each substance it was necessary to use some second neighbor constants in order to fit the experimental information.

It is already clear on fundamental grounds that our calculation will have to be superseded by a more accurate one. The quantum-mechanical justification of the model by Tolpygo[7] is based on the Hartree-Fock one-electron approximation and, therefore, does not properly include electron correlation effects. The quantum-mechanical treatments of Cowley[8] and Mashkevich[9] are schematic and are based on assumptions that have not been rigorously justified, and probably imply a neglect of at least some correlation effects. A recent calculation by Adler[16] shows how the high-frequency dielectric constant can be modified to incorporate electron correlation effects in the random-phase approximation while simultaneously including local field effects. The results have important bearing on the interpretation of ionic charge parameters. Similar calculations for the elastic constants and other properties which include ionic motion, perhaps using the formalism of Baym,[17] and the development of an appropriate mechanical model for the quantum-mechanical results are necessary before the next level of understanding is reached in the theory of lattice vibrations.

In Sec. II we present our general results. Section III describes the application of these results to the four crystals mentioned above. The results are discussed in Sec. IV. The evaluation of various lattice sums is treated in an Appendix.

## II. VIBRATIONS OF ZINCBLENDE STRUCTURE CRYSTALS

The geometry of the zincblende structure and many formal features of the vibration spectrum problem for this structure have been discussed in great detail by Merten.[1] We will not repeat any of this work but merely mention a few essential points in the way of orientation.

Each of the two types of ions in the zincblende structure occupies the sites of a face-centered cubic lattice, where we take the cube side to have a length $2a$. The second such lattice is displaced along the body diagonal of the first lattice by one quarter of the cube diagonal $(\sqrt{3}/2)a$. The three basis vectors that define the rhombohedral parallelepiped unit cell are

$$\mathbf{a}_1=a(0,1,1),\quad \mathbf{a}_2=a(1,0,1),\quad \mathbf{a}_3=a(1,1,0).$$

We place the negative ion in the position $\mathbf{x}_1=(0,0,0)$ and the positive ion at the position $\mathbf{x}_2=\frac{1}{2}a(1,1,1)$ within the cell. It is necessary to specify which ion is at the origin because an interchange of the ions causes a change in sign of the piezoelectric constant. The volume of the unit cell is $v=2a^3$. The mass of the negative ion core is $M_1$ and that of the positive ion core is $M_2$. Both shells are massless.

General first and second neighbor force constant matrices for zincblende structure crystals are:

first neighbor at $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$,

$$\begin{bmatrix} \alpha & \beta & \beta \\ \beta & \alpha & \beta \\ \beta & \beta & \alpha \end{bmatrix};$$

second neighbor at (1,1,0),

$$\begin{bmatrix} \mu & \nu & \delta \\ \nu & \mu & \delta \\ -\delta & -\delta & \lambda \end{bmatrix}.$$

When one uses the shell model, there is a matrix of the first neighbor type for core-core (CC), shell-shell (SS) and each of two types of core-shell (CS) interactions (see Fig. 1). There are separate second neighbor matrices for the two types of atoms in the unit cell, and for each of these there are core-core, shell-shell, and one core-shell types. The shell charges are $Y_1$ and $Y_2$ and the core charges are $X_1$ and $X_2$. The total ionic charges are $Z_1=X_1+Y_1$ and $Z_2=X_2+Y_2$. Charge neutrality requires $X_1+X_2+Y_1+Y_2=0$. The constants $k_1$ and $k_2$ represent isotropic coupling of each core to its own shell.

With the parameters of our model specified we may

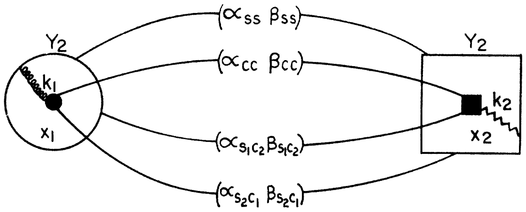

FIG. 1. The most general nearest-neighbor shell model for zincblende structure vibrations showing the force constants connecting the different degrees of freedom $(\alpha,\beta,k)$ and the charges of the different degrees of freedom $(X,Y)$.

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[16] Stephen L. Adler, Phys. Rev. **126**, 413 (1962).

[17] G. Baym, Ann. Phys. (N. Y.) **14**, 1 (1961).

follow the procedure indicated in the previous shell-model calculations [8,12,13] in order to find dispersion curves $\omega(\mathbf{y})$ for various directions in reciprocal space, and expressions for various macroscopic parameters of interest. The shells and cores are treated as separate degrees of freedom, but since the shells are massless the equations of motion for the shells do not add additional branches to the vibration spectrum. These equations establish a relation between core and shell displacements and thus serve to eliminate the shell displacements from the core equations of motion, while simultaneously introducing the shell polarization effects into the core motions. We will write down a few important formulas here and refer the reader to the above references for a more detailed treatment.

The dispersion curves $\omega(\mathbf{y},j)$ are obtained by solving the secular equation:

$$|\omega^2(\mathbf{y},j)\delta_{kk'}\delta_{\alpha\beta}-M_{\alpha\beta}(\mathbf{y};kk')|=0, \tag{1}$$

where $\mathbf{y}$ is the wave vector, $j$ is the branch of the vibration spectrum, $\alpha$ and $\beta$ are cartesian indices, and $k$ and $k'$ are indices corresponding to the different cores in the unit cell. The relative amplitudes of the various cores in the normal mode $\mathbf{y}$, $j$ are obtained from the equations:

$$\omega^2(\mathbf{y},j)w_\alpha(k)=\textstyle\sum_{k'\beta} M_{\alpha\beta}(\mathbf{y};kk')w_\beta(k'). \tag{2}$$

The time-dependent core amplitudes in a normal mode are

$$u_\alpha{}^{\mathrm{C}}(k,l)=\exp\{2\pi i\mathbf{y}\cdot[\mathbf{x}(l)+\mathbf{x}(k)]-i\omega t\}w_\alpha(k)/[M_k]^{1/2}, \tag{3}$$

and the shell amplitudes are

$$u_\alpha{}^{\mathrm{S}}(k,l)=-\exp\{2\pi i\mathbf{y}\cdot[\mathbf{x}(l)+\mathbf{x}(k)]-i\omega t\}\sum_{\gamma,\beta,k_1,k'} D_{\alpha\gamma}{}^{\mathrm{SS}}(kk_1)C_{\gamma\beta}{}^{\mathrm{SC}}(k_1k')w_\beta(k')/[M_{k'}]^{1/2}, \tag{4}$$

where $\mathbf{x}(l)+\mathbf{x}(k)$ is the undisplaced position of a core or shell at the $k$th site in the $l$th unit cell. The matrix elements $M_{\alpha\beta}(\mathbf{y},kk')$ are given by

$$M_{\alpha\beta}(\mathbf{y};kk')=[M_kM_{k'}]^{-1/2}\{C_{\alpha\beta}{}^{\mathrm{CC}}(kk')-\sum_{\gamma,\delta,k_1,k_2} C_{\alpha\gamma}{}^{\mathrm{CS}}(kk_1)D_{\gamma\delta}{}^{\mathrm{SS}}(k_1k_2)C_{\delta\beta}{}^{\mathrm{SC}}(k_2k')\}, \tag{5}$$

where $D^{\mathrm{SS}}=(C^{\mathrm{SS}})^{-1}$, and the $C$ matrices are given by

$$C_{\alpha\beta}{}^{\mathrm{CC}}(kk')=\sum_{l'}\exp\{2\pi i\mathbf{y}\cdot[\mathbf{x}(l')+\mathbf{x}(k')-\mathbf{x}(l)-\mathbf{x}(k)]\}\Phi_{\alpha\beta}{}^{\mathrm{CC}}(l-l';kk'), \tag{6}$$

with similar expressions for $C_{\alpha\beta}{}^{\mathrm{CS}}(k,k')$, $C_{\alpha\beta}{}^{\mathrm{CS}}(k,k')$, and $C_{\alpha\beta}{}^{\mathrm{SS}}(k,k')$. Here the $\Phi$'s are force constants connecting the indicated degrees of freedom. Note that the first shell or core superscript belongs with particle $k$ and the second with particle $k'$.

For symmetry directions in the Brillouin zone the above expressions simplify considerably. For example, for propagation in the [100] direction we find a separation into transverse and longitudinal modes; the transverse optic and transverse acoustic branches of the spectrum are twofold degenerate. The symmetry properties of the zincblende structure have been treated in detail by Parmenter[18] and Dresselhaus[19]; Merten[1] and Srinivasan and Rajagopal[2] have made specific application of symmetry considerations to zincblende vibration problems. We will not discuss symmetry here but merely use its consequences when necessary.

In all above expressions we have followed, as closely as possible, the notation of Born and Huang.[10] It should be pointed out that the force constants must be divided into Coulomb and non-Coulomb contributions. We have given the nonzero, non-Coulomb constants of our model, above. The Coulomb effect has been discussed for the shell model by Cochran[12,13] and is also treated for rigid ion lattices in references 1, 2, and 10, the last reference being particularly thorough. The results of calculations of some lattice sums at special points in the Brillouin zone are given in Appendix A.

In order to evaluate some number of parameters of our model with the aid of experimental data we need, in addition to the solutions of Eq. (1) for particular points in $\mathbf{k}$ space, expressions for a number of long-wavelength parameters: the elastic constants $C_{11}$, $C_{12}$, and $C_{44}$, the piezoelectric constant $e_{14}$, and the total and electronic polarizabilities $\alpha_t$ and $\alpha_e$. Expression for $C_{11}$, $C_{12}$, $C_{44}$, $e_{14}$, and $\alpha_t$ can be derived by using the procedure of paragraphs 31, 32 of reference 10. In applying this procedure to the shell model we treat the cores and shells equivalently, formally ascribing a mass to each shell. In the final expressions all masses, both shell and core, cancel out justifying the procedure. The

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[18] R. H. Parmenter, Phys. Rev. **100**, 573 (1955).

[19] G, Dresselhaus, Phys. Rev. **100**, 580 (1955),

electronic polarizability, $\alpha_e$, can be found by taking a limit of the total polarizability in which the cores cannot move. The simplest way to do this is to let all core-core constants become indefinitely large.

Rather than stating our results in terms of shell-model constants it is convenient to use constants closely related to those used by Tolpygo and his school.[6,15] This change of notation is desirable because the new constants, which are based closely on the quantum-mechanical justification of the shell model, are two fewer in number than the shell-model constants. This reduction takes place because the quantum-mechanical derivation relates the polarizability of an ion to one constant, $\alpha$, rather than to two constants, the shell charge $Y$ and the polarization spring $k$, as in the shell model. The correct combinations of shell-model constants may be found by writing the potential energy for the system in terms of core displacements and electronic dipoles associated with each ion rather than in terms of shell and core displacements, using a procedure similar to that followed by Cochran for germanium. The results are as follows:

$$\begin{aligned}
\alpha_1&=(k_1+4\alpha_{\mathrm{S_2C_1}}+4\alpha_{\mathrm{S_1S_2}}+8\mu_{\mathrm{S_1C_1}}+4\lambda_{\mathrm{S_1C_1}})/Y_1^2,\\
\alpha_2&=(k_2+4\alpha_{\mathrm{S_1C_2}}+4\alpha_{\mathrm{S_1S_2}}+8\mu_{\mathrm{S_2C_2}}+4\lambda_{\mathrm{S_2C_2}})/Y_2^2,\\
G&=4(\alpha_{\mathrm{SS}}+\alpha_{\mathrm{S_1C_2}}+\alpha_{\mathrm{S_2C_1}}+\alpha_{\mathrm{CC}}),\\
H&=4(\beta_{\mathrm{SS}}+\beta_{\mathrm{S_1C_2}}+\beta_{\mathrm{S_2C_1}}+\beta_{\mathrm{CC}}),\\
g_1&=4(\alpha_{\mathrm{S_1C_2}}+\alpha_{\mathrm{SS}})/Y_1,\\
g_2&=4(\alpha_{\mathrm{S_2C_1}}+\alpha_{\mathrm{SS}})/Y_2,\\
h_1&=4(\beta_{\mathrm{S_1C_2}}+\beta_{\mathrm{SS}})/Y_1,\\
h_2&=4(\beta_{\mathrm{S_2C_1}}+\beta_{\mathrm{SS}})/Y_2,\\
\mathcal{G}&=4\alpha_{\mathrm{SS}}/(Y_1Y_2),\\
\mathcal{H}&=4\beta_{\mathrm{SS}}/(Y_1Y_2).
\end{aligned}$$

For $i=1$, 2,

$$\begin{aligned}
K_i&=4(\mu_{\mathrm{S}_i\mathrm{S}_i}+2\mu_{\mathrm{S}_i\mathrm{C}_i}+\mu_{\mathrm{C}_i\mathrm{C}_i}),\\
L_i&=4(\lambda_{\mathrm{S}_i\mathrm{S}_i}+2\lambda_{\mathrm{S}_i\mathrm{C}_i}+\lambda_{\mathrm{C}_i\mathrm{C}_i}),\\
N_i&=4(\nu_{\mathrm{S}_i\mathrm{S}_i}+2\nu_{\mathrm{S}_i\mathrm{C}_i}+\nu_{\mathrm{C}_i\mathrm{C}_i}),\\
k_i&=4(\mu_{\mathrm{S}_i\mathrm{C}_i}+\mu_{\mathrm{S}_i\mathrm{S}_i})/Y_i,\\
l_i&=4(\lambda_{\mathrm{S}_i\mathrm{C}_i}+\lambda_{\mathrm{S}_i\mathrm{S}_i})/Y_i,\\
n_i&=4(\nu_{\mathrm{S}_i\mathrm{C}_i}+\nu_{\mathrm{S}_i\mathrm{S}_i})/Y_i,\\
\mathcal{K}_i&=4\mu_{\mathrm{S}_i\mathrm{S}_i}/Y_i^2,\\
\mathcal{L}_i&=4\lambda_{\mathrm{S}_i\mathrm{S}_i}/Y_i^2,\\
\mathcal{N}_i&=4\nu_{\mathrm{S}_i\mathrm{S}_i}/Y_i^2.
\end{aligned}\tag{7}$$

We have ignored the force constant $\delta$ because it does not occur in any of our results.

Several points should be noted:

(1) $\alpha_1$ and $\alpha_2$ reflect the fact that ions one and two are polarizable. Second neighbor shell-model constants of core-shell type occur in their definitions. Thus the use of the new form suppresses the occurrence of second neighbor constants in many expressions.

(2) We could have made the transformation from shell and core amplitudes to shell and dipole amplitudes *before* finding the long-wavelength limit. However, we would not then have been able to use the general formulas of Born and Huang because the eigenvalue equation would have involved the frequency in the off diagonal as well as in the diagonal terms.

(3) The capital italic letters can be interpreted as rigid atom constants, i.e., the force constants that would obtain if each nucleus and its electron cloud suffered no relative motion during an oscillation. The lower case italic letters are rigid-atom, dipole constants; and the capital script letters are dipole, dipole constants.

The long-wavelength parameters are given below:

$$2aC_{11}=\tfrac{1}{4}G+0.25Z_1^2/v+K_1+K_2;\tag{8a}$$

$$2aC_{12}=\tfrac{1}{2}H-\tfrac{1}{4}G-2.64Z_1^2/v+N_1+N_2-\tfrac{1}{2}(L_1+L_2+K_1+K_2);\tag{8b}$$

$$2aC_{44}=\tfrac{1}{4}G+\tfrac{1}{2}(L_1+L_2+K_1+K_2)-0.12Z_1^2/v+10.04Z_1e_{14}/a+[1-(4\pi/3v)\alpha_t]^{-1}\{25.2(Z_1/v)^2\alpha_t-C/B\},\tag{8c}$$

where

$$B=G(\alpha_1\alpha_2-\mathcal{G}^2)+g_1(g_2\mathcal{G}-\alpha_2g_1)+g_2(g_1\mathcal{G}-\alpha_1g_2),$$

and

$$\begin{aligned}
4C=H^2(\alpha_1\alpha_2-\mathcal{G}^2)&+2H[h_2(\mathcal{G}g_1-\alpha_1g_2)+h_1(\mathcal{G}g_2-\alpha_2g_1)]+2h_1h_2(g_1g_2-\mathcal{G}G)+h_2^2(G\alpha_1-g_1^2)+h_1^2(\alpha_2G-g_2^2)\\
&-(4\pi/3v)[G(h_1+h_2)^2+\alpha_2(H-h_1Z_1)^2+\alpha_1(H+h_2Z_1)^2+2\mathcal{G}(H-h_1Z_1)(H+h_2Z_1)+Z_1(h_1+h_2)(h_1g_2-h_2g_1)\\
&\qquad-2(g_1+g_2)(h_1+h_2)H];
\end{aligned}$$

$$e_{14}=(2a/v)[1-(4\pi/3v)\alpha_t]^{-1}[E/4B-2.51\alpha_tZ_1/v],\tag{8d}$$

where

$$\begin{aligned}
E=Z_1[H(\alpha_1\alpha_2-\mathcal{G}^2)+h_1(\mathcal{G}g_2-\alpha_2g_1)+h_2(\mathcal{G}g_1-\alpha_1g_2)]&+(\alpha_2+\mathcal{G})(-Hg_1+h_1G)+(\alpha_1+\mathcal{G})(-h_2G+Hg_2)\\
&+(g_1+g_2)(-h_1g_2+h_2g_1);
\end{aligned}$$

$$\alpha_e=(\alpha_1+\alpha_2+2\mathcal{G})/(\alpha_1\alpha_2-\mathcal{G}^2);\tag{8e}$$

$$\alpha_t=(1/B)[Z_1^2(\alpha_1\alpha_2-\mathcal{G}^2)+2Z_1(g_2(\alpha_1+\mathcal{G})-g_1(\alpha_2+\mathcal{G}))+G(\alpha_1+\alpha_2+2\mathcal{G})-(g_1+g_2)^2].\tag{8f}$$

We also display expressions for particular frequencies of interest,

(a) $\omega_{L0}$, the frequency of the longitudinal mode at $\mathbf{y}=0$:

$$\bar{M}\omega_{L0}^2=\left[G+\frac{g_1(g_2\mathcal{G}-\alpha_2 g_1)+g_2(g_1\mathcal{G}-\alpha_1 g_2)}{\alpha_1\alpha_2-\mathcal{G}^2}\right]\left[\frac{1+(8\pi/3v)\alpha_t}{1+(8\pi/3v)\alpha_e}\right], \tag{8g}$$

where $\bar{M}=M_1M_2/(M_1+M_2)$. It is convenient for numerical work to combine Eqs. (8f) and (8g) to obtain the result

$$(\alpha_t-\alpha_e)\bar{M}\omega_{L0}^2=\left[Z_1+\frac{g_2(\mathcal{G}+\alpha_1)-g_1(\mathcal{G}+\alpha_2)}{\alpha_1\alpha_2-\mathcal{G}^2}\right]^2\left[\frac{1+(8\pi/3v)\alpha_t}{1+(8\pi/3v)\alpha_e}\right]. \tag{8h}$$

(b) $\omega_{L_1}$ and $\omega_{L_2}$, the longitudinal frequencies at the point $X$ (see Fig. 2):

$$M_1\omega_{L_1}^2=G+4K_1+4.333Z_1^2/v-\frac{(g_1+4k_1+4.333Z_1/v)^2}{\alpha_1+4\mathcal{K}_1+4.333/v}; \tag{9a}$$

$$M_2\omega_{L_2}^2=G+4K_2+4.333Z_1^2/v-\frac{(g_2+4k_2-4.333Z_1/v)^2}{\alpha_2+4\mathcal{K}_2+4.333/v}. \tag{9b}$$

(c) $\omega_{T_1}$ and $\omega_{T_2}$, the transverse frequencies at the point $X$. These expressions are complex and will be given in condensed form:

$$\omega_{(T_1,T_2)}^2=SM_1+QM_2\pm\frac{[(SM_1-QM_2)^2+4R^2M_1M_2]^{1/2}}{2M_1M_2}, \tag{9c,d}$$

where

$$Q=E_{11}-(E_{13}^2E_{44}-2E_{13}E_{14}E_{34}+E_{14}^2E_{33})/(E_{33}E_{44}-E_{34}^2),$$
$$R=E_{12}+(E_{23}E_{13}E_{44}-E_{23}E_{14}E_{34}+E_{13}E_{34}E_{24}-E_{14}E_{24}E_{33})/(E_{33}E_{44}-E_{34}^2),$$
$$S=E_{22}-(E_{24}^2E_{33}+2E_{24}E_{34}E_{23}+E_{23}^2E_{44})/(E_{33}E_{44}-E_{34}^2),$$

and

$$E_{11}=G+2L_1+2K_1-2.166Z_1^2/v,$$
$$E_{12}=-H+10.624Z_1^2/v,$$
$$E_{13}=-g_1-2l_1-2k_1+2.166Z_1/v,$$
$$E_{14}=h_2+10.624Z_1/v,$$
$$E_{22}=G+2L_2+2K_2-2.166Z_1^2/v,$$
$$E_{23}=-h_1+10.624Z_1/v,$$
$$E_{24}=-g_2-2l_2-2k_2-2.166Z_1/v,$$
$$E_{33}=\alpha_1+2\mathcal{K}_1+2\mathcal{L}_1-2.166/v,$$
$$E_{34}=-\mathcal{K}-10.624/v,$$
$$E_{44}=\alpha_2+2\mathcal{K}_2+2\mathcal{L}_2-2.166/v.$$

Our long-wavelength results reduce to results given by Cochran[3] if we make the simplifications:

$$H=\gamma G,\quad h_1=\gamma g_1,\quad h_2=\gamma g_2, \tag{10}$$

and set all second neighbor constants equal to zero. Our piezoelectric constant also agrees with the result obtained by Merten[4] when appropriate simplifications are made. It should be noted, however, that the simplified expressions are not capable to fitting all of the experimental results for any substance that we considered. If Eq. (10) holds, the piezoelectric constant is zero if $Z=0$; this is not true for the general expression. The Szigeti relation,

$$Z^*=\omega_{T0}[(\epsilon_0-\epsilon_\infty)/4\pi]^{1/2}[3/(\epsilon_\infty+2)][\bar{M}v]^{1/2}, \tag{11}$$

holds for our model. Here, $Z^*$ is the Szigeti ionic charge. In particular, $Z_1=0$ does not imply $Z^*=0$, as has been discussed by Cochran.[20] Other general relations that our model satisfies are the Clausius-Mosotti and

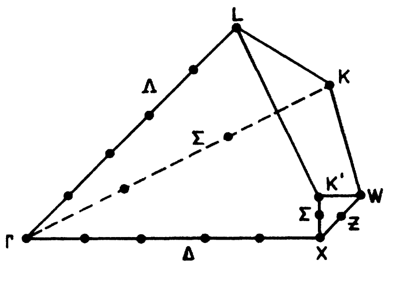

FIG. 2. The black dots indicate the locations of the wave vectors in the central Brillouin zone of the zincblende structure for which dipole sums are reported here. The letters identifying symmetry points and directions in the Brillouin zone follow the notation of reference 18. Because of a reciprocal lattice translation, the line $K'\Sigma X$ can be regarded as the extension of $\Gamma\Sigma K$ into another Brillouin zone.

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[20] W. Cochran, Nature **191**, 60 (1961).

TABLE I. Experimental data concerning the lattice vibration spectra of some zincblende structure crystals.

| Substance | $a$ ($10^{-8}$ cm) | $M_1$ ($10^{-23}$ g) | $M_2$ ($10^{-23}$ g) | $C_{11}$ ($10^{11}$ dynes/cm$^2$) | $C_{12}$ ($10^{11}$ dynes/cm$^2$) | $C_{44}$ ($10^{11}$ dynes/cm$^2$) | $e_{14}$ ($10^4$ esu/cm$^2$) |
|---|---|---|---|---|---|---|---|
| GaAs | 2.818 | 12.47 | 11.6 | 11.88[a] | 5.38[a] | 5.94[a] | +3.6[e] |
| InSb | 3.231 | 20.2 | 19.1 | 6.72[b] | 3.67[b] | 3.02[b] | 0 |
| AlSb | 3.065 | 20.2 | 4.44 | 8.94[c] | 4.42[c] | 4.15[c] | 0 |
| ZnS | 2.706 | 5.33 | 10.86 | 10.0[d] | 6.5[d] | 3.4[d] | −4.2[f] |

| Substance | $\alpha_e$ ($10^{-24}$ cm$^3$) | $\alpha_t$ ($10^{-24}$ cm$^3$) | $\omega_{L_0}$ ($10^{13}$ sec$^{-1}$) | $\omega_{L_1}$ ($10^{13}$ sec$^{-1}$) | $\omega_{L_2}$ ($10^{13}$ sec$^{-1}$) | $\omega_{T_1}$ ($10^{13}$ sec$^{-1}$) | $\omega_{T_2}$ ($10^{13}$ sec$^{-1}$) |
|---|---|---|---|---|---|---|---|
| GaAs | 8.31[g] | 8.64[i] | 5.55[j] | 4.42[j] | 3.54[j] | 4.88[j] | 1.37[j] |
| InSb | 13.52[g] | 13.80[i] | 3.82[k] | 2.95[k] | 2.23[k] | 3.41[k] | 0.82[k] |
| AlSb | 10.7[g] | 11.2[i] | 6.55[l] | 5.60[l] | 2.49[l] | 5.95[l] | 1.22[l] |
| ZnS | 6.48[h] | 5.36[h] | 7.27[h] | 7.14[h] | 4.95[h] | 5.60[h] | 4.30[h] |

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[i] M. Haas and B. W. Henvis, J. Chem. Phys. Solids **23**, 1099 (1962).

[j] W. Cochran, S. J. Fray, F. A. Johnson, J. E. Quarrington, and N. Williams, J. Appl. Phys. **32**, 2102 (1961).

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Lorenz-Lorentz relations and the equation $(\omega_{L0}/\omega_{T0}) = (\epsilon_0/\epsilon_\infty)^{1/2}$.

There does not seem to be a simple physical picture to describe the roles of the different parameters in the general case even when all second neighbor force constants vanish. On the other hand, none of the results, e.g., the nonvanishing of the piezoelectric constant when the ionic charge $Z_1$ vanishes, are incompatible with the complexity of the model.

## III. APPLICATIONS OF THE THEORY

In this section we evaluate some of the force constants that appear in the general results, Eqs. (8) and (9), for each of several 3–5 and 2–6 compounds, by using available experimental information. The experimental data are given in Table I. In connection with this data the following points should be noted:

(1) The piezoelectric constant measurements are the least satisfactory of the results we use: The work on ZnS is very old; the result for GaAs is tentative; and the value $e_{14}=0$, used for InSb and AlSb, is a speculation based on the fact that the values of $e_{14}$ for ZnS and GaAs, two rather different materials, are small compared to $10^6$ esu/cm$^2$, a value which our work shows to be a natural size for this constant.

(2) In some cases, $\omega_{T0}$ rather than $\omega_{L0}$ was measured. We then used the relation $\omega_{L0}/\omega_{T0} = (\epsilon_0/\epsilon_\infty)^{1/2}$ to obtain $\omega_{L0}$.

(3) The assignments of modes to the four frequencies at point $X$ were not obtained from experiment. We used the assignments of the experimenter where these were indicated and in the remaining cases we made plausible guesses.

(4) Table I contains eleven experimental values for each substance, and thus at most eleven theoretical parameters can be evaluated for each substance. Because of the nature of quantum-mechanical overlap, one would expect second neighbor force constants to be, in general, smaller than first neighbor force constants of the same type. Furthermore, it was shown in references 7 and 15 that among the force constants connecting a given pair of atoms the atom-atom constant should generally be the largest, the dipole-atom constant next in size, and the dipole-dipole constant the smallest. Using these guides and the fact that there are eleven first neighbor and other large constants $(Z_1,\alpha_1,\alpha_2)$ in our model, it was decided to introduce second neighbor constants only when first neighbor constants would fail to fit all of the data.

Because of this conditional use of second neighbor constants it is necessary to discuss briefly the details of our fitting procedure. This procedure was strongly influenced by the ways in which the various parameters entered Eqs. (8) and (9). We first consider the long-wavelength equations. If $\alpha_1$, $\alpha_2$, and $Z_1$ are assigned numerical values, then Eq. (8a) determines $G$, Eq. (8b) determines $H$, Eq. (8e) determines $\mathcal{G}$ and any two of Eqs. (8f), (8g), and (8h) determine $g_1$ and $g_2$. Once these parameters are determined, Eqs. (8c) and (8d) determine $h_1$ and $h_2$. In carrying out this procedure several square roots occur, and thus it is not certain that all sets $(\alpha_1,\alpha_2,Z_1)$ will give solutions for the indicated constants. An inspection of the short-wavelength expressions now shows that Eqs. (9a) and (9b) contain no new first neighbor constants and that (9c) and (9d) both contain $\mathcal{H}$. One might then hope that some set $(\alpha_1,\alpha_2,Z_1,\mathcal{H})$ would exist allowing Eqs. (9) to be satisfied.

Fortunately the realistic ranges of values of $(\alpha_1,\alpha_2,Z_1)$ are limited. For 3–5 compounds one would expect a low value of $Z_1$, perhaps less than $\pm 0.5e$. ($Z_1$ is always taken to be the conventionally negative ion in a com-

TABLE II. Some sets of theoretical parameters that fit the experimental data in Table I for GaAs.[a]

| $Z_1/e$ | $\alpha_1$ ($10^{24}$ cm$^{-3}$) | $\alpha_2$ ($10^{24}$ cm$^{-3}$) | $K_1=K_2$ | $L_1=L_2$ | $N_1=N_2$ | $G$ | $g_1e$ | $g_2e$ |
|---|---|---|---|---|---|---|---|---|
| −0.25 | 0.498 | 0.249 | −0.5 | −0.5 | 0 | 30.75 | −9.71 | −6.81 |
| +0.25 | 0.249 | 0.498 | −0.5 | −0.5 | 0 | 30.75 | −6.81 | −9.71 |
| 0 | 0.249 | 0.498 | −0.5 | 0 | 0 | 30.78 | 5.55 | 11.63 |
| $\mathcal{G}e^2$ | $H$ | $h_1e$ | $h_2e$ | $\mathcal{H}e^2$ | $k_1e$ | $k_2e$ | % error in $\omega_{T_2}$ | |
| 2.31 | 19.61 | −8.72 | −4.37 | 0.52 | −0.81 | −0.21 | 2.0 | |
| 2.31 | 19.61 | −2.17 | −4.62 | −4.03 | −1.01 | 0.25 | 3.6 | |
| 2.31 | 20.45 | 5.21 | 10.41 | 1.18 | 1.42 | −0.61 | 1.0 | |

[a] The quantities in columns 4–16 are in units of $10^4$ dyn/cm.

pound: the "5" in 3–5 compounds and the "6" in 2–6's.) For zinc sulfide the allowable range extends from perhaps $+0.5e$ to $-2.0e$. The magnitudes of $\alpha_1$ and $\alpha_2$ are severely limited by Eq. (8e) which determines the dipole-dipole constant $\mathcal{G}$, because one would expect $\mathcal{G}e^2$ to be at most one or two tenths the size of the comparable atom-atom constant, $G$. Unfortunately, using even wider ranges of $\alpha_1$, $\alpha_2$, and $Z_1$ than indicated as acceptable we were not able to find solutions of all of the long-wavelength equations for any of the four substances we studied. We therefore introduced values of the constants $K$, $L$, $N$ whose magnitudes were between 2% and 6% of the value of $G$. In all cases we arbitrarily assumed $K_1=K_2$, $L_1=L_2$, and $N_1=N_2$. Under these conditions the long-wavelength data could be fitted for several sets $(K,L,N)$ and many sets $(\alpha_1,\alpha_2,Z_1)$.

The short-wavelength data, Eqs. (9a) and (9b), necessitated the introduction of further constants in order that $K_1$ and $K_2$ not be required to be large. We thus used Eqs. (9a) and (9b) to determine the values of $k_1$ and $k_2$. Finally, the trace $\omega_{T_1}{}^2+\omega_{T_2}{}^2$ was used to determine $\mathcal{H}$ and the separate values of $\omega_{T_1}{}^2$ and $\omega_{T_2}{}^2$ that resulted were compared with experiment. In view of the large number of force constants that we used it is perhaps not surprising that we found a very large number (many hundred) of sets of force constants that would fit the experimental data. It must, however, be remembered that we have tried to limit the ranges of many of the constants to values which could reasonably be expected to result from a fundamental quantum-mechanical calculation. A few better fits are shown in Tables II, III, IV, V, for GaAs, InSb, AlSb, and ZnS, respectively. Our criterion of a good fit was that the force constants roughly obey the relative magnitude arguments mentioned above. The accuracy of the value of $\omega_{T_2}$ was also considered but was not the prime criterion. In order to facilitate the comparison of force constant magnitudes all atom-dipole constants are multiplied by $e$ and all dipole-dipole constants by $e^2$. All force constants should then be multiplied by $10^4$ dyn/cm.

It may be noticed from Tables II–V that $G$ is always the largest force constant and that $H$ is almost always the second largest force constant. (As a reference to the type of binding, equality of any "$g$-$h$ pair" indicates a central force between the two entities that the pair couples.) The other relations between force constants indicated by Tolpygo[7] are not often satisfied in all respects. Some deviations from Tolpygo's criteria should not be considered unusual. His argument is based upon an expansion in powers of overlap integrals. Although overlap integrals are most often reasonably small, there are also cases in which they are large, of

TABLE III. Some sets of theoretical parameters that fit the experimental data in Table I for InSb.[a]

| $Z_1/e$ | $\alpha_1$ ($10^{24}$ cm$^{-3}$) | $\alpha_2$ ($10^{24}$ cm$^{-3}$) | $K_1=K_2$ | $L_1=L_2$ | $N_1=N_2$ | $G$ | $g_1e$ | $g_2e$ |
|---|---|---|---|---|---|---|---|---|
| ∓0.25 | 0.180 | 0.360 | −0.5 | −0.5 | 0 | 21.35 | ∓5.10 | ∓5.39 |
| ∓0.25 | 0.180 | 0.360 | 0 | 0.5 | 0.5 | 17.35 | ∓3.58 | ∓2.88 |
| 0 | 0.360 | 0.180 | −0.5 | −0.5 | 0 | 21.37 | ±7.47 | ±3.41 |
| 0 | 0.082 | 0.164 | 0 | 0 | 0.5 | 17.37 | ∓1.44 | ±3.17 |
| ∓0.25 | 0.164 | 0.082 | −0.5 | −0.5 | 0.5 | 21.35 | ∓4.79 | ±0.04 |
| $\mathcal{G}e^2$ | $H$ | $h_1e$ | $h_2e$ | $\mathcal{H}e^2$ | $k_1e$ | $k_2e$ | % error in $\omega_{T_2}$ | |
| 2.31 | 13.53 | ∓2.61 | ∓0.57 | −2.85 | ∓0.45 | ∓0.06 | 1.2 | |
| 2.31 | 12.53 | ∓0.78 | ±2.65 | 1.07 | ±2.61 | ∓0.08 | 1.2 | |
| 2.31 | 13.43 | ±2.56 | ±0.67 | −0.55 | ±0.53 | ∓1.84 | 0 | |
| −2.33 | 11.43 | ∓1.40 | ±3.86 | −2.23 | ±1.61 | ∓1.29 | 3.7 | |
| −1.09 | 11.53 | ∓1.10 | ±1.53 | −2.99 | ∓0.47 | ±0.67 | 0 | |

[a] The quantities in columns 4–16 are in units of $10^4$ dyn/cm.

TABLE IV. Some sets of theoretical parameters that fit the experimental data in Table I for AlSb.[a]

| $Z_1/e$ | $\alpha_1$ ($10^{24}$ cm$^{-3}$) | $\alpha_2$ ($10^{24}$ cm$^{-3}$) | $K_1=K_2$ | $L_1=L_2$ | $N_1=N_2$ | $G$ | $g_1e$ | $g_2e$ |
|---|---|---|---|---|---|---|---|---|
| $\mp0.25$ | 0.209 | 0.418 | $-0.5$ | 0.5 | 0 | 25.90 | $\mp6.75$ | $\mp6.56$ |
| 0 | 0.209 | 0.418 | $-0.5$ | 0 | 0 | 25.92 | $\pm6.41$ | $\pm7.45$ |
| $\mp0.25$ | 0.188 | 0.094 | $-0.5$ | 0.5 | 0 | 25.90 | $\mp6.28$ | $\pm2.12$ |

| $\mathcal{G}e^2$ | $H$ | $h_1e$ | $h_2e$ | $\mathcal{H}e^2$ | $k_1e$ | $k_2e$ | % error in $\omega_{T_2}$ |
|---|---|---|---|---|---|---|---|
| 2.31 | 18.50 | $\mp7.42$ | $\mp8.24$ | 1.55 | $\mp0.37$ | $\mp1.14$ | 1.0 |
| 2.31 | 15.38 | $\pm6.14$ | $\pm9.43$ | 1.50 | $\pm0.56$ | $\pm0.80$ | 6.9 |
| $-2.32$ | 18.50 | $\mp3.52$ | $\pm2.29$ | $-4.42$ | $\mp0.41$ | $\pm0.93$ | 4.5 |

[a] The quantities in columns 4–16 are in units of $10^4$ dyn/cm.

order unity. As a second point, once it became apparent that a unique fit to the experimental data was not possible, we did not try to find the solution which most closely obeyed Tolpygo's criteria.

The error in $\omega_{T_2}$ for any given fit could be removed by small adjustments of some of the force constants.

It is unfortunate that for $Z_1=0$, the experiments do not distinguish between two models having opposite signs for all atom-dipole constants. Other similar lacks of sensitivity may be noticed in Tables II–V.

Among the solutions are a number in which a pair of what one might think would be roughly equal valued parameters have markedly different values (e.g., $g_1$ and $g_2$ for 3–5 compounds). Although one's intuition argues against such solutions, they cannot be rejected without further examination. It must be remembered that the curvature of a typical plot of potential energy vs internuclear spacing, for a diatomic molecule, changes sign outside of the equilibrium spacing of the nuclei. The generalization of this observation to the solid makes clear the danger of rejecting the above type of solution on intuitive grounds: One of a pair of force constants may have passed the point at which the curvature changes sign and the other one may not have done so.

## IV. DISCUSSION

Our original purpose in carrying through a detailed study of the vibration spectra of zincblende structure substances was to determine a value of the effective ionic charge, $Z_1$, as defined by lattice dynamics,[8] for each substance. We hoped that such effective ionic charge values would be related to the usual qualitative ionic charge concept and might be useful for purposes such as the selection of a potential energy for energy-band calculations. The results of Sec. III have destroyed this program. The available experimental data in conjunction with our model are incapable of distinguishing between ionic charges $Z_1=+0.5$, $-0.5$, $-1.5$, $-2.0$ for the sulfur ion in zinc sulfide, and cannot distinguish between many low ionic charge values for several 3–5 compounds. We are led to the conclusion that the distortion dipole model is flexible enough, as a method of parameterizing lattice dynamics, to fit a very wide range of experimental possibilities, each in many different, apparently realistic ways. This flexibility removes any concern we might have had about inconsistencies in the experimental data arising from the fact that all experiments were not performed on the same sample.

TABLE V. Some sets of theoretical parameters that fit the experimental data in Table I for ZnS.[a]

| $Z_1/e$ | $\alpha_1$ ($10^{24}$ cm$^{-3}$) | $\alpha_2$ ($10^{24}$ cm$^{-3}$) | $K_1=K_2$ | $L_1=L_2$ | $N_1=N_2$ | $G$ | $g_1e$ | $g_2e$ |
|---|---|---|---|---|---|---|---|---|
| $-2.0$ | 0.4 | 0.4 | $-1.4$ | 0 | 0 | 30.52 | $-11.18$ | $-1.76$ |
| $-1.5$ | 0.8 | 0.4 | $-1.4$ | 0 | 0 | 31.54 | 11.08 | 10.61 |
| $-2.0$ | 0.4 | 0.4 | $-0.93$ | 0 | 0 | 26.72 | 0.96 | 9.52 |
| $+0.5$ | 0.6 | 1.2 | $-2.4$ | 1.0 | 1.0 | 40.70 | $-16.60$ | $-21.51$ |
| $-0.5$ | 0.6 | 1.2 | $-2.4$ | 1.0 | 1.0 | 40.70 | 16.60 | 21.51 |
| $+0.5$ | 1.2 | 0.6 | $-2.4$ | 1.0 | 1.0 | 40.70 | $-25.00$ | $-13.11$ |
| $-0.5$ | 1.2 | 0.6 | $-2.4$ | 1.0 | 1.0 | 40.70 | 25.00 | 13.11 |

| $\mathcal{G}e^2$ | $H$ | $h_1e$ | $h_2e$ | $\mathcal{H}e^2$ | $k_1e$ | $k_2e$ | % error in $\omega_{T_2}$ |
|---|---|---|---|---|---|---|---|
| 0.62 | 31.79 | $-16.57$ | 6.59 | $-4.02$ | 1.66 | 1.66 | 5.3 |
| 4.04 | 26.92 | $-5.80$ | 5.12 | 1.66 | $-4.23$ | $-5.52$ | 10.0 |
| 0.62 | 30.84 | $-5.71$ | 17.56 | 4.08 | 3.32 | $-1.46$ | 9.8 |
| 10.63 | 21.36 | $-11.22$ | $-25.57$ | 5.44 | 1.68 | 2.58 | 0.2 |
| 10.63 | 21.36 | 11.28 | 25.85 | 5.02 | $-1.68$ | $-2.58$ | 2.3 |
| 10.63 | 21.36 | $-19.33$ | $-17.46$ | 3.89 | $-3.00$ | 1.30 | 5.8 |
| 10.63 | 21.36 | 18.46 | 17.84 | 3.85 | $-3.00$ | $-1.30$ | 2.9 |

[a] The quantities in columns 4–16 are in units of $10^4$ dyn/cm.

In reference 5 the conclusion is reached that the ionic charge $Z$, of GaAs is zero. The model used in that work incorporates the simplification Eq. (10) above. While it is true that with this simplification one minimizes the errors in the elastic constants with the choice $Z_1=0$, an exact fit to the elastic constants is not possible. Our more general model, which fits the elastic constants exactly, allows, as we have seen, a range of plausibly small values of $Z_1$.

There are two basic methods of improving the situation. We may increase the amount of available experimental data and/or we may calculate some force constants from first principles.

From the experimental point of view, determinations of the dispersion curves in symmetry directions by inelastic neutron scattering experiments would be very valuable in further restricting force constant values, although there is some evidence that even this amount of data is insufficient to lead to an unambiguous force constant determination.[21] Knowledge of the Debye temperature as a function of temperature $[\Theta(T)]$ would also be of value. These data exist for ZnS and we hope to test our various sets of force constants against this criterion in the near future. However, the effect of averaging over the vibration spectrum probably means that a variety of spectra can lead to the same $\Theta(T)$.

We are inclined to the view that no large amount of progress will be made in the unambiguous determination of force constants of most substances without the help of some detailed quantum-mechanical calculations. If the values of even a few force constants were limited by basic theory the range of fits to a given set of experimental data would shrink significantly. As a first step, an effort might be made to estimate some of the matrix elements in Tolpygo's force constant expressions,[7] based on the one-electron approximation. However, the framework for a better determination exists in the Green's function formulation of Baym[17] and ultimately calculations based on this or an equally general model will be carried out.

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## APPENDIX A

Dipole sums have been calculated for the zincblende structure along three symmetry directions in the Brillouin zone and at several points on the zone boundary. The point group symmetry of zincblende together with time reversal symmetry allows us to consider only points in an element containing one forty-eighth of the volume of the Brillouin zone. The locations of the wave vectors for which dipole sums are reported here are indicated in Fig. 2.

The dipole sums were computed by the Ewald method, as described in reference 11, which makes use of a theta function transformation to establish the following identity:

$$
\begin{aligned}
Q_{\alpha\beta}(\mathbf{y};kk') &= \frac{4\pi}{v}\frac{y_\alpha y_\beta}{|\mathbf{y}|^2} + \sum_l \frac{3x_\alpha(lk';0k)x_\beta(lk';0k) - |\mathbf{x}(lk';0k)|^2\delta_{\alpha\beta}}{|\mathbf{x}(lk';0k)|^5} \exp[2\pi i\mathbf{y}\cdot\mathbf{x}(lk';0k)] \\
&= \frac{4\pi}{v}\frac{y_\alpha y_\beta}{|\mathbf{y}|^2}[1-\exp(-\pi|\mathbf{y}|^2/s^2)] + \frac{4\pi}{3}s^3\delta_{\alpha\beta}\delta_{kk'} + \sum_l \left\{ \frac{3x_\alpha(lk';0k)x_\beta(lk';0k) - |\mathbf{x}(lk';0k)|^2\delta_{\alpha\beta}}{|\mathbf{x}(lk';0k)|^5} \frac{2}{\pi^{1/2}} \right. \\
&\quad \times \int_{s\pi^{1/2}|\mathbf{x}(lk';0k)|}^{\infty} e^{-u^2}du + \left[ \frac{3x_\alpha(lk';0k)x_\beta(lk';0k) - |\mathbf{x}(lk';0k)|^2\delta_{\alpha\beta}}{|\mathbf{x}(lk';0k)|^2} + 2x_\alpha(lk';0k)x_\beta(lk';0k)s^2\pi \right] \\
&\quad \left. \times \frac{2s}{|\mathbf{x}(lk';0k)|^2} \exp[-s^2\pi|\mathbf{x}(lk';0k)|^2] \right\} \exp[2\pi i\mathbf{y}\cdot\mathbf{x}(lk';0k)] - \frac{4\pi}{v}\sum_h{}' \frac{(y_\alpha(h)+y_\alpha)(y_\beta(h)+y_\beta)}{|\mathbf{y}(h)+\mathbf{y}|^2} \\
&\quad \times \exp\{-\pi|\mathbf{y}(h)+\mathbf{y}|^2/s^2 + 2\pi i\mathbf{y}(h)\cdot[\mathbf{x}(k)-\mathbf{x}(k')]\}. \qquad \text{(A1)}
\end{aligned}
$$

The notation is the same as that of Sec. II except that the sum over $h$ is over reciprocal lattice vectors and the prime on the sum over $h$ indicates that the term $h=0$ is to be omitted. The parameter $s$ is chosen to obtain rapid convergence of the two sums. We used the value $s=(1/v)^{1/3}$. The computations were performed by an IBM 650 computer. The results are shown in Table VI.

Note that the coefficients $\mathcal{C}$ are independent of any particular lattice constant $a$ and ionic charges $e_k$, $e_{k'}$.

Where possible the values in Table VI were checked against those given by Merten[2] and Kellermann.[22] We used the condition, trace $\mathcal{C}(\mathbf{y},k,k')=0$, to obtain an estimate of the accuracy of our machine calculations.

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[21] W. Cochran (private communication).

[22] E. W. Kellermann, Phil. Trans. Roy. Soc. (London) **A238**, 513 (1940).

TABLE VI. Dipole sums $\mathcal{C}(\mathbf{y},k,k')$ for the zincblende structure where $\mathcal{C}(\mathbf{y},k,k')=C(\mathbf{y},k,k')/[e_ke_{k'}/v]=4\pi\mathbf{yy}/|\mathbf{y}|^2-vQ(\mathbf{y},k,k')$.

Along $\Delta$ $(y,0,0)$, $\mathcal{C}(\mathbf{y},k,k')$ has the forms:

$$k=k',\ \begin{pmatrix}2A & 0 & 0\\ 0 & -A & 0\\ 0 & 0 & -A\end{pmatrix};\quad k\neq k',\ \begin{pmatrix}2B & 0 & 0\\ 0 & -B & -iC\\ 0 & -iC & -B\end{pmatrix}$$

| $2ya$ | $A$ | $B$ | $C$ |
|---|---|---|---|
| 0.0 (Γ) | 4.189 | 4.189 | 0.0 |
| 0.2 | 4.006 | 3.979 | 3.123 |
| 0.4 | 3.517 | 3.374 | 6.022 |
| 0.6 | 2.893 | 2.444 | 8.424 |
| 0.8 | 2.370 | 1.281 | 10.046 |
| 1.0 ($X$) | 2.166 | 0.0 | 10.624 |

Along $\Lambda$ $(y,y,y)$, $\mathcal{C}(\mathbf{y},k,k')$ has the forms:

$$k=k',\ \begin{pmatrix}0 & A & A\\ A & 0 & A\\ A & A & 0\end{pmatrix};\quad k\neq k',\ \begin{pmatrix}0 & B+iC & B+iC\\ B+iC & 0 & B+iC\\ B+iC & B+iC & 0\end{pmatrix}$$

| $2ya$ | $A$ | $B$ | $C$ |
|---|---|---|---|
| 0.0 (Γ) | 4.189 | 4.189 | 0.0 |
| 0.1 | 4.131 | 4.266 | −1.547 |
| 0.2 | 3.986 | 4.471 | −2.920 |
| 0.3 | 3.812 | 4.706 | −4.011 |
| 0.4 | 3.668 | 4.928 | −4.657 |
| 0.5 ($L$) | 3.615 | 4.948 | −4.948 |

Along $\Sigma$ $(y,y,0)$, $\mathcal{C}(\mathbf{y},k,k')$ has the forms:

$$k=k',\ \begin{pmatrix}A & B & 0\\ B & A & 0\\ 0 & 0 & -2A\end{pmatrix};\quad k\neq k',\ \begin{pmatrix}C & D & iE\\ D & C & iE\\ iE & iE & -2C\end{pmatrix}$$

| $2ya$ | $A$ | $B$ | $C$ | $D$ | $E$ |
|---|---|---|---|---|---|
| 0.0 (Γ) | 2.095 | 6.283 | 2.095 | 6.283 | 0.0 |
| 0.1 | 2.048 | | | | |
| 0.25 | 1.780 | 5.874 | 1.770 | 6.769 | −3.668 |
| 0.4 | 1.224 | | | | |
| 0.5 | 0.669 | 4.262 | 1.018 | 8.117 | −5.694 |
| 0.6 | −0.015 | | | | |
| 0.75 ($K$) | −1.132 | 1.546 | 0.173 | 9.683 | −4.524 |

Along $\Sigma$ $(1/2a,y,y)$, $\mathcal{C}(\mathbf{y},k,k')$ has the forms:

$$k=k',\ \begin{pmatrix}-2A & 0 & 0\\ 0 & A & B\\ 0 & B & A\end{pmatrix};\quad k\neq k',\ \begin{pmatrix}2iC & -E & -E\\ -E & -iC & -iD\\ -E & -iD & -iC\end{pmatrix}$$

| $2ya$ | $A$ | $B$ | $C$ | $D$ | $E$ |
|---|---|---|---|---|---|
| 0.25 ($K'$) | −1.132 | 1.546 | 0.173 | 9.683 | −4.524 |
| 0.125 | −1.878 | 0.430 | 0.078 | 10.389 | −2.544 |
| 0.0 ($X$) | −2.167 | 0.0 | 0.0 | 10.624 | 0.0 |

Along $Z$ $(1/2a,y,0)$, $\mathcal{C}(\mathbf{y},k,k')$ has the forms:

$$k=k',\ \begin{pmatrix}A & 0 & 0\\ 0 & -A-B & 0\\ 0 & 0 & B\end{pmatrix};\quad k\neq k',\ \begin{pmatrix}0 & C & 0\\ C & 0 & -iD\\ 0 & -iD & 0\end{pmatrix}$$

| $2ya$ | $A$ | $B$ | $C$ | $D$ |
|---|---|---|---|---|
| 0.0 ($X$) | 4.333 | −2.166 | 0.0 | 10.624 |
| 0.25 | 3.224 | −1.355 | 4.808 | 10.138 |
| 0.5 ($W$) | 0.788 | 0.788 | 8.364 | 8.364 |

We find that our numbers are accurate to about ±0.002 near $\mathbf{y}=0$. The accuracy improves by a factor of ten as we approach the zone boundary.

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# Conductivity of Polycrystals

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The problem of the prediction of the effective electric or thermal conductivity of a polycrystal in terms of the conductivities of the constituting single crystals is treated by a variational method. It is assumed that the crystals are all of the same kind and randomly oriented. Consequently, the polycrystal is assumed to be homogeneous and isotropic in the large. However, no assumptions about the shape of the crystals have to be introduced.

Lower and upper bounds for the effective conductivity are derived on the basis of a new variational formulation of the conductivity problem in anisotropic and nonhomogeneous media. For reasons of mathematical analogy the results are also valid for the effective dielectric constant and magnetic permeability of polycrystals. The bounds obtained are close when the anisotropy of the single crystals is not too large.

## I. INTRODUCTION

THE present paper is concerned with the problem of the determination of the gross isotropic conductivity $\sigma$ of a polycrystal in terms of the principal conductivities $\sigma_1<\sigma_2<\sigma_3$, of the constituting anisotropic crystals.[1] This problem may be considered as one of the determination of effective properties of a heterogeneous

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[1] For reference to previous work on this subject, see J. K. Alstad, R. V. Colvin, and S. Legvold, Phys. Rev. **123**, 418 (1961). Volume and page in reference 2 should read **A138**, 348 (1932).