

# Elastic Properties of ZnS Structure Semiconductors

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A simple phenomenological theory of the elastic constants of sphalerite structure crystals is presented and shown to apply within reasonable errors to the known experimental constants. The theory utilizes a form for bond-stretching ( $\alpha$ ) and bending ( $\beta$ ) forces first used by Keating, to which are added effective point-ion Coulombic forces. Also it is pointed out that regularities in the experimental elastic constants of these crystals are readily explained in terms of the ionicity  $f_i$  defined by Phillips and Van Vechten. Of particular note are the shear constants which decrease markedly with ionicity. It is found that this decrease is described quantitatively by  $\beta/\alpha \propto (1-f_i)$ , which confirms the interpretation of  $\beta$ , since bond-bending forces should vanish in the ionic limit  $f_i \rightarrow 1$ . Other equally simple formulas for the forces in terms of only the bond length and  $f_i$  are shown to predict all the constants with a rms accuracy of 10%.

## I. INTRODUCTION

THE most useful phenomenological description of the short-range valence forces in the tetrahedrally coordinated crystals is the valence-force-field (VFF) approach,<sup>1</sup> in which all interatomic forces are resolved into bond-stretching and bond-bending forces. A description of the VFF method has been given by Musgrave and Pople,<sup>1</sup> where explicit formulas for the elastic constants are given. Also the method has been applied with much success to the calculation of the entire dispersion curves by McMurtry *et al.*,<sup>2</sup> Nusimovici and Birman,<sup>3</sup> and others. A similar derivation by Keating<sup>4</sup> is here shown to be a useful special case of the VFF model.

There are two primary virtues of the VFF model. First, because all distortions are described in terms of bond lengths and angles, the model is automatically rotationally invariant so that serious errors that may arise in the ordinary force-constant approach are avoided.<sup>4</sup> Second, in crystals in which atom pair bonds play an essential role, the VFF model is the most natural description of interatomic forces. Thus one expects the VFF model to involve the smallest possible number of parameters.

In the first part of this paper the VFF approach is extended to the heteropolar cubic ZnS [sphalerite or zinc-blende (ZB)] structure crystals by adding Coulombic forces assumed to be described by rigid point charges at the atom sites. The approach is essentially the same as that of Nusimovici and Birman,<sup>3</sup> but here special attention is paid to the long-wavelength limit and only the sphalerite structure is considered.

In the second part of the paper the regularities in the elastic properties of the ZB structure crystals are examined. We show that the trends, first pointed out by

Keyes,<sup>5</sup> are understandable in terms of the formulas of Sec. II and the qualitative effects of the changes in the ionicity<sup>6,7</sup> of the various compounds.

## II. THEORY

The VFF model for diamond-structure crystals has been described by Musgrave and Pople.<sup>1</sup> For the purpose of this paper we simplify their expressions omitting the less important forces. The simplified expression for the VFF part of the distortion energy of each unit cell is

$$U = \frac{1}{2} \sum_{i=1}^4 k_r (\Delta r_i)^2 + \sum_{s=1}^2 \left[ \frac{1}{2} \sum_{i,j>i} k_{\theta}^s (r \Delta \theta_{ij}^s)^2 + \sum_{i,j \neq i} k_{r\theta}^s (\Delta r_i^s) (r \Delta \theta_{ij}^{s'}) + \sum_{i,j>i} k_{rr}^s (\Delta r_i^s) (\Delta r_j^s) \right], \quad (1)$$

in the notation of Musgrave and Pople.<sup>1</sup> In (1) we have allowed the force constants  $k_{\theta}^s$ , etc., to differ for the two atoms in the unit cell denoted by  $s=1, 2$ . The bonds about each atom are denoted by  $i, j=1, \dots, 4$ ,  $r$  is the equilibrium bond length,  $\Delta r_i^s$  is the scalar change in length of bond  $i$  about atom  $s$ , and  $\Delta \theta_{ij}^s$  is the change in angle formed by bonds  $i$  and  $j$  about  $s$ , as shown in Fig. 1. Only the bonds about one atom are included in the first term in (1) to avoid double counting in the sum over unit cells.

In the present paper we deal only with long-wavelength acoustic or optic modes in which case the force constants for the two atoms in the unit cell always enter the relevant quantities in the form  $k = k^1 + k^2$ . Thus in the remainder of the paper we need only deal with the smaller set of independent constants,  $k_r, k_{\theta} = \frac{1}{2}(k_{\theta}^1 + k_{\theta}^2)$ ,  $k_{r\theta} = \frac{1}{2}(k_{r\theta}^1 + k_{r\theta}^2)$ , etc.

For the Coulomb part of the energy, we assume rigid point ions with charges  $\pm Z^*$  which interact via the screened coulomb potential  $\pm Z^{*2} e^2 / \epsilon R$ , where  $R$  is the

<sup>1</sup> M. J. P. Musgrave and J. A. Pople, Proc. Roy. Soc. (London) **A268**, 474 (1962).

<sup>2</sup> H. L. McMurtry, A. W. Solbrig, Jr., J. K. Boyter, and C. Noble, J. Phys. Chem. Solids **28**, 2359 (1967).

<sup>3</sup> M. A. Nusimovici and J. L. Birman, Phys. Rev. **156**, 925 (1967); M. A. Nusimovici, M. Balkanski, and J. L. Birman, Phys. Rev. **B1**, 595 (1970).

<sup>4</sup> P. N. Keating, Phys. Rev. **145**, 637 (1966).

<sup>5</sup> R. W. Keyes, J. Appl. Phys. **33**, 3371 (1962).

<sup>6</sup> J. C. Phillips, Phys. Rev. Letters **20**, 550 (1968); Chem. Phys. Letters **3**, 286 (1969); J. C. Phillips and J. A. Van Vechten, Phys. Rev. Letters **22**, 705 (1969).

<sup>7</sup> J. A. Van Vechten, Phys. Rev. **187**, 1007 (1969).

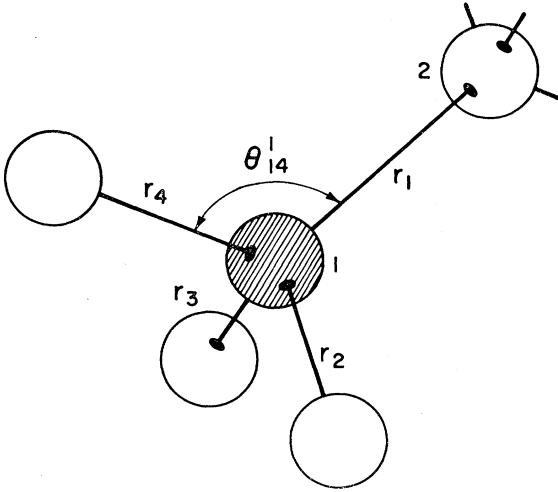


FIG. 1. Cubic ZnS (ZB or sphalerite) structure. The bonds shown are considered to belong to the unit cell containing atoms 1 and 2, and a typical angle  $\theta_{14}$  is shown.

separation and  $\epsilon$  is the electronic dielectric constant. The contribution of the Coulomb forces to the elastic constants has been given by Blackman.<sup>8</sup> In addition to the purely Coulombic forces, one must also include the effects of the linear repulsive term which must be present for the crystal to be stable. In the simple bond picture, this means that there must be a linear bond-stretching term in addition to (1),

$$U = \sum_{i=1}^4 f_r \Delta r_i + \text{second-order terms.} \quad (2)$$

The condition that the crystal be in equilibrium requires

$$f_r = -\frac{1}{4} \alpha_M Z^{*2} e^2 / \epsilon r^2, \quad (3)$$

where  $\alpha_M = 1.6381$  is the Madelung constant. Since this term is also proportional to  $Z^{*2}/\epsilon$ , it is conveniently included with the Coulomb terms. (We note that only if the effects of  $f_r$  are included in the force constants do the resulting elastic constants have the proper symmetry.)

The expressions for the elastic constants are most straightforwardly derived by directly expanding  $U$  in (1) in the manner described by Keating.<sup>4</sup> Using Blackman<sup>8</sup> and Eq. (3), the results are

$$C_{11} = (\sqrt{3}/12r)(k_r + 6k_{rr} + 12k_\theta) - 0.0829SC_0, \quad (4a)$$

$$C_{12} = (\sqrt{3}/12r)(k_r + 6k_{rr} - 6k_\theta) - 0.136SC_0, \quad (4b)$$

and

$$C_{44} = C_{44}' - C\zeta^2, \quad (4c)$$

where

$$C_{44}' = (\sqrt{3}/12r)(k_r - 2k_{rr} + 2k_\theta + 8k_{r\theta''}) - 0.136SC_0, \quad (4d)$$

$$C = (\sqrt{3}/12r)(k_r - 2k_{rr} + 8k_\theta - 16k_{r\theta''}) - 0.266SC_0, \quad (4e)$$

<sup>8</sup> M. Blackman, Phil. Mag. **3**, 831 (1959).

and

$$\zeta = \frac{1}{C} [(\sqrt{3}/12r)(k_r - 2k_{rr} - 4k_\theta - 4k_{r\theta''}) - 0.294SC_0]. \quad (4f)$$

Here we have defined  $k_{r\theta''} = k_{r\theta}'/\sqrt{2}$ ,

$$S = Z^{*2}/\epsilon, \quad (5)$$

and

$$C_0 = e^2/r^4, \quad (6)$$

which has the dimensions of an elastic constant. Note that  $\zeta$  is the internal-strain parameter defined by Kleinman<sup>9</sup> which is related to the internal-strain tensor<sup>10,11</sup> by

$$\gamma_{14} = -(r/\sqrt{3})\zeta. \quad (7)$$

The derivation of the formulas (4) explicitly employed the rigid point-ion approximation. No polarizability of the "effective" ions has been taken into account and the same effective charge was assumed to apply for all modes, optic and acoustic, and to the linear term (2). This is a convenient assumption that reduces the number of parameters. The justification is that no quantity considered is critically dependent on the effective charge so that even such a simple approximation can aid our quantitative understanding of the elastic properties. In the numerical results,  $Z^*$  will be taken to be the dynamic effective charge defined by the optic-mode splitting

$$S = Z^{*2}/\epsilon = (\Omega/4\pi e^2)m(\omega_l^2 - \omega_t^2), \quad (8)$$

where  $\Omega$  is the unit cell volume,  $m$  the reduced mass, and  $\omega$  the optic frequency.

The formulas for the elastic constants can be further simplified by an approximation suggested by Keating.<sup>4</sup> Assume that the expansion of the VFF energy (1) involves only the squares of the scalar variations  $\Delta(\mathbf{r}_i^s \cdot \mathbf{r}_j^s)$ , where  $\mathbf{r}_i^s$  and  $\mathbf{r}_j^s$  are bond vectors about atom  $s$ . Then in Keating's notation, we have

$$U = \frac{1}{2} \alpha \left( \frac{3}{4r^2} \right) \sum_{i=1}^4 [\Delta(\mathbf{r}_i^1 \cdot \mathbf{r}_i^1)]^2 + \frac{1}{2} \sum_{s=1}^2 \beta^s \left( \frac{3}{4r^2} \right) \sum_{i,j>i} [\Delta(\mathbf{r}_i^s \cdot \mathbf{r}_j^s)]^2. \quad (9)$$

One may readily show by expressing (9) in terms of changes in bond lengths and angles that Keating's approximation is realized in the VFF model by requiring

$$\begin{aligned} k_r &= 3\alpha + \frac{1}{2}\beta, & k_\theta &= \frac{2}{3}\beta, \\ k_{r\theta}' &= (3\sqrt{2})^{-1}\beta, & k_{rr} &= \frac{1}{2}\beta, \end{aligned} \quad (10)$$

where, as before,  $\beta = \frac{1}{2}(\beta^1 + \beta^2)$ .

<sup>9</sup> L. Kleinman, Phys. Rev. **128**, 2614 (1962).

<sup>10</sup> J. L. Birman, Phys. Rev. **111**, 1510 (1958).

<sup>11</sup> A. Segmüller and H. R. Neyer, Physik Kondensierten Materie **4**, 63 (1965).

From Eqs. (4) and (10), one may easily show that the elastic constants have the simple form

$$C_{11}+2C_{12}=(\sqrt{3}/4r)(3\alpha+\beta)-0.355SC_0, \quad (11a)$$

$$C_{11}-C_{12}=(\sqrt{3}/r)\beta+0.053SC_0, \quad (11b)$$

$$C_{44}=(\sqrt{3}/4r)(\alpha+\beta)-0.136SC_0 -C\zeta^2, \quad (11c)$$

where

$$C=(\sqrt{3}/4r)(\alpha+\beta)-0.266SC_0 \quad (11d)$$

and

$$\zeta=C^{-1}[(\sqrt{3}/4r)(\alpha-\beta)-0.294SC_0]. \quad (11e)$$

In particular, note that Eqs. (11a), (11b), and (11e) may be used to derive a simple expression for the internal-strain parameter

$$\zeta=(2C_{12}-C')/(C_{11}+C_{12}-C'), \quad (12a)$$

where

$$C'=0.314SC_0. \quad (12b)$$

The formulas for the elastic constants now involve only three parameters of which one,  $S$ , is fixed by the optic mode data. Thus the Eqs. (11) predict a relation among the elastic constants which may be checked experimentally. The relation may be written

$$\frac{2C_{44}(C_{11}+C_{12}-C')}{(C_{11}-C_{12})(C_{11}+3C_{12}-2C')+0.831C'(C_{11}+C_{12}-C')}=1, \quad (13)$$

which reduces to the form given by Keating<sup>4</sup> if we set  $C'=0$ .

In Table I are listed the experimental elastic constants of the ZB crystals, the parameter  $S$  derived via Eq. (8), and the constant  $C_0$ . From the experimental values the parameters for Keating's approximation are derived and shown in Table II. The first two columns contain  $\alpha$  and  $\beta$  calculated from (11a) and (11b) and in the third column the ratio on the left-hand side of (13)

TABLE I. Experimental bond lengths, elastic constants, and effective charge parameter  $S$  for the diamond or sphalerite structure materials. The elastic constants and effective charge parameters are for room temperature for each case in which that data was available.

Material	$r$ (a.u.)	$C_0$	$C_{11}$ ( $10^{11}$ dyn/cm <sup>2</sup> )	$C_{44}$ ( $10^{11}$ dyn/cm <sup>2</sup> )	$C_{12}$	$S$
C	2.919	40.523	107.6	57.68	12.50 <sup>a</sup>	0
Si	4.444	7.538	16.57	7.96	6.39 <sup>b</sup>	0
Ge	4.629	6.401	12.89	6.71	4.83 <sup>b</sup>	0
AlSb	5.020	4.630	8.94	4.16	4.43 <sup>c</sup>	0.364 <sup>d</sup>
GaP	4.460	7.430	14.12	7.05	6.25 <sup>e</sup>	0.514 <sup>f</sup>
GaAs	4.626	6.418	11.81	5.92	5.32 <sup>e</sup>	0.441 <sup>d</sup>
GaSb	5.006	4.681	8.84	4.32	4.03 <sup>g</sup>	0.331 <sup>h</sup>
InP	4.802	5.529	10.22	4.60	5.76 <sup>i</sup>	0.682 <sup>d</sup>
InAs	4.939	4.941	8.33	3.96	4.53 <sup>e</sup>	0.579 <sup>h</sup>
InSb	5.301	3.723	6.67	3.02	3.65 <sup>e</sup>	0.369 <sup>h</sup>
ZnS	4.426	7.660	10.40	4.62	6.50 <sup>j</sup>	0.887 <sup>k</sup>
ZnSe	4.638	6.356	8.10	4.41	4.88 <sup>j</sup>	0.688 <sup>k</sup>
ZnTe	4.984	4.765	7.13	3.12	4.07 <sup>j</sup>	0.539 <sup>k</sup>
CdTe	5.303	3.718	5.35	1.99	3.68 <sup>e</sup>	0.838 <sup>h</sup>
CuCl	4.423	7.681	2.72	1.57	1.87 <sup>l</sup>	0.266 <sup>m</sup>

<sup>a</sup> H. J. McSkimin and W. L. Bond, Phys. Rev. **105**, 116 (1957).  
<sup>b</sup> H. B. Huntington, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1958), Vol. 7.  
<sup>c</sup> *Londoll-Börnstein Numerical Data and Functional Relationships in Science and Technology, New Series*, edited by K. H. Hellwege (Springer, Berlin, 1966), Group 3, Band 5.  
<sup>d</sup> A. Mooradian and G. B. Wright, Solid State Commun. **4**, 431 (1966).  
<sup>e</sup> R. Weil and W. O. Groves, J. Appl. Phys. **39**, 4049 (1968).  
<sup>f</sup> A. S. Barker, Phys. Rev. **165**, 917 (1968).  
<sup>g</sup> H. J. McSkimin, A. Jayaraman, P. Andreatch, and T. B. Bateman, J. Appl. Phys. **39**, 4127 (1968).  
<sup>h</sup> D. H. Martin, Advan. Phys. **14**, 39 (1965).  
<sup>i</sup> F. S. Hickernell and W. R. Gayton, J. Appl. Phys. **37**, 462 (1966).  
<sup>j</sup> Reference 16.  
<sup>k</sup> W. G. Nilsen, in *Light Scattering Spectra of Solids*, edited by G. B. Wright (Springer, New York, 1969), p. 129.  
<sup>l</sup> Reference 15.  
<sup>m</sup> A. Hadni, F. Brehat, J. Claudel, and P. Strimer, J. Chem. Phys. **49**, 471 (1968).

is given. Note that with the exception of CuCl and ZnSe (more is said about these crystals in Sec. III), relation (13) is satisfied to within  $\sim 10\%$ . In contrast to the original relation given by Keating,<sup>4</sup> the ratio is as well satisfied for the ionic crystals as it is for the homopolar diamond-type crystals.

Of particular importance is the present calculation of the internal-strain parameter  $\zeta$ , the values of which are derived from (12) and given in Table II. The internal strain is, for example, essential for understanding the piezoelectric effect.<sup>12</sup> However, it has been pointed out<sup>10</sup> that a direct x-ray measurement of  $\zeta$  in the sphalerite structure crystals would be extremely difficult so that we must rely on derived values of  $\zeta$ . The only experimentally measured values<sup>11</sup> are for the homopolar crystals Si and Ge, both of which have  $\zeta \sim 0.63$  or about 15% greater than the derived value. The accuracy with

TABLE II. Theoretical quantities derived from the data of Table I.  $\alpha$  and  $\beta$  are the short-range force parameters and  $\zeta$  is Kleinman's internal displacement parameter.

Material	$\alpha$ $n/m$	$\beta$	$\beta/\alpha$	Ratio <sup>a</sup>	$\zeta$	Optic-mode check <sup>b</sup>
C	129.33	84.76	0.655	1.002	0.208	1.159
Si	48.50	13.81	0.285	1.005	0.557	1.044
Ge	38.67	11.35	0.294	1.081	0.546	1.019
AlSb	35.35	6.77	0.192	1.056	0.649	1.083
GaP	47.32	10.44	0.221	1.044	0.589	1.105
GaAs	41.19	8.95	0.217	1.068	0.600	1.085
GaSb	33.16	7.22	0.218	1.059	0.612	1.039
InP	43.04	6.24	0.145	1.075	0.699	1.136
InAs	35.18	5.50	0.156	1.109	0.682	1.054
InSb	29.61	4.77	0.161	1.103	0.695	1.029
ZnS	44.92	4.78	0.107	1.082	0.736	1.300
ZnSe	35.24	4.23	0.120	1.319	0.723	1.210
ZnTe	31.35	4.45	0.142	1.059	0.706	1.250
CdTe	29.02	2.43	0.084	1.045	0.793	1.220
CuCl	12.60	1.00	0.079	1.532	0.785	0.978

<sup>a</sup> Left-hand side of Eq. (13).

<sup>b</sup>  $\omega_i(\text{model})/\omega_i(\text{expt.})$ . See Eq. (16).

<sup>12</sup> W. Cady, *Piezoelectricity* (McGraw-Hill, New York, 1946).

which relation (13) (which is strongly dependent upon  $\zeta$ ) is satisfied suggests that the values of  $\zeta$  in the heteropolar compounds should not be in error by much greater amounts.

Let us now discuss the approximations made in more detail. From (10) we see that Keating's approximation is equivalent to taking  $k_r$  and  $k_\theta$  as independent parameters in the VFF model but requiring

$$k_{r\theta}' = (1/\sqrt{8})k_\theta,$$

and

$$k_{rr} = \frac{1}{3}k_\theta. \quad (14)$$

We might compare this approximation with one which appears more obvious in the VFF approach—setting the smaller constants  $k_{r\theta}' = k_{rr} = 0$ . The force constants have been determined in only a limited range of examples, notably diamond,<sup>2</sup> Si,<sup>13</sup> and many hydrocarbons.<sup>14</sup> In none of the cases is (14) well satisfied; however, the force constants do fall off with  $k_\theta > k_{r\theta}' > k_{rr}$ . The latter constants  $k_{r\theta}'$  and  $k_{rr}$  are by no means negligible, and it appears that (14) is a better choice than neglecting  $k_{r\theta}'$  and  $k_{rr}$  entirely.

It may also be noted that the alternative approximation with  $k_{r\theta}' = k_{rr} = 0$  leads to a relation among the elastic constants similar to (13). Even for the homopolar case, for which one finds

$$\frac{7}{6} \frac{2C_{44}[C_{11} + (2/7)C_{12}]}{(C_{11} + 2C_{12})(C_{11} - C_{12})} = 1, \quad (15)$$

the relation is not well satisfied. The left-hand side of (15) is 1.18, 1.14, and 1.23 for diamond, Si, and Ge, respectively—greater deviations than was found for (13) in any of the crystals except ZnSe and CuCl.

There is, however, a simple check which reveals clearly the inadequacy of the simple model used in the present work. One may show that the transverse optic-mode frequency in the model is given by

$$\omega_t(\text{model}) = [(16r/\sqrt{3}m)C]^{1/2}, \quad (16)$$

where  $C$  is given in (11d). The ratio  $\omega_t(\text{model})/\omega_t(\text{expt.})$  is listed in the last column of Table II. We see that in general the deviations increase as the value of  $S$  increases. The primary reason for the discrepancies is the rigid point-ion approximation. In order to fit the optic modes (and, of course, other modes at finite wave vector), a more complex model with more parameters must be used. This has not been done in the present work.

### III. TRENDS IN ELASTIC CONSTANTS

Regularities in the elastic properties of the semiconductors with the sphalerite structure have been

<sup>13</sup> A. W. Solbrig, Jr., and H. L. McMurtry (private communication).

<sup>14</sup> J. H. Schachtschneider and R. G. Snyder, *Spectrochim. Acta* 19, 117 (1963).

TABLE III. Fractional ionic character  $f_i$  from Ref. 7 and the reduced elastic constants derived from Table I.

Material	$f_i$	$B^*$	$C_s^*$	$C_{44}^*$
C	0	1.091	1.173	1.421
Si	0	1.298	0.675	1.056
Ge	0	1.173	0.627	1.048
AlSb	0.426	1.282	0.487	0.899
GaP	0.374	1.194	0.530	0.949
GaAs	0.310	1.166	0.506	0.926
GaSb	0.261	1.203	0.514	0.923
InP	0.421	1.311	0.403	0.832
InAs	0.357	1.173	0.385	0.801
InSb	0.321	1.251	0.406	0.811
ZnS	0.623	1.018	0.255	0.603
ZnSe	0.676	0.937	0.253	0.694
ZnTe	0.546	1.068	0.321	0.655
CdTe	0.675	1.139	0.225	0.535
CuCl	0.746	0.280	0.055	0.204

previously pointed out by Keyes.<sup>5</sup> The purpose of the remainder of the present paper is to put these regularities on a more quantitative basis and to discuss in a simple way the physics underlying the trends.

Following Keyes we consider the reduced elastic constants  $C_{11}^* = C_{11}/C_0$ , etc., where  $C_0$  is the normalization modulus defined in Eq. (6) and listed in Table I. This choice of the normalization modulus is suggested by the fact that all forces in the crystal are basically

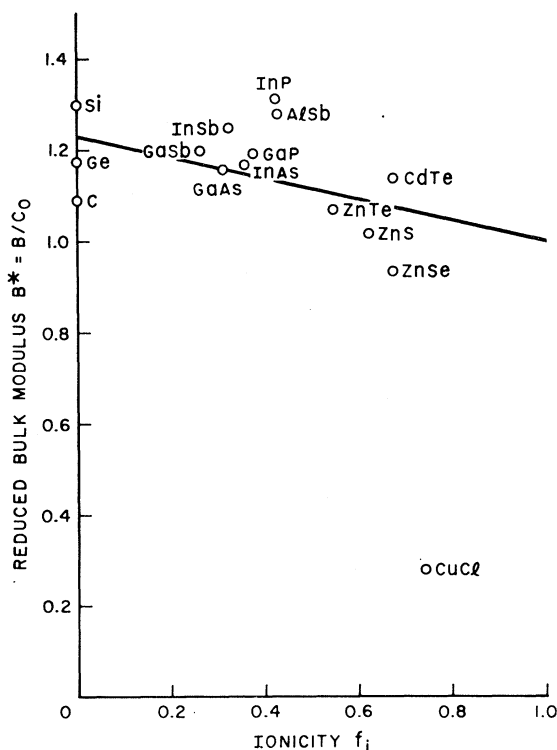


FIG. 2. Reduced bulk modulus  $B^* = B/C_0$  as a function of ionicity  $f_i$ . In Figs. 2-4 the solid line is the theoretical result derived from Eqs. (11) and (18) and fitted to the average value for Si and Ge.

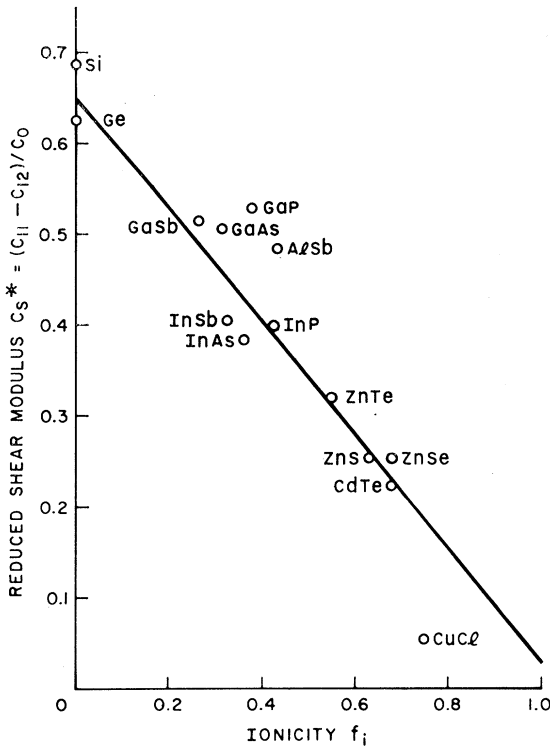


FIG. 3. Reduced shear modulus  $C_s^* = (C_{11} - C_{12})/2C_0$  as a function of  $f_i$ . Note that the value for diamond (not shown) is much larger than for the other crystals. See caption of Fig. 2.

electrostatic in origin. Since the crystals under consideration all have the same symmetry, the same number of electrons per atom pair, and thus similar bonding, the dependence of the moduli on the bond length is largely removed. The trends in the reduced moduli thus should be directly correlated with the character of the bond.

Here we examine the dependence of the reduced moduli upon the most important characterization of the bond, its ionicity. The scale of ionicity used is that defined by Phillips and Van Vechten,<sup>6,7</sup> which is the best available scale for  $A^N B^{8-N}$  heteropolar crystals. It has already been demonstrated that the ionicity  $f_i$  correlates well with the crystal structure; that is, it is found<sup>6,7</sup> that those and only those crystals with  $f_i$  less than a critical value are stable in a tetrahedrally coordinated structure.

It is most informative to examine the reduced bulk and shear moduli

$$B^* = (C_{11} + 2C_{12})/3C_0, \quad (17)$$

$$C_{44}^* = C_{44}/C_0,$$

and

$$C_s^* = (C_{11} - C_{12})/2C_0.$$

The formulas given in Sec. II show that the reduced shear moduli  $C_{44}^*$  and  $C_s^*$  should decrease as the ionicity increases because  $C_{44}^*$  and  $C_s^*$  are primarily

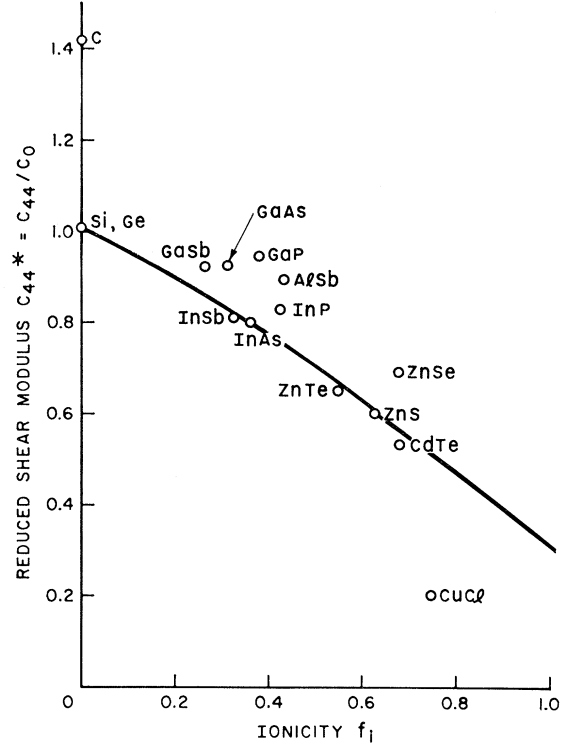


FIG. 4. Reduced shear modulus  $C_{44}^* = C_{44}/C_0$  as a function of  $f_i$ . See caption of Fig. 3.

determined by  $\beta$ , the noncentral force constant, which should decrease and tend to zero in the ionic limit  $f_i \rightarrow 1$ .

In Table III are listed the ionicity  $f_i$ <sup>7</sup> and the reduced elastic constants and in Figs. 2-4 are shown the reduced moduli as functions of the ionicity. We see that the reduced bulk moduli do not show a systematic variation with  $f_i$ , but rather reflect more strongly variations between the different rows of the Periodic Table. These variations are small and will not be discussed here. The reduced shear moduli, on the other hand, decrease markedly with increasing  $f_i$ . As was noted by Keyes,<sup>5</sup>  $C_s^*$  decreases more rapidly than  $C_{44}^*$ . The behavior of the elastic constants is best understood by examining the derived parameters  $\alpha$ ,  $\beta$ , and  $S$  as functions of  $f_i$ . This is done below where it is shown that simple approximations for the parameters in terms of  $f_i$  lead to the results displayed as the continuous lines in Figs. 2-4.

The reduced moduli of only one compound CuCl are in great disagreement with the trends. The measured elastic constants<sup>15</sup> are very low considering the small lattice constant. CuCl is the only one of the compounds (CuCl, CuBr, AgI) found in the ZB structure which have ionicity very near the critical value<sup>6,7</sup> for which measurements have been carried out. It would be useful

<sup>15</sup> T. Inoguchi, T. Okamoto, and M. Koba, Sharp Tech. J. 12, 59 (1969).

to verify the results of CuCl and to obtain the moduli for CuBr and AgI. It is possible that the low values for CuCl herald an approaching acoustic instability for crystals near the point of transition to the rock salt structure.

Note that the shear moduli for diamond are anomalously large. Presumably this reflects a real difference in the bonding caused by the fact that *s-p* hybridization is much more complete for first row atoms than for the heavier elements. Thus we would not expect the reduced moduli for compounds containing a first row element to be directly comparable with those from the other rows.

Also, it was noted in the previous section that for ZnSe the relation (13) is not well satisfied. The deviation is caused by the large value of  $C_{44}$  as may be seen by comparing the elastic constants of ZnSe with those of CdTe which has essentially the same ionicity. Since there is no *a priori* reason to suspect that ZnSe would be different from the other similar crystals, this result suggests that the experimental<sup>16</sup> elastic constants for ZnSe, in particular  $C_{44}$ , may be in error.

We may utilize the results of Sec. II and examine the derived parameters  $\alpha$ ,  $\beta$ , and  $S$  as functions of  $f_i$ . The elastic constants are, of course, composite functions of all the forces, whereas  $\alpha$ ,  $\beta$ , and  $S$  have simple interpretations as bond-stretching, bond-bending (non-central), and Coulombic force constants, respectively. We note from Tables II and III that  $\beta$  decreases much faster than  $\alpha$  as the ionicity  $f_i$  increases. Of particular interest is the dimensionless ratio  $\beta/\alpha$ , which is plotted versus  $f_i$  in Fig. 5. It was noted above that the non-central force constant  $\beta$  should decrease and approach zero for large ionicity. This is the result found experimentally; in Fig. 5 we see that the values of  $\beta/\alpha$  fall close to the straight line drawn from the Si-Ge average to  $\beta/\alpha=0$  at  $f_i=1$ . That is, the primary trends in the elastic constants are described quantitatively by

$$\beta/\alpha \propto 1 - f_i, \quad (18a)$$

which is the simplest possible form having the required result  $\beta=0$  for  $f_i=1$ . This result provides both a simple picture of the experimental force constants as a function of the ionicity and supports the approximations made in the theoretical analysis of Sec. II.

The functional forms of the derived parameters are completed by observing that to a first approximation

$$\alpha(r^3/e^2) = \text{const}, \quad (18b)$$

and

$$S = f_i. \quad (18c)$$

Each of these relations is supported by the experimental data. The left-hand side of (18b) is, apart from small corrections, proportional to  $B^*$ , which was shown in Fig. 2 to be approximately constant. The form (18c) for

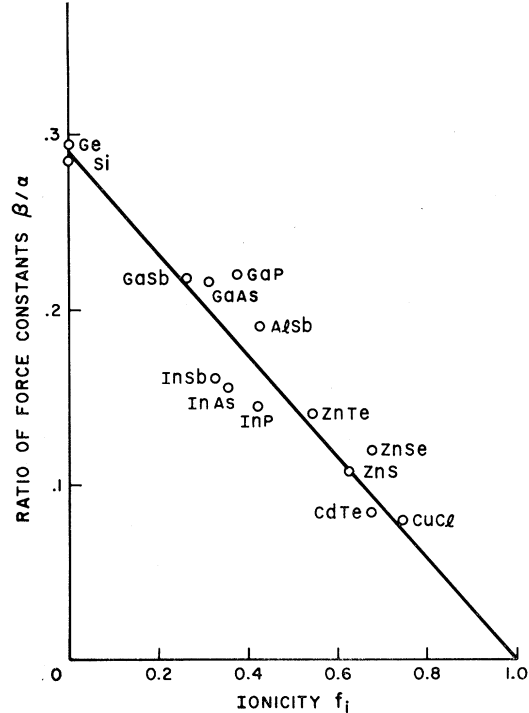


FIG. 5. The ratio of the noncentral to the central force constants  $\beta/\alpha$  in Keating's approximation [see Eqs. (11) and Table II] as a function of the ionicity  $f_i$ . The straight line is drawn from the Si-Ge average to the point  $\beta/\alpha=0$  at  $f_i=1$ , as anticipated by the theoretical discussion of Sec. II.

$S$  is chosen because it is the linear interpolation between the homopolar case where  $S=0$  and the completely ionic case where  $S=1$ , representing rigid ions of unit charge.

The set of formulas (18) may now be combined with Eqs. (11) to provide a useful prescription whereby the elastic constant of any ZB crystal can be calculated solely in terms of its bond length  $r$  and ionicity  $f_i$ . The only additional input required are the magnitudes of  $\alpha$  and  $\beta$  for one crystal. The results are most clearly presented in terms of the reduced elastic constants, the predicted values of which are functions of  $f_i$  alone. The results for the three reduced constants are shown as the solid lines in Figs. 2-4; the only adjustable parameters have been chosen to fit the average values of  $B^*$  and  $C_s^*$  for Si and Ge. The experimental points deviate somewhat from the theoretical curves, for example, the predicted constants for GaP and AlSb are too low, but it is clear that the theory is in generally good agreement with the trends in the experimental numbers. The rms deviations from the theoretical curves (excluding diamond and CuCl for which there are large deviations) are 8, 11, and 10%, respectively, for  $B$ ,  $C_s$ , and  $C_{44}$ .

The large bond-bending forces in the crystals which have any row-I atoms require that they be considered separately from crystals which do not contain row-I atoms. The same equations (11) and (18) would be used

<sup>16</sup> D. Berlincourt, H. Jaffe, and L. R. Shiozawa, Phys. Rev. **129**, 1009 (1963).

[except that (18c) is badly violated in some cases involving row-I atoms], but the parameters would be chosen to fit  $\alpha$  and  $\beta$  for a more appropriate crystal. For example, the elastic constants of  $BN$  would be predicted from those of diamond.

In summary, the elastic properties of the sphalerite structure semiconductors, especially the shear moduli, have been shown to follow simple trends as functions of the ionicity  $f_i$ , as defined by Phillips and Van Vechten. These results (Figs. 2-4) give quantitative form to the observations made by Keyes.<sup>5</sup> Also the present work has presented a simple theory of the elastic constants of tetrahedrally coordinated crystals which involves only two parameters fitted to the elastic data. The theoretical formulation yielded four important results; (a) a relation [Eq. (13)] among the elastic constants and the optical effective charge which was shown to be satisfied to  $\sim 10\%$ , (b) a calculation of the internal strain parameter<sup>9,11</sup>  $\zeta$  from the elastic data, (c) the trends (as function of  $f_i$ ) in the fitted parameters  $\alpha$ ,  $\beta$ , and  $S$  which

supports the interpretation given them in the theory, and (d) a set of formulas from which the elastic constants of a ZB crystal can be predicted from its bond length and ionicity<sup>7</sup> with an expected accuracy of 10%.

*Note added in proof.* The suggestion made in the present paper that the experimental elastic constants of  $ZnSe$  were erroneous has been verified. Recent measurements reported by Lee<sup>17</sup> yield  $C_{11}=8.59$ ,  $C_{44}=4.06$ , and  $C_{12}=5.06$ . With the new constants Eq. (13) is satisfied to 11% in accord with similar compounds. No other results for  $ZnSe$  are greatly changed. The author is indebted to Dr. Y. S. Park for bringing to his attention the work of Dr. Lee.

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<sup>17</sup> B. H. Lee (to be published).

## *F* Center in Cesium Fluoride: Properties of the Optically Excited Center\*

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Studies of the luminescence, photoconductivity, Schottky ionization, bleaching, and ground-state repopulation of the optically excited *F* center in  $CsF$  are reported, with these main results: (a) Excitation in the *F* absorption band centered at 1.88 eV gives rise with high efficiency to a luminescence band (at 1.43 eV) whose unusual properties include the small Stokes shift (0.45 eV), narrow low-temperature width (0.10 eV), and short lifetime (50 nsec). (b) Photoconductivity, Schottky ionization, and optical bleaching show a wavelength dependence in the *F*-band region. Thermal ionization of the optically excited center is found to be more efficient for excitation in the high-energy component of the triplet *F* absorption band, which corresponds to the  $P_{1/2}$  level of the spin-orbit-split *P*-like excited states. This implies that the lattice relaxation processes are influenced by the initial state. (c) The characteristic time for return to the ground state for an optically excited *F* center is found to be 1.0  $\mu$ sec, much longer than the luminescence lifetime. This suggests the occurrence of a bottleneck in the lattice relaxation following the emission.

### I. INTRODUCTION

THE unusual properties of the optical absorption of the *F* center in cesium fluoride have been described in a previous paper,<sup>1</sup> in which a number of

phenomena not usually associated with *F*-center optical properties were shown to be important. Among these are a combination of spin-orbit and Jahn-Teller interactions of comparable strength in the *P*-like excited states, leading to an optical-absorption band (*F* band) consisting of three narrow resolved components, on which structure due to discrete optical-phonon transi-

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quirements for the Ph.D. degree at Cornell University, Ithaca, N. Y.

<sup>1</sup> T. A. Fulton and D. B. Fitchen Phys. Rev. **179**, 846 (1969).