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PHYSICAL REVIEW B

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Relation between Elastic Tensors of Wurtzite and Zinc-Blende Structure Materials

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A transformation is derived which relates the fourth-rank elastic tensors of the two common modifications of tetrahedrally coordinated compounds, cubic zinc blende (ZB), and hexagonal wurtzite (Wz). The basic assumptions are that the local tetrahedra extending to second neighbors about each atom are rotated but otherwise identical in the two structures, and that differences between ZB and Wz for third and more distant neighbors are negligible. The procedure involves Robinson's rotations which apply to any tensorial property, to which is added internal strain between the two inequivalently oriented tetrahedra in the Wz structure. Good agreement is found with empirical constants of ZnS which have been measured in both structures. The transformation permits a simple derivation of "effective" cubic constants for Wz compounds, which are sufficient to extract the most important information on average tetrahedral forces. Effective constants are compared with measured ZB constants for the entire range of tetrahedrally coordinated compounds.

I. INTRODUCTION

It has long been recognized that crystals having the wurtzite (Wz) or sphalerite (zinc blende or ZB) structures are fundamentally similar despite differences between the two structures. ZB crystals are fcc (T_d) with two atoms per primitive cell, whereas Wz crystals are hexagonal (C_{6v}) with four atoms per cell. The fundamental relation between the two structures is that the local environment of any atom in either ZB or ideal Wz ($c/a = 1.633$) is exactly the same through the second neighbor. The two lattices differ only in the arrangement of third and more distant neighbors. Robinson¹ has expressed the relation between ZB and ideal Wz succinctly: Each lattice can be constructed from tetrahedral building blocks. In ZB all tetrahedra are equivalent, but in Wz there are two inequivalently oriented tetrahedra each of which can be related to the standard orientation of ZB tetrahedra by a simple rotation. Thus we expect that a given chemical compound is basically the same, independent of the structure in which it crystallizes, and that, to a good approximation, the tensorial representations of any physical property in the two systems are related by simple rotations.

The fundamental correctness of this comparison of Wz and ZB crystals is most clearly seen by comparing empirical data for compounds (such as ZnS) which can crystallize in either form. For a large range of materials, both modifications have essentially the same first- and second-neighbor separations.^{2,3} Furthermore, the lattice constants for Wz crystals reveal only small deviations from the ideal c/a ratio^{2,3} so the ideal approximation is justified for many properties. Close correspondence between Wz and ZB crystals may be seen in the total energies,³⁻⁵ Raman frequencies,⁶ electronic bands,^{7,8} dielectric constants,⁴ as well as other properties.

The close correspondence of Wz and ZB crystals has been documented by Phillips⁴ and Van Vechten⁴ in terms of a "universal semiconductor model." They have shown that many properties of the entire range of tetrahedrally coordinated compounds are continuous functions of two variables, lattice constant and ionicity, independent of the structure Wz or ZB. Similar conclusions may be drawn from chemical bond analyses, such as that of Pauling,⁹ who implicitly ignores the difference between the structures in his molecular approach. The common feature of the above analyses^{4,9} is

that dominant chemical trends are determined solely by the chemical constituents and the tetrahedral coordination.

Robinson's tensorial relations¹ between properties of ZB and Wz crystals have previously been tested for two third-rank tensor properties, the piezoelectric constant¹⁰ e_{ijk} and nonlinear susceptibility d_{ijk} .¹ The only compound for which these constants have been measured in both modifications is ZnS; in that case agreement is very good. The close relations among these constants for several other similar materials further supports the relations.

In the present paper the relation between ZB and Wz is extended to a fourth-rank tensor, the elastic tensor C_{ijkl} . In this case it is conceptually essential to go beyond the work of Robinson to allow the inequivalent tetrahedra in the Wz crystal to be strained by different amounts. This is incorporated as a generalized internal strain¹¹ which completely accounts for the inequivalent Wz tetrahedra within the force-constant approximations used here. The relation of ZB to Wz phonon dispersion curves has been described by Birman¹² who simply folded the ZB curves into the Wz Brillouin zone. In the acoustic regime this amounts to the approximation that ZB and Wz are indistinguishable. The present results amend his zeroth-order approach in the elastic region to include the effects of the inequivalent tetrahedral orientations.

The primary achievement of the present work is the derivation of simple formulas for effective cubic constants in terms of experimental wurtzite elastic constants. The formulas are accurate to a few percent for ZnS and are generally within the experimental uncertainty. Effective cubic constants lucidly describe the most important information concerning interatomic forces.¹³ Without such simplifications the basic tetrahedral forces are buried in parametrized models made tedious by the presence of complicated forces peculiar to the wurtzite structure. In addition, the present approach is but one example of a general procedure which should be applicable to other structures, for example, the many hexagonal stacking polytypes of SiC or the chalcopyrites¹⁴ which are composed of structurally inequivalent tetrahedra.

It must be emphasized that we are neglecting the deviations from the ideal Wz structure and the difference between ZB and Wz of all forces between third and longer-range neighbors. The success of the method with these approximations underscores the importance of the fundamental tetrahedral units in both structures and supports the arguments that the basic chemical properties are independent of whether the compound crystallizes with ZB or Wz symmetry.

The paper is organized to present in Sec. II the

basic relations between ZB and Wz including the internal strain and to test these relations using empirical data for ZnS. In Sec. III transformed constants for a range of compounds are presented and the effective cubic constants for Wz crystals are quantitatively compared with empirical constants for cubic ZB compounds.

II. BASIC TRANSFORMATIONS

Our starting point is the ansatz that the properties of ZB and Wz crystals are determined by the properties of the constituent tetrahedra. The only interaction between the tetrahedra that is considered here is the essential feature of a connected network—neighboring tetrahedra are joined so that their distortions are not independent. With this ansatz we neglect the *difference* between Wz and ZB in all interactions involving third and more distant neighbors. This procedure is justified by the comments in the Introduction and the fact that long-range forces are known to play only a small role in the elastic properties of ZB crystals.¹³

In addition, we neglect all deviations from the ideal Wz structure.² That is, we neglect both the deviations of c/a from the ideal value and the internal displacement² u of the sublattices. Each of these deviations in real Wz crystals modifies the precise tetrahedral coordination around each atom. However, the deviations are small and are not expected to modify the present results significantly (except possibly for ZnO). Let us note that the displacement parameter u is often referred to as an "internal strain." It must be emphasized that the internal strain discussed below is an internal strain of the ideal Wz structure; here we neglect both u and changes in u with strain.

The first step is to relate the orientations of the tetrahedra in the two structures. The standard¹⁵ axes for tensorial properties of ZB crystals are the cubic axes ($x_1 = x$, $x_2 = y$, $x_3 = z$), in terms of which the four tetrahedral bonding directions are $[111]$, $[1\bar{1}\bar{1}]$, $[\bar{1}1\bar{1}]$, and $[\bar{1}\bar{1}1]$. The two inequivalent tetrahedra in a Wz crystal in the standard configuration¹⁵ (x_3 axis along c axis) are found by rotating the standard ZB tetrahedra with transformation matrices, respectively,¹

$$R^{(1)} = \frac{1}{\sqrt{6}} \begin{bmatrix} \sqrt{3} & 0 & \sqrt{3} \\ -1 & 2 & 1 \\ -\sqrt{2} & -\sqrt{2} & \sqrt{2} \end{bmatrix} \quad (1)$$

and

$$R^{(2)} = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} R^{(1)}. \quad (2)$$

Each rotation $R^{(1)}$ and $R^{(2)}$ transforms the ZB crys-

tal to one of two inequivalent trigonal orientations. Hexagonal symmetry results from the superposition of the two trigonal orientations.

Let T_{ijkl}^{ZB} be the representation of any tensorial property of ZB in the standard orientation. In each of the two trigonal systems the tensor T is represented by

$$T_{ijkl}^{(n)} \dots = R_{ii'}^{(n)} R_{jj'}^{(n)} R_{kk'}^{(n)} R_{ll'}^{(n)} \dots T_{i'j'k'l'}^{ZB} \dots, \quad (3)$$

where summation over repeated indices is understood. For the third-rank nonlinear susceptibility $\chi^{(2)}$, Robinson neglected all interactions between the tetrahedra so that the corresponding tensor for the hexagonal Wz crystal is the average of the two trigonal tensors:

$$\bar{T}_{ijkl}^{Wz} \dots = \frac{1}{2}(T_{ijkl}^{(1)} \dots + T_{ijkl}^{(2)} \dots). \quad (4)$$

It is easily verified that \bar{T}^{Wz} has the correct C_{6v} symmetry.

The averaging procedure (4) is reasonable for the nonlinear susceptibility, since it is exact in the usual approximation that local-field effects are accounted for simply by a phenomenological prefactor. However, for an elastic strain the tetrahedra cannot be thought of as independent—the corners of the neighboring tetrahedra are firmly attached so that the response of each to external forces is not independent. This constraint is correctly taken into account by allowing for strain tensor $\epsilon_{ij}^{(1)}$ for tetrahedra of orientation 1 to differ from that of orientation 2, $\epsilon_{ij}^{(2)}$, subject to the constraint that the average

$$\epsilon_{ij} = \frac{1}{2}(\epsilon_{ij}^{(1)} + \epsilon_{ij}^{(2)}) \quad (5)$$

is the macroscopic strain. The difference between the strains

$$\delta_{ij} = \frac{1}{2}(\epsilon_{ij}^{(1)} - \epsilon_{ij}^{(2)}) \quad (6)$$

is not fixed by the macroscopic strain, but is an internal strain which adjusts to minimize the total energy of the strained crystal.

Let us define the elastic tensors for the two trigonal orientations to be $C_{ijkl}^{(1)}$ and $C_{ijkl}^{(2)}$. Then the strain energy per tetrahedron is

$$\begin{aligned} U &= \frac{1}{4}(\epsilon_{ij}^{(1)} C_{ijkl}^{(1)} \epsilon_{kl}^{(1)} + \epsilon_{ij}^{(2)} C_{ijkl}^{(2)} \epsilon_{kl}^{(2)}) \\ &= \frac{1}{2}(\epsilon_{ij} \bar{C}_{ijkl}^{Wz} \epsilon_{kl} + \delta_{ij} \bar{C}_{ijkl}^{Wz} \delta_{kl} \\ &\quad + \epsilon_{ij} \Delta_{ijkl} \epsilon_{kl} + \delta_{ij} \Delta_{ijkl} \delta_{kl}), \end{aligned} \quad (7)$$

where \bar{C}^{Wz} is the average elastic tensor

$$\bar{C}_{ijkl}^{Wz} = \frac{1}{2}(C_{ijkl}^{(1)} + C_{ijkl}^{(2)}), \quad (8)$$

and Δ is the difference

$$\Delta_{ijkl} = \frac{1}{2}(C_{ijkl}^{(1)} - C_{ijkl}^{(2)}). \quad (9)$$

The internal strain δ_{ij} is fixed by minimizing the energy U in Eq. (7), i. e., requiring $\partial U / \partial \delta_{ij} = 0$. Equation (7) then yields the predicted constants for

the Wz structure:

$$U = \frac{1}{2} \epsilon_{ij} C_{ijkl}^{Wz} \epsilon_{kl}, \quad (10)$$

with

$$C_{ijkl}^{Wz} = \bar{C}_{ijkl}^{Wz} - \Delta_{ijj'j'} (\bar{C}^{Wz})^{-1}_{i'j'k'l'} \Delta_{k'l'kl}. \quad (11)$$

Thus the correct transformation from ZB to the ideal Wz structure is given by (11), where \bar{C}^{Wz} is the average elastic tensor and the correction term has the prototype form¹¹ for an internal strain contribution. The matrix inverse $(\bar{C}^{Wz})^{-1}$ is just the "average" elastic compliance tensor \bar{S}^{Wz} . For any simple crystal system such as C_{6v} the matrix inversion reduces to a simple set of algebraic relations¹⁵ between components of the C and S matrices.

At this point it is pertinent to write out explicitly the transformation for the elastic tensor. Define a three-component vector C^{ZB} , with components $C_1^{ZB} = C_{11}^{ZB}$, $C_2^{ZB} = C_{12}^{ZB}$, and $C_3^{ZB} = C_{44}^{ZB}$, the three independent constants for the cubic structure. For both C^{Wz} and \bar{C}^{Wz} we define the six-component vectors $C_1^{Wz} = C_{11}^{Wz}$, $C_2^{Wz} = C_{33}^{Wz}$, $C_3^{Wz} = C_{12}^{Wz}$, $C_4^{Wz} = C_{13}^{Wz}$, $C_5^{Wz} = C_{44}^{Wz}$, and $C_6^{Wz} = C_{66}^{Wz}$ and similarly for \bar{C}^{Wz} . There is only one independent component of Δ_{ijkl} , $\Delta = \Delta_{14}$, which determines all coefficients which are nonzero in the trigonal system but zero in the hexagonal system [see Ref. 15, p. 229 (class 3M) and p. 300 (class 6MM)]. It is then straightforward to carry out the multiplications in (3) using the matrices (1) and (2) to find

$$\bar{C}_i^{Wz} = \sum_{j=1}^3 P_{ij} C_j^{ZB}, \quad i = 1, 6 \quad (12)$$

and

$$\Delta = \sum_{j=1}^3 Q_j C_j^{ZB}, \quad (13)$$

where P is the 6×3 matrix

$$P = \frac{1}{6} \begin{bmatrix} 3 & 3 & 6 \\ 2 & 4 & 8 \\ 1 & 5 & -2 \\ 2 & 4 & -4 \\ 2 & -2 & 2 \\ 1 & -1 & 4 \end{bmatrix}, \quad (14)$$

and Q is the 1×3 matrix

$$Q = (1/3\sqrt{2}) [1 \quad -2 \quad -2]. \quad (15)$$

The internal strain contribution can be worked out readily for the present case using the form of the \bar{C}^{Wz} and Δ matrices from Ref. 15. Let us define the vector corresponding to the internal strain contribution in Eq. (11) by D ,

$$C_i^{Wz} = \bar{C}_i^{Wz} - D_i, \quad i = 1, 6. \quad (16)$$

One finds the simple results

$$\begin{aligned} D_1 = -D_3 = D_6 = \Delta^2 / \bar{C}_5^{Wz}, \\ D_2 = D_4 = 0, \quad D_5 = \Delta^2 / \bar{C}_6^{Wz}. \end{aligned} \quad (17)$$

The set of Eqs. (16), into which are inserted the formulas (12)–(15) and (17), completely specifies the transformation from three elastic constants of the cubic structure to the predicted six constants of the ideal wurtzite structure. The test of the validity of the transformation is to compare experimental constants for a compound in the Wz structure with those found by transforming the constants measured experimentally for the same compound in the ZB structure.

Tables I and II show the results for ZnS, the only compound for which complete elastic data are available in both structures. In Table I we see that the transformed cubic values agree very well with the experimental¹⁶ constants for hexagonal ZnS. There is a range of experimental values^{17–19} of the cubic constants as shown in Table II. All values were measured by dynamic techniques. The “average” constants listed in Table II are the averages of the two independent experiments^{17,18} which agree closely, disregarding the third set of data¹⁹ for which the bulk modulus differs significantly. With experimental uncertainties of several percent, the present agreement of predicted and experimental values is entirely satisfactory. The final column of Table I lists the average constants \bar{C}^{Wz} neglecting the internal strain. The internal strain contribution is a small correction, but the fractional improvement in agreement is significant. It is noteworthy that the internal strain brings all constants into the same general agreement as are C_{33} and C_{13} , which have no internal strain contribution.

The reverse transformation from Wz to ZB (i. e., defining effective cubic parameters for wurtzite crystals) is probably more important because it

TABLE I. Experimental elastic constants for hexagonal ZnS compared with transformed values from cubic ZnS. Constants for cubic ZnS are the average experimental values shown in Table II. Columns 2 and 3 show, respectively, the transformed values with (C^{Wz}) and without (\bar{C}^{Wz}) the internal strain (IS) contribution. All data are taken at room temperature. Units are 10^{11} dyn/cm².

	Expt ^a	Transformed cubic	
		With IS	Without IS
C_{11}	12.42	12.78	13.07
C_{33}	14.00	13.96	13.96
C_{12}	6.02	5.90	5.61
C_{13}	4.55	4.72	4.72
C_{44}	2.86	2.78	2.84
C_{66}	3.20	3.44	3.73

^aReferences 16.

allows one to derive clearly and simply the average tetrahedral forces in wurtzite crystals. This is an important step in simplifying otherwise complicated parametrization of forces²⁰ peculiar to the wurtzite structure. Of course, the transformation from Wz to ZB is not unique. We choose to define effective cubic parameters by a least-squares fit to the six WZ constants weighted equally.

The most concise procedure for carrying out the least-squares fit utilizes the average constants \bar{C}^{Wz} in an intermediate step. Given the transformation (12), it is straightforward to show that in terms of the \bar{C}^{Wz} the least-squares fit can be expressed by a matrix transformation²¹:

$$\begin{aligned} C_i^{eff} &= \sum_{j=1}^3 \sum_{k=1}^6 [P^T P]_{ij}^{-1} P_{jk}^T \bar{C}_k^{Wz} \\ &\equiv \sum_{k=1}^6 S_{ik} \bar{C}_k^{Wz}. \end{aligned} \quad (18)$$

The matrix S is found numerically to be

$$S = \begin{bmatrix} 0.603 & -0.515 & -0.103 & 1.015 & 1.470 & 0.353 \\ 0.015 & 0.426 & 0.485 & 0.074 & -0.647 & -0.235 \\ 0.118 & 0.412 & -0.118 & -0.412 & -0.176 & 0.118 \end{bmatrix}. \quad (19)$$

Determination of the effective cubic constants is accomplished by calculating \bar{C}^{Wz} which are related to the empirical elastic constants C^{Wz} by a nonlinear relation (16). Coupling Eqs. (11), (13), and (18), the relation can be written in matrix form as

$$\bar{C}^{Wz} = C^{Wz} + (QS\bar{C}^{Wz})^T (\bar{C}^{Wz})^{-1} (QS\bar{C}^{Wz}). \quad (20)$$

Equation (20) can be straightforwardly evaluated for \bar{C}^{Wz} by iteration using the known C^{Wz} as starting values for \bar{C}^{Wz} . The reduced form of the final

term, which is given in Eq. (17), greatly simplifies the matrix manipulations. Finally the effective cubic constants may be evaluated using Eq. (18).

In Table II is shown the comparison for ZnS of the effective cubic constants determined from the Wz data¹⁶ with the experimental constants^{17–19} for the cubic structure. In Table II are listed the most meaningful constants, the bulk modulus $B = \frac{1}{3}(C_{11} + 2C_{12})$, and the two shear constants $C_s = \frac{1}{2}(C_{11} - C_{12})$, and C_{44} . There is very good agree-

TABLE II. Experimental elastic constants of cubic ZnS compared with effective cubic derived (see text of Sec. II) from experimental data for hexagonal ZnS (per Table I). All data are taken at room temperature. Units are 10^{11} dyn/cm².

	Ref. 19	Expt Ref. 17	Ref. 18	Average Refs. 17 and 18	Effective cubic values for Wz
B	7.19	7.75	7.84	7.80	7.70
C_s	1.93	1.93	1.96	1.94	1.81
C_{44}	4.51	4.62	4.61	4.62	4.62

ment between the effective and the experimental cubic values, the worst discrepancy being 7% for C_s . Thus it is quite sufficient to use the effective cubic parameters for quantitative characterization of average tetrahedral forces in Wz structure crystals.

The internal strain between the tetrahedra in the Wz crystal always tends to soften the Wz structure relative to the average of the two trigonal orientations of the ZB crystal. The magnitude of its contribution decreases for materials with large shear constants C_{44}^{Wz} and C_{66}^{Wz} ; internal strain is entirely negligible in diamond or SiC, but is important in soft materials such as CuCl. Within the present approximations we find that crystals with the wurtzite structure are always softer against shear than a ZB counterpart constructed from identical tetrahedra.

The present approach could be straightforwardly extended to the various polytypes, which have more inequivalent tetrahedra although the inclusion of internal strain would be more tedious. Note, however, it was found that the internal strain contribution is negligible in compounds such as SiC. Therefore, the present theory predicts that all polytypes of SiC have essentially identical elastic behavior. Somewhat more variation within the range between columns two and three of Table I is predicted for ZnS polytypes.

III. APPLICATION

In this section is presented the application to several interesting crystals of the formulas derived in Sec. II. First, elastic constants are predicted for several compounds occurring in the Wz structure but whose elastic properties have been measured only in the cubic structure. Next effective cubic constants are derived for Wz crystals and compared with experimental constants of similar cubic crystals.

In Table III are listed predicted hexagonal elastic constants for several crystals which can occur in the Wz structure. Experimental cubic constants are taken from references listed in Ref. 13 (henceforth referred to as I), except as noted. Predicted

TABLE III. Predicted elastic constants for wurtzite structure calculated from experimental data (see Ref. 13, except as noted) taken on compounds in the cubic modification. Units are in 10^{11} dyn/cm².

Material	C_{11}	C_{33}	C_{12}	C_{13}	C_{44}	C_{66}
C	117.65	121.00	9.17	5.81	50.90	54.24
SiC ^a	47.90	52.14	9.78	5.53	14.84	19.06
ZnSe ^b	10.72	11.65	4.46	3.53	2.50	3.13
ZnTe	8.56	9.26	3.70	3.00	2.02	2.43
CdTe	6.22	6.89	3.59	2.91	1.16	1.31
CuCl ^c	5.25	6.16	4.13	3.22	0.70	0.56

^aTheoretical values for cubic constants from Ref. 22.

^bCubic constants from Ref. 25.

^cCubic constants from Ref. 26.

constants were derived from Eqs. (12)–(17). Diamond has been included to illustrate the transformation for a very hard crystal. Also included is SiC using theoretically calculated cubic constant.²²

The internal strain contribution varies greatly. It is important for soft crystals, but entirely negligible for hard crystals. For example, in CuCl the shear constant C_{66}^{Wz} is reduced by 50% from the average constant \bar{C}_{66}^{Wz} . On the other hand, in SiC and C all internal strain contributions are less than 0.1% in the present calculations. For this reason, the present results are the same as found by Arlt and Schodder²³ for SiC, who also transformed the cubic constants of Ref. 22 to the rotated frame. They found good agreement of the rotated values with experimental measurements on the 6H polytype of SiC. The present theory supports the arguments of Arlt and Schodder²³ and, as noted in Sec. II, predicts that all polytypes of SiC will have essentially the same elastic behavior.

Let us now turn to the effective cubic constants for Wz crystals. The constants are evaluated from Eqs. (18)–(20) using the iterative procedure described in Sec. II. The results for several

TABLE IV. Effective cubic constants for wurtzite crystals derived by the procedure of Sec. II. Experimental data for the wurtzite structure are from source noted. Units are 10^{11} dyn/cm².

Material	B^{eff}	C_s^{eff}	C_{44}^{eff}
SiO ^a	22.06	11.90	25.15
BeO ^b	22.52	11.69	19.96
ZnO ^c	14.33	4.55	5.49
CdS ^c	6.11	1.26	2.41
CdSe ^c	5.31	1.02	2.23

^aReference 23, except C_{13} is the theoretical value predicted by Ref. 22.

^bReference 16.

^c*Londolt-Bornstein Numerical Data and Functional Relationships in Science and Technology, New Series*, edited by K. H. Hellwege (Springer, Berlin, 1966), group 3, band 5.

wurtzite crystals are listed in Table IV. As was done in Table II, the most significant moduli $B = \frac{1}{3}(C_{11} + 2C_{12})$, $C_s = \frac{1}{2}(C_{11} - C_{12})$, and C_{44} are listed. The most immediate result is that, except for SiC and ZnO, the effective constants are very close to those of similar ZB crystals.¹³

Quantitative comparison of the elastic properties of the various ZB and Wz crystals can be accomplished by the procedure of I. The dimensionless reduced constants, first introduced by Keyes,²⁴

$$C^* = C/C_0, \quad C_0 = e^2/r^4, \quad (21)$$

where r is the average nearest-neighbor distance, have been shown^{13,24} to be the fundamental measures of elasticity. Size factors have been well accounted for by Keyes's reduction, so that variations in the reduced moduli are related to changes in the nature of the bonding. The second requirement is a scale describing the bonding upon which all the compounds are placed. Such a scale is the ionicity scale of Phillips and Van Vechten⁴ (PVV) or that of Pauling.⁸ The PVV scale is used here following Ref. 13; however, very similar results hold for Pauling's scale. In Table V are listed the values of the ionicity f_i and reduced effective constants.

Comparison of reduced effective constants for Wz crystals with the reduced constants for ZB crystals is presented in Figs. 1-3. For ZB crystals, the ionicities f_i and reduced constants are the same as in Ref. 13, except for new elastic data for ZnSe,²⁵ CuCl,²⁶ CuBr,²⁶ and CuI,²⁶ and corrections^{4,27} to the PVV scale of ionicity. The points for ZnS derived from independent measurements in the two structures are included to show the accuracy of the comparison of ZB and Wz crystals. The differences between the respective ZnS points is always less than the scatter of experimental points about the indicated trends.

The solid lines in Figs. 1-3 are the results of a simple model presented in I. For our purposes here, we can regard the solid lines as merely indicators of general trends with ionicity. Just as

TABLE V. Ionicity and reduced dimensionless effective constants for wurtzite crystals derived from Tables II and IV with definition of C^* given in Eq. (21).

Material	f_i^a	B^{*eff}	C_s^{*eff}	C_{44}^{*eff}
SiC	0.18	1.20	0.65	1.37
BeO	0.60	0.72	0.37	0.64
ZnO	0.66 ^b	0.95	0.30	0.36
ZnS	0.62	1.01	0.24	0.60
CdS	0.68	1.09	0.22	0.43
CdSe	0.70	1.12	0.20	0.47

^aReference 4.

^bReference 3.

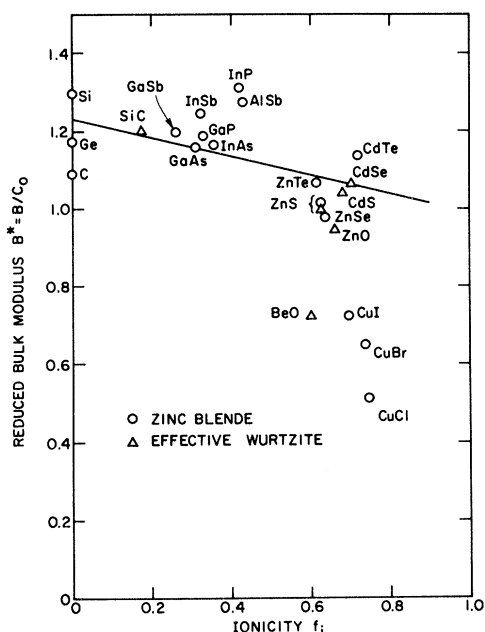


FIG. 1. Reduced dimensionless bulk modulus B^* vs ionicity f_i (Ref. 4). Effective constants for wurtzite crystals are derived following the procedure described in the text and are indicated by triangles. The solid line is the result of a simple model derived in Ref. 13.

was found for ZB crystals,¹³ effective constants for Wz crystals involving no atoms from the first row of the Periodic Table follow the same simple trends

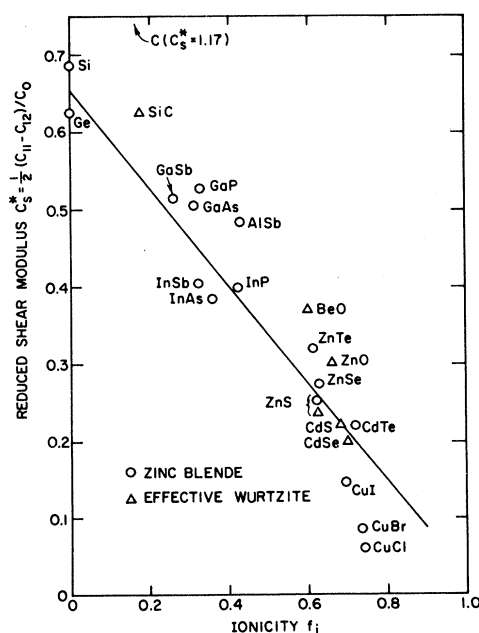


FIG. 2. Reduced dimensionless shear constant C_s^* vs ionicity. The solid line is the result of a simple model derived in Ref. 13.

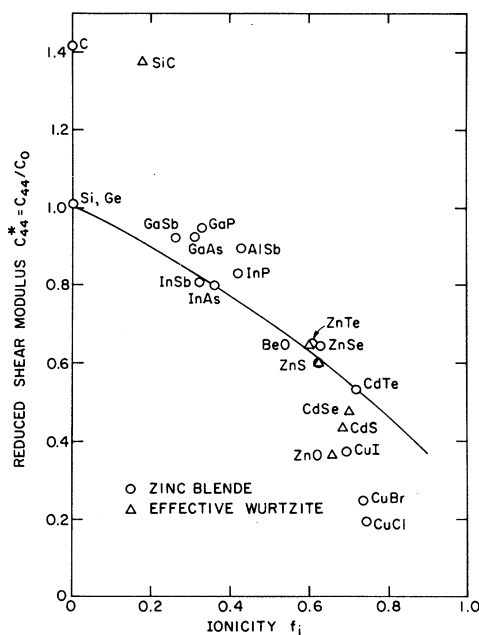


FIG. 3. Reduced dimensionless shear constant C_{44}^* vs ionicity. The solid line is the result of a simple model derived in Ref. 13.

with ionicity. Therefore, we have shown that for these crystals, dominant interatomic forces are basically determined by the tetrahedral unit and are independent of crystal symmetry. This further supports the conclusion that differences between ZB and Wz crystals can be ignored to a good approximation in the analysis of chemical trends.

The most striking deviations from the trends are for crystals with one or both atoms from the first row of the Periodic Table. The cases where both atoms are from the first row, however, appear to be systematic. The proposal that C, BN, and BeO should form a separate family was made in I; here, we find that the effective constants for BeO support that conclusion. No experimental data for BN have been reported. The present results suggest that reduced constants for cubic BN can be estimated by interpolating between diamond and BeO in Figs. 1-3.

On the other hand, there seem to be no simple categories for mixed compounds with one row-one atom. For example, SiC appears to be very similar to Si in its shear constant C_{44}^* , but similar to diamond in the other shear constant C_{44}^* . The low value of C_{44}^* in ZnO is particularly puzzling and is unresolved. Possible anomalous forces in ZnO

such as oxygen-oxygen overlap would be expected to increase C_{44}^* . It may be that deviations from the ideal Wz structure are responsible for the anomalies in ZnO.

IV. SUMMARY

A transformation relating the respective elastic tensors of ZB and Wz modifications of a compound has been derived. With it one can calculate either the six predicted Wz constants from three ZB constants or vice versa. The transformation from Wz to ZB results in cubic constants which are termed "effective," since their values depend upon the manner in which one fits the six Wz constants. In this paper are given specific formulas which achieve a least-squares fit to the six Wz constants, weighted equally.

The transformations are checked in Sec. II by application to ZnS, the only compound for which elastic data have been measured in both structures. The accuracy of a few percent in the transformed values is probably sufficient both for any theoretical calculation based on the elastic data and for many practical applications.

In Sec. III are presented the results of the transformations for all Wz crystals and several ZB crystals for which experimental elastic data are available. The effective cubic constants for Wz crystals are especially interesting because they can provide a simple picture of the average tetrahedral forces in a Wz compound. One result is that for Wz compounds with no atoms from the first row of the Periodic Table, the tetrahedral building blocks are virtually indistinguishable from those of ZB counterparts. The simple trends with ionicity presented in I are further supported by these Wz crystals.

In the present approach the deviations of real Wz crystals from the ideal Wz structure and the differences between ZB and Wz of third- and more-distant-neighbor interactions are entirely neglected. The success of the theory is further evidence of the basic correctness of the assertion⁴ that all important chemical properties are determined by the tetrahedral coordination and are very insensitive to the differences between ZB and Wz.

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Calculation of Light Scattering from Anisotropic Semiconductors

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The Raman-scattering cross section from anisotropic semiconductors, such as PbTe, Ge, etc., has been calculated. Detailed computation of the scattered spectra from spin-density fluctuations (SDF) and charge-density fluctuations (CDF) is presented. It is shown that, for linearly polarized light, the contributions from SDF and CDF to the scattered spectrum can be separately obtained by an appropriate choice of the polarization directions. Finally, the possible detection of the ion acoustic wave, which to date has not been observed experimentally, has been considered.

I. INTRODUCTION

The inelastic or Raman scattering of electromagnetic radiation from a plasma provides useful information about the spectrum and the nature of its elementary excitations. The Raman-scattering cross section is completely characterized by the wave-number transfer $\vec{q} = \vec{k}_{in} - \vec{k}_{out}$ and $\omega = \omega_{in} - \omega_{out}$, where \vec{k}_{in} (\vec{k}_{out}) and ω_{in} (ω_{out}) are, respectively, the incoming (outgoing) wave number and frequency. It is useful to classify the scattering according to the magnitude of \vec{q} (fixed-angle scattering) and then for this fixed angle to analyze the intensity and polarization of the scattered radiation as a function of ω (spectrum analysis). For most light-scattering experiments from semiconducting plasmas the

wave-number transfer is smaller than the inverse screening length, i. e., $q\lambda_s < 1$. For a one-component isotropic plasma, the cross section is proportional to the charge-density fluctuations (CDF) of the electron gas. For the case $q\lambda_s < 1$ the scattered intensity resides almost entirely in the so-called plasma line.

However, in solids there are three known mechanisms which produce single-particle scattering and lead to direct measurements of the momentum distribution of electrons (holes) in the conduction (valence) band. Firstly, a finite spin-orbit coupling in the valence bands allows scattering from spin-density fluctuations (SDF) of the electrons. Here the scattered spectrum is that of a single particle.^{1,2}

Secondly, the plasma in many semiconductors,