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Theory of the Piezoelectricity of Zinc-Blende-Type and Wurtzite-Type Crystals

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A theory of piezoelectricity in zinc-blende-type and wurtzite-type crystals is given. The charge-transfer effect contributes mainly to the piezoelectric constant. The assumption of the second-nearest-neighbor electron interaction (π-electronic energy) in the crystal enables us to predict theoretically the charge-transfer value, so that the piezoelectric coefficients can be calculated. The π-electronic interaction energy is found to be $0.5 \sim 0.8$ times the σ-bonding (tetrahedral-bonding) energy in wurtzite crystals.

I. INTRODUCTION

Zinc-blende-type (ZB) and wurtzite-type (Wu) crystals are piezoelectric. The piezoelectric coefficients of these crystals have been obtained experimentally.[1,2] The most striking aspect of the experimental data for the piezoelectric constants of ZB and Wu crystals is that $\sqrt{3}\,e_{14}$(ZB), or its equivalent e_{33}(Wu), reverses sign on going from II-VI to III-V crystals. But no successful theory has been proposed which enables us to predict the piezoelectric constants or to understand the origin of the effect.

To explain these data, a simple theory of the rigid-ion model had been proposed.[1] In that theory it is assumed that the charges of anion and cation in the crystals under stress remain constant, and only the relative bond angle changes. Then, for ZB, the piezoelectric constant e_{14} is given by

$$e_{14} = \tfrac{3}{16} e^*/d^2 \quad , \tag{1}$$

where e^* is the effective charge of the lattice and d is the bond length from anion to cation. The piezoelectricity of the cubic ZnS crystal shows good agreement with the theory,[3] but this is not the case for all other crystals.[1,]

Arlt and Quadflieg[2] introduced the charge redistribution effect (i.e., change in ionicity) for the explanation of experimental data on piezoelectricity. They gave the relation

$$\begin{aligned} e_{14} = {} & \text{(the displacement of ionic charge)} \\ & + \text{(the internal displacement of the electron cloud relative to the atomic nucleus)} \\ & + \text{(the effect due to the strain-induced change in ionicity)}. \end{aligned} \tag{2}$$

The first and second terms in Eq. (2) are equal to Eq. (1), because the effective charge e^* includes the effect of the displacement of the electronic charge, i.e., electronic polarization.[4] The third term is the charge-transfer effect under the strain. They estimated the contribution of the change in ionicity such that the positively charged atoms lose their charges linearly in expanding the bond length; i.e., if the bond length is expanded a factor of 2, all atoms would become neutral.

Phillips and Van Vechten[5] showed that there is some correlation between the magnitude of the charge-transfer effect and the ionicity f_i of the crystal. They gave the relation

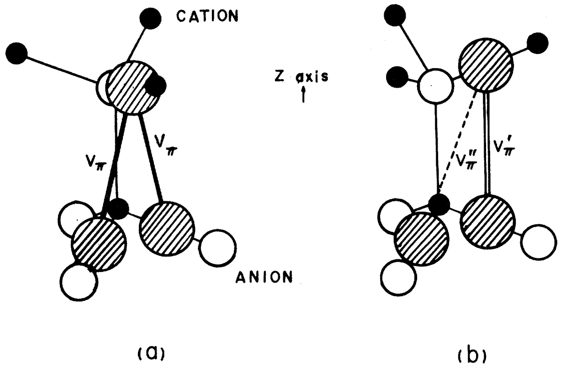

FIG. 1. Structure of cation, anion, and covalent electron in (a) zinc-blende-type crystals and (b) wurtzite-type crystals. Solid circles show the cation, open circles show the anion, and cross-hatched circles show the spherical covalent electrons. V_π, V_π', and V_π'' denote the π-electronic, or the second-nearest-neighbor electron interaction.

$$e_{\mathrm{po1}} = (\zeta - \tfrac{1}{4} s)\sqrt{3}\, e^* \times (\text{lattice-constant-dependent part}) \ , \quad (3)$$

where $e_{\mathrm{po1}} = \sqrt{3}\, e_{14}(\mathrm{ZB})$ or $e_{33}(\mathrm{Wu})$, ζ is the ionic part (in the presence of the nearest-neighbor central force only, $\zeta = 1.0$, whereas the second-neighbor bond-bending force makes $\zeta = 0.6$ [5]), and s shows the charge-transfer effect, i.e., charge redistribution. The s term in Eq. (3) is the same effect as the third term in Eq. (2). The sign of e_{po1} is determined by whether the ionic polarization or charge-transfer effect is the dominant factor. s changes from 10.21 (GaSb) to -3.86 (ZnO). Generally speaking, s is large if the ionicity is small. These s values can not be explained by Arlt and Quadflieg's idea. No successful theory has been proposed which enables us to understand the origin of the charge-transfer effect or to predict an index s which is not yet measured. In this article, a theory to explain the charge-transfer effect and to calculate the index s will be given.

II. CRYSTAL STRUCTURE AND SECOND-NEAREST-NEIGHBOR ELECTRON BONDING

Since ZB and Wu structure have the same unit tetrahedron, the cohesive energy[6] and the band structures of these crystals[7] are nearly equal to each other. But there is some difference of properties between ZB and Wu. It has been observed that the charge-transfer index s for ZB crystals is always plus except for ZnS, but for Wu crystals, it is minus except for BeO.[5] There is a difference in bond length between ZB and Wu structures of the same compounds.[8] In addition, Wu crystals have an anisotropy of the thermal expansion coefficient.[9] It should be a reasonable assumption that the different properties of two structures ZB and Wu may be caused by the secondary structure of these crystals. The primary structure is the unit tetrahedron, and the secondary structure means the $\bar{4}3m$ (ZB) or $6mm$ (Wu) crystal structure. The primary structures of ZB and Wu are equal to each other.

Since the sp^3 tetrahedrally bonding energy is of course due to the electronic interaction, we may assume that the difference of properties between ZB and Wu is assumed by the second-nearest-neighbor electron (denoted by SNE for simplicity hereafter) bond. The SNE interaction is clarified in Fig. 1. The nearest-neighbor bond electrons are the sp^3 tetrahedrally bonded electrons belonging to the same unit tetrahedron. The nearest-neighbor electron bond is constant with respect to the change of the secondary structure. The second-nearest-neighbor electron bond is the interaction between a bond charge (original charge) and the charge which appears second along the bonding chain counting from the original charge.

The SNE interaction is the same as the π-electronic interaction in ethylene.[10] In Fig. 2, the electronic structure of the ethylene is shown. The bond electron between carbon C_1 and carbon C_2 is described as σ bonding. The nearest-neighbor electron bond in ZB or Wu, which constitutes the tetrahedron, is the same as the σ bonding in ethylene. The SNE interaction in ZB and Wu is quite similar to the π-electronic interaction in ethylene. The π-electronic interaction in ethylene changes with the change of the secondary structure of ethylene. If the C_2-HH part (primary structure of ethylene) rotates along the C_1-C_2 bond axis, the length of π-electronic interaction changes. In Fig. 1, if the upper tetrahedron rotates along the z axis, the SNE bond length changes. Thus the SNE interaction is the same as the π-electronic interaction in ethylene.

The SNE interaction length of ZB is different from that of Wu, so that we may conclude that the

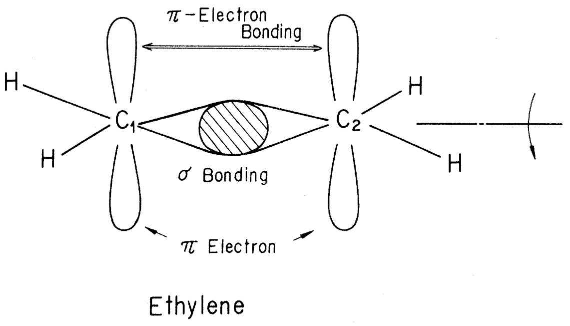

FIG. 2. Electron structure of ethylene. C_1 and C_2 show the carbon atoms and H shows the hydrogen atom.

difference in properties between ZB and Wu is caused by the difference of the SNE, or π-electronic, interaction from ZB to Wu. We denote the sp^3 tetrahedrally bonding as σ bonding and the bonding energy as V_σ. The SNE interaction energy is described by V_π in analogy with the π-electronic interaction in ethylene.

The aim of this paper is to clarify the relation between SNE interaction and the properties of piezoelectricity, or others. Assuming the V_π as the Morse-type potential energy, we will get the quantitative theory to explain the charge-transfer index s.

III. INTERACTION LENGTH OF SNE

Wu crystals have piezoelectric constants e_{33}, e_{31} and e_{15}, but ZB crystals show only e_{14}. Transforming the z axis of ZB structure from $\langle 001\rangle$ to $\langle 111\rangle$, we have the relation[1]

$$e_{33}{}' = \sqrt{3}\, e_{14} \quad , \tag{4}$$

where $e_{33}{}'$ is the piezoelectric constant referred to the new z axis of ZB. Therefore we may only treat e_{33} of Wu and $e_{33}{}'$ of ZB for simplicity.

In the theory in this article, the following three assumptions are made. The first is that the bond electron is spherical (electron cloud) and its radius is proportional to the bond length. In Fig. 1, the constitutions of the anion, cation, and bond electrons in ZB [Fig. 1(a)] and Wu [Fig. 1(b)] are shown (only one pair of interacting SNE are shown). This spherical bond-electron model is adequate for the experimental data[11] and the theoretical calculation.[12] Walter and Cohen[12] calculated the ground-state bond-electron distribution. The second assumption is that the position of the bond electron deviates from the center of anion-cation bond, and can move only along the bond axis under the stress. In Ge, the bond charge stands on the center of two Ge atoms, whereas in GaAs, it shifts towards the anion site (see Ref. 12). Ge's ionicity is of course zero, and GaAs's ionicity is 0.31. Thus, accompanying the increase of ionicity, the bond charge shifts from the center of anion-cation bond to anion site along the bond axis. The third assumption is that there is SNE interaction energy.

The equilibrium position of bond charge is determined by the V_σ and V_π (SNE interaction energy). The bond-electron cloud may move as a result of the change of V_π, i.e., the change of interaction length of SNE. In Fig. 1, one sees that the interaction length of SNE changes with the strain along with the z axis. Of course, the SNE interaction along the x-directional bonding exists, but, since the change of interaction length of the x-directional SNE bonding is small compared to that of z-directional bonding under the z-directional strain, we ignore the effect of the x-directional interaction.

The center of the bond-electron cloud is shifted from halfway between the anion-cation bond towards the anion site by an amount proportional to the ionicity f_i. The position of the electron cloud is given as

$$x_0 = (a_0/2\sqrt{3})(1-\alpha f_i) \quad , \tag{5}$$

where x_0 is the x component of the center of the electron cloud measured from the anion site, a_0 is the size of the unit tetrahedron and α is a constant. From the paper of Walter *et al.*, one sees that in $f_i = 0.31$ crystals (GaAs), the bond charge shifts towards the anion from the bond center by an amount of 10% of the anion-cation bond length. α is then nearly 0.6. But in GaAs the total bond charge is smaller than the Ge's bond charge. Then, we may assume that effective α is smaller than 0.6 under the constant bond-charge model. While we do not have the exact base to determine α, it will be assumed to have a value suitable for the coincidence of theory and experimental data: $\alpha \approx 0.3$. Discussion of the α value will be given in Sec. VII.

By a simple geometric consideration, the SNE interaction length between one pair of SNE is given as

$$l_e = l_{e0} + A\delta_\parallel + B\Delta f_i \quad , \tag{6}$$

where $\delta_\parallel$ is the strain of the lattice constant along with z axis and Δf_i is the deviation of the ionicity from the ionicity under no SNE interaction. l_{e0}, A, and B are given in Table I. Detailed mathematical calculations are given in the Appendix. For Wu in Fig. 1(b), there are two different SNE interaction energies $V_\pi{}'$ and $V_\pi{}''$. Since the influence of $V_\pi{}''$ is small (A and B for $V_\pi{}''$ is small), we ignore the $V_\pi{}''$ in Wu. Generally, l_{e0}, A, and B for Wu are not equal to those for ZB. Since the SNE interaction energy is the function of the l_e, a difference of properties which are affected by SNE interaction will appear between ZB and Wu.

IV. SNE INTERACTION ENERGY AND CHARGE-TRANSFER MECHANISM

Now the explicit formulation of the SNE interaction energy will be introduced. The σ-bonding (tetrahedral-bonding) energy is described as

$$V_\sigma = K_1(\pm\Delta f_i)^2 \quad , \tag{7}$$

where K_1 is the σ-bonding force constant against the motion of the spherical bond electron which is denoted by the change of ionicity, Δf_i. In analogy to V_σ, we assume the V_π as follows:

$$V_\pi = K_2(l_e/d_0)^2 \quad , \tag{8}$$

where K_2 is a constant and l_e is given by Eq. (6) and Table I. d_0 is the bond length from anion to

TABLE I. The second-nearest-neighbor electron interaction length $l_e = l_{e0} + A\delta_{\parallel} + B\Delta f_i$ under the strain $\delta_{\parallel}$ parallel to the z axis. Δf_i shows the change of ionicity under the stress. d_0 is the anion-to-cation bond length.

Structure	l_{eo}	A	B
Wurtzite	$\frac{4}{3} d_0(1+\frac{1}{4}\alpha^2 f_i)$	$-\frac{4}{3} d_0$	$\frac{2}{3}\alpha^2 f_i d_0$
Zinc-blende	$\sqrt{2}\, d_0(1+\frac{1}{6}\alpha^2 f_i)$	$-(5/3\sqrt{2})\, d_0$	$(\sqrt{2}/3)\alpha^2 f_i d_0$

cation. Then the total energy is described as

$$V(\mathrm{ZB}) = V_\sigma + 2V_\pi = K_1(\pm\Delta f_i)^2 + 2K_2(l_e/d_0)^2 \ , \qquad (9a)$$

$$V(\mathrm{Wu}) = V_\sigma + V_\pi{}' = K_1(\pm\Delta f_i)^2 + K_2(l_e{}'/d_0)^2 \ , \qquad (9b)$$

where $V(\mathrm{ZB})$ and $V(\mathrm{Wu})$ show the total energy of ZB and Wu, respectively. $l_e{}'$ in Eq. (9b) is the SNE interaction length of Wu. In Eq. (9a), the factor 2 for V_π is caused by the existence of two V_π in Fig. 1(a). Δf_i is given by the relation $\partial V/\partial(\Delta f_i) = 0$, and we have

$$\Delta f_i(\mathrm{ZB}) = \frac{-4K_2(B/d_0)[(l_{e0}+A\delta_{\parallel})/d_0]}{[2K_1+4K_2(B/d_0)^2]} \ , \qquad (10a)$$

$$\Delta f_i(\mathrm{Wu}) = \frac{-2K_2(B'/d_0)\,[(l_{e0}+A'\delta_{\parallel})/d_0]}{[2K_1+2K_2(B'/d_0)^2]} \ . \qquad (10b)$$

where l_{e0}', A', and B' in Eq. (10b) are given by Table I. The redistributed charge per $\delta_{\parallel}$ is given by $\partial(\Delta f_i)/\partial\delta_{\parallel}$ and

$$e_r(\mathrm{ZB}) = C\,\frac{2K_2(AB)/d_0{}^2}{\pm K_1 + 2K_2(B/d_0)^2} \ , \qquad (11a)$$

$$e_r(\mathrm{Wu}) = C\,\frac{K_2(A'B')/d_0{}^2}{\pm K_1 + K_2(B'/d_0)^2} \ , \qquad (11b)$$

where C is a constant and e_r shows the transferred charge. The sign ± of K_1 is as follows: If e_r is negative, the sign is plus, and if it is positive, the sign is negative. The reason why this relation is assumed will be discussed in Sec. VII.

Using Eq. (11), l_{e0}, $l_{e0}{}'$, A, A', B and B' from Table I, we get

$$e_r(\mathrm{ZB}) = C\,\frac{\frac{10}{9}(K_2/K_1)\,\alpha^2 f_i}{1+\frac{4}{9}(K_2/K_1)\alpha^4 f_i{}^2} \ , \qquad (12a)$$

$$e_r(\mathrm{Wu}) = C\,\frac{\frac{8}{9}(K_2/K_1)\,\alpha^2 f_i}{-1+\frac{4}{9}(K_2/K_1)\alpha^4 f_i{}^2} \ . \qquad (12b)$$

Introducing the new normalized parameter $K_2{}' = \frac{4}{9}(K_2/K_1)\,\alpha^4$, Eqs. (12) are transformed into

$$e_r(\mathrm{ZB}) = C'\,\frac{K_2{}' f_i}{1+K_2{}' f_i{}^2} \ , \qquad (12a')$$

$$e_r(\mathrm{Wu}) = C'\,\frac{\frac{4}{5} K_2{}' f_i}{-1+K_2{}' f_i{}^2} \ , \qquad (12b')$$

where $C' = \frac{10}{9} C\,\alpha^{-2}$ is a newly defined constant. Our purpose in this article is to calculate the $K_2{}'$ and e_r. The difference of e_r from ZB to Wu is due to the difference of $K_2{}'$, which is proportional to K_2 in Eq. (8). One should be careful to note the factor $\frac{4}{5}$ in Eq. (12b′).

The redistributed charge is proportional to se^* in Eq. (3), which should be equal to e_r of Eqs. (12′). The measured s values[5] for several ZB and Wu crystals are tabulated in column 2 of Table II. The theoretical result for ZB is shown in Fig. 3, in which we assume $K_2{}' = -28$ and $C' = 0.282$. These values $K_2{}'$ and C' are determined by the method of least squares. The solid line is the equation (12a′), using $K_2{}' = -28$ and $C' = 0.282$, and the dotted lines in Fig. 3 are the calculated values using $K_2{}' = -28 \pm 12$ and $C' = 0.282$. Now we may conclude that $K_2{}'$ is nearly constant for all ZB except ZnS and the origin of the charge-transfer mechanism is the existence of the SNE interaction. Deviation of the experimental se^* from the calculated line in several crystals will be discussed in Sec. VII.

Figure 4 shows the $K_2{}'$ for Wu calculated from Eq. (12b′), in which C' is assumed to be 0.282 the same as in ZB. At $f_i = 0.88$, $K_2{}'$ seems to go to zero; this suggests the fact that the SNE interaction energy has the Morse-type potential energy. Detailed discussions will be given in Sec. V. For BeO, the index s shows the positive sign and $K_2{}'$ is calculated as 3.92, which deviates from the other all-Wu crystals.

V. DISCUSSION FOR THE $K_2{}'$ VALUE

Now we discuss the difference of $K_2{}'$ between Wu and ZB crystals. ZB have $K_2{}' \approx -28$, whereas

TABLE II. The experimental data of the charge-transfer value for several tetrahedral compounds (Ref. 5). s shows the charge-transfer index, e^* is the effective charge of the lattice, se^* is the charge-transfer value, and f_i is the ionicity (Ref. 13).

Crystals		s	e^*	se^*	f_i
(Wu)	AlN	−2.76	0.47	−1.3	0.449
	CdS	−2.85	0.41	−1.17	0.685
	CdSe	−2.39	0.39	−0.97	0.699
	ZnO	−3.86	0.53	−2.02	0.614
	BeO	2.08	0.61	1.27	0.602
II-Vi (ZB)	ZnSe	1.29	0.35	0.45	0.675
	ZnTe	1.48	0.28	0.414	0.596
	CdTe	1.44	0.34	0.49	0.675
	ZnS	−0.37	0.39	−0.144	0.623
III-V (ZB)	GaSb	10.2	0.15	1.53	0.261
	GaAs	8.96	0.20	1.74	0.31
	InSb	7.37	0.15	1.10	0.321
	GaP	5.53	0.24	1.33	0.374
	AlSb	5.36	0.22	1.18	0.426
	InAs	4.29	0.22	0.94	0.367

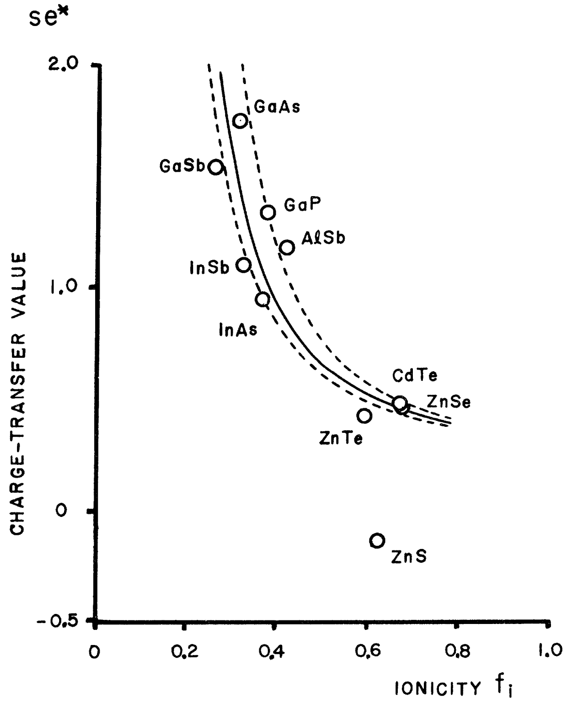

FIG. 3. Comparison of the theoretically calculated charge-transfer value (solid line) and the experimental data for zinc-blende-type crystals. Solid line is calculated from Eq. (12a′), where $K_2' = -28$ and $C' = 0.282$ are used. Dashed lines are $K_2' = -28 \pm 12$ lines.

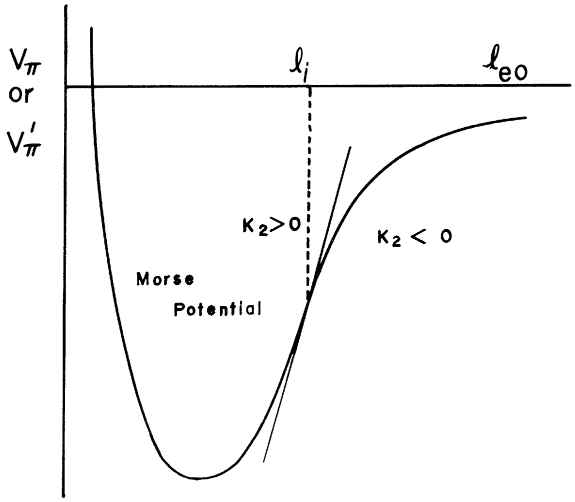

FIG. 5. Morse-potential-type second-nearest-neighbor electron interaction energy. l_{eo} is the interaction length. For large l_{eo}, K_2 has the negative sign, whereas for $l_{eo} < l_i$, it has a positive sign. l_i is the inflection point for the Morse potential.

Wu have +1.5~+4.0. This difference of K_2' from ZB to Wu will be due to the difference of l_{e0} from ZB to Wu. The assumption of the Morse-type energy for the SNE interaction will give a reasonable prediction for different values of K_2' from ZB to Wu. Figure 5 denotes the Morse-type potential for the SNE interaction which has the inflection point l_i. In the region $l_{e0} > l_i$, K_2' is negative, and for $l_{e0} < l_i$, it is positive. The value K_2' may be obtained from

$$K_2' = D(l_{e0} - l_i) \quad . \tag{13}$$

l_{e0} is dependent upon f_i and the difference in structures, ZB or Wu. D is a constant, which is the tangent of the line in Fig. 5. From Fig. 4, one knows the inflection point to be the l_{e0} of Wu at $f_i = 0.88$. Then, extrapolating the relation between K_2' and l_{e0} from the Wu region to the ZB region, we will predict the value K_2' for ZB. Figure 6 gives

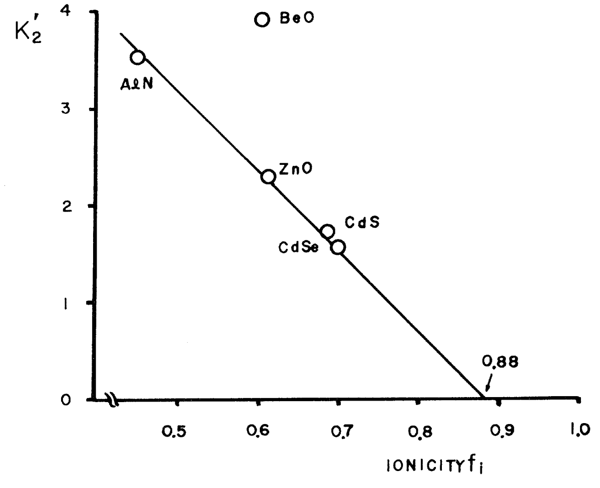

FIG. 4. K_2' for several wurtzite-type crystals. At $f_i = 0.88$, K_2' goes to zero.

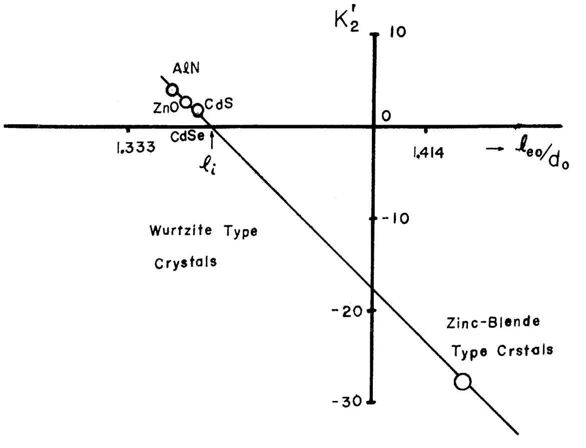

FIG. 6. Relation of the K_2' between zinc-blende-type and wurzite-type crystals. K_2' is given as $K_2' = D(l_{eo} - l_i)$ [see Eq. (13) in text], and l_{eo} s are given in Table I. l_i is the inflection point of the Morse potential in Fig. 5.

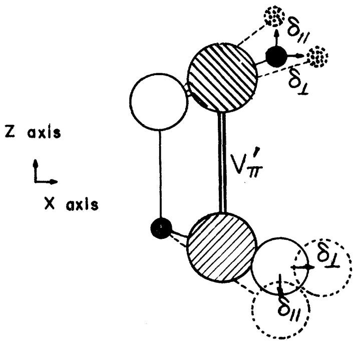

FIG. 7. Thermal expansion of $\delta_\parallel$ parallel to z axis and $\delta_\perp$ perpendicular to z axis.

these relations. Now the value $K_2' = -28$ for ZB can be demonstrated using the line in Fig. 6. The agreement with the theory and the experiment is good. In Fig. 6, $\alpha^2 = 0.1$ ($\alpha = 0.31$) is assumed for the calculation of l_i. One may conclude that the origin of the charge transfer is due to the SNE interaction, which is described by the Morse potential.

VI. ANISOTROPY OF THERMAL EXPANSION COEFFICIENT OF Wu CRYSTALS

The SNE interaction is anisotropic in Wu crystals. In Fig. 1, V_π' for Wu is not equal to V_π in ZB which is equal to the x-directional SNE energy in Wu. Thus, Wu crystals have anisotropy in thermal expansion coefficient, which relates to the anisotropy of the SNE interaction. Since the charge-transfer mechanism is due to the SNE interaction, one expects that the anisotropy of the thermal expansion coefficient relates to the index s. In Wu, let the small expansions of the lattice constants of the z axis and x axis be $\delta_\parallel$ and $\delta_\perp$, respectively (Fig. 7). The bonding energy V_σ (V_σ is the tetrahedral isotropic bonding energy) for $\delta_\parallel$ and $\delta_\perp$ is

$$V_\sigma = K_1'[(\delta_\parallel)^2 + b(\delta_\parallel)^3 + (\delta_\perp)^2 + b(\delta_\perp)^3] , \qquad (14)$$

where the third-order terms are the anharmonicity of the bonding energy. K_1' is a constant, which is proportional to K_1 in Eq. (7), but does not have the same numerical value, because in Eq. (14) the variables are $\delta_\parallel$ and $\delta_\perp$, whereas in Eq. (7) it is Δf_i. The potential energy V_π' of the SNE interaction in Wu is

$$V_\pi' = K_2''[(\delta_\parallel)^2 + b(\delta_\parallel)^3] , \qquad (15)$$

because in Wu the expansion of the x axis does not affect the SNE interaction length along the z axis. Figure 7 shows this situation. K_2'' is proportional to K_2 in Eq. (8). From Eqs. (14) and (15), we have for the expansions $\delta_\parallel$ and $\delta_\perp$

$$V_\parallel = (K_1' + K_2'')[(\delta_\parallel)^2 + b(\delta_\parallel)^3] ,$$

$$V_\perp = K_1'[(\delta_\perp)^2 + b(\delta_\perp)^3] , \qquad (16)$$

where $V_\parallel$ and $V_\perp$ are the potential energies of the expansions of the z axis and x axis, respectively. The anisotropy of the thermal expansion coefficient is given as[14]

$$(\alpha_\parallel - \alpha_\perp)/\alpha_\parallel = K_2''/K_1' , \qquad (17)$$

where $\alpha_\parallel$ and $\alpha_\perp$ are the thermal expansion coefficients of the z axis and x axis, respectively. From Eq. (8) and Eq. (15), K_2'' should be proportional to K_2' and from Eq. (14), K_1' is proportional to K_1. Then, K_2''/K_1' in Eq. (17) should be proportional to K_2' given from the charge-transfer effect in the piezoelectricity by Eq. (12b'). Figure 8 shows this proportionality for ZnO and CdS.[9] The proportionality is fairly good. One can estimate the value of K_2''/K_1', which is 0.8 for ZnO and 0.6 for CdS.

VII. DISCUSSION

A. Difference of Anion-to-Cation Bond Length d_0 between ZB and Wu for Same Compounds

Some compounds (ZnS, ZnSe, ZnTe, and CdS, etc.) have the two structures ZB and Wu.[8] The SNE interaction length l_e along with the z axis of Wu structure is different from that in ZB structure (Fig. 1). SNE interaction energy is different in the two structures. Since the z-directional anion-to-cation bond length d_0 (not l_e) is affected by the SNE interaction energy, it is expected that there is a correlation between the difference of the bond length d_0 from Wu to ZB, and the charge-transfer index s. Figure 9 shows this relation. d_0 is cal-

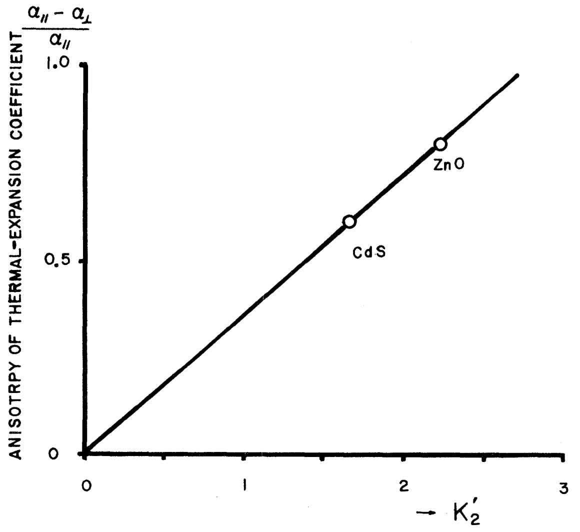

FIG. 8. Proportionality between the anisotropy of the thermal expansion coefficient $(\alpha_\parallel - \alpha_\perp)/\alpha_\parallel$ and the SNE energy K_2' for ZnO and CdS (Ref. 9).

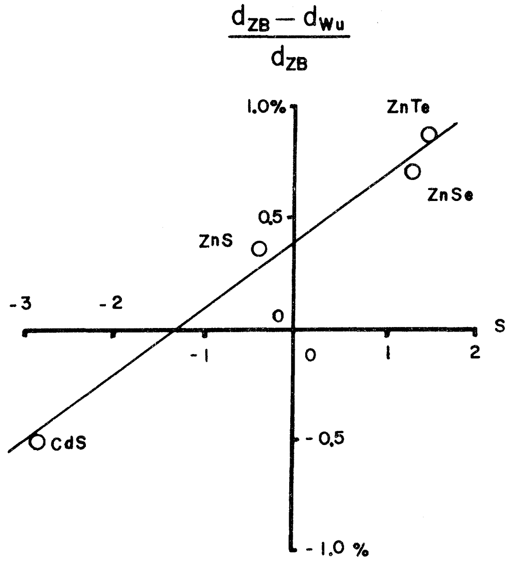

FIG. 9. Correlation between the difference of the bond length from zinc-blende and wurtzite structures of same compounds (Ref. 8) and the charge-transfer index s. d_{ZB} and d_{Wu} show the z-directional anion-to-cation chemical bond length d_0 (not l_{e0}).

culated from Ref. 8. For the quantitative calculation of the bond length d_0, we have to have an accurate formulation of V_π and V_π', which we do not have at this time. In this paper, only the second-order term in V_π or V_π' was determined.

B. Values K_2 and α

From $K_2' = \frac{4}{9}(K_2/K_1)\,\alpha^4$ and the assumption $\alpha^2 = 0.1$, the value of K_2/K_1 is of the order of 200~ 500 for Wu, which is an anomalously large value. From the thermal expansion coefficients, K_2''/K_1' is of the order of 0.5 to 0.8. Thus the estimations of the absolute value of K_2/K_1 by two methods give values which differ by a factor of 500.

But this abnormal K_2/K_1 value is deceptive. The variable in Eq. (7) is Δf_i, whereas in Eq. (8), it is l_e/d_0. Using the l_e value of Table I for Wu, Eq. (8) is transformed into

$$V_\pi' = \tfrac{4}{9}K_2\alpha^4 f_i^2(\Delta f_i)^2 + \text{other terms}. \qquad (18)$$

Now the variable in Eq. (18) is Δf_i, and the force constant for Δf_i is $\frac{4}{9}K_2\alpha^4 f_i^2$. Thus the anisotropy of potential energy V_π'/V_σ based on the same variables in V_π' and V_σ for Wu, which should be equal to Eq. (17), is

$$\begin{aligned} V_\tau'/V_\sigma &= (\tfrac{4}{9}K_2/K_1)\,\alpha^4 f_i^2 \\ &= K_2'' f_i^2 \;\; [= K_2''/K_1' \text{ in Eq. (17)}]. \qquad (19) \end{aligned}$$

For ZnO, since $K_2' = 2.231$ and $f_i = 0.616$, $V_\pi'/V_\sigma = 0.84$. This agrees well with value obtained by the anisotropy of the thermal expansion. Again, we can conclude that the charge-transfer mechanism and the anisotropy of the thermal expansion have the same origin: SNE interaction in crystals.

The value of α in Eq. (5) was taken to be 0.31 so that the theoretical and the experimental values for K_2' of ZB and Wu would agree with each other. Walter and Cohen calculated the electron distribution for several crystals.[12] In GaAs ($f_i = 0.31$), the center of the spherical electron cloud shifts from the center of anion-to-cation bond by an amount of 10% of the bond length d_0. This means that α is nearly 0.62. But the covalent electron in GaAs is smaller than Ge. Thus the effective α for the constant spherical electron model is smaller than 0.62. In GaAs, the number of bonding charge is 0.55 times that of Ge's bonding charge. Now we may conclude that the effective α value of electron cloud in GaAs is $0.62 \times 0.55 = 0.34$, which well explains the assumed value 0.31.

C. Oxygen Compounds

The oxygen compounds (ZnO and BeO) have the largest SNE energy of all compounds. We found that the magnitude of the SNE energy is as large as 0.8 times the tetrahedrally bonding energy in ZnO or BeO. ZnO crystal has an abnormally large distortion from the ideal wurtzite structure,[15] which could not be explained by a simple electrostatic theory.[16] BeO's K_2' deviates from the K_2' of other all-Wu crystals (Fig. 4). It will be expected that the large SNE energy in ZnO and BeO is the main cause of the abnormally large distortion in the case of ZnO structure and of the abnormal K_2' value for BeO.

D. Sign of K_1 in Eqs. (10) and (11)

In Eqs. (10) and (11), we assume that, for ZB ($e_r > 0$), the sign of K_1 is positive, whereas for Wu ($e_r < 0$), the sign of K_1 is negative. In Sec. V, it was shown that the SNE interaction energy is the same as the Morse potential. Then, K_2 for ZB with long l_{e0} is always negative (Fig. 5). With regard to experimental results, it seems that for ZB the charge-transfer effect should be dispersive at $f_i \approx 0.2$ so that the sign of K_1 should be positive for negative K_2. For Wu, K_2 is positive. From Eq. (11b), the sign of K_1 should be negative to get the negative charge-transfer effect.

E. Random Deviation of Experimental se^* for ZB

In Fig. 3, one sees that the experimental se^* for ZB are randomly deviated from the calculated value. On the contrary in Wu, the experimental values agree well with the theory (Fig. 4) except BeO. One cause of random deviations in ZB is that the measured ionicity f_i may have a small error as yet. For example in AlSb, if its f_i is 20% smaller than the value defined by Phillips,[13] then the experimental se^* is consistent with the calculated value. The ionicity f_i is not so accurately determined as yet. Pauling's[17] f_i is sometimes different from Phillips's f_i for several crystals.

Also, the e_{14} values are not so accurately measured,[2] so that it is expected that the experimental se^* have small fluctuation.

F. C Value

Physical meaning of coefficient C in Eqs. (11) and (12) is as follows: se^* in Eq. (3) is the screening effect of the bond charge associated with the distortion of lattice, because the charge redistribution weakens or cancels the movement of nuclear charge. The screening effect is proportional to the number of movable bond charges times the mobility of the charge, where the mobility is described by $\partial \Delta f_i / \partial \delta_{\parallel}$. Therefore the parameter C means the value of bond charge e_b. From $C = \frac{10}{9} C' \alpha^2$, using $C' = 0.282$ and $\alpha^2 = 0.1$, $C \approx 0.03$ is obtained. From Fig. 3 of the paper of Walter *et al.*,[12] one sees that the number of movable bond charges e_b at $f_i = 0.5$ (average of all crystals) is 0.03, which agrees reasonably with our parameter C. The difference of bond charge from a crystal to others is included in the effective α discussed in Sec. VIIB. Our simple model is the constant-bond-charge model and the α includes the difference of bond charge accompanying the difference of ionicity f_i.

VIII. CONCLUSION AND REMARKS

The microscopic mechanism of the piezoelectricity for zinc-blende- and wurtzite-type crystals was investigated. The main contribution to the piezoelectric constant is the charge-transfer effect. The charge-transfer effect is due to the second-nearest-neighbor electron (SNE) bond energy. This energy is the same as the π-electronic energy in ethylene. Since SNE energy is different from ZB to Wu crystals, there exists the difference of the properties in piezoelectricity and the thermal expansion coefficient of ZB to Wu.

In oxygen compounds, the SNE energy is very large. The magnitude of the SNE energy in oxygen compounds is 0.8 times the tetrahedrally σ-bonding energy.

It is expected that in $AB\text{O}_3$ oxygen-perovskite crystals, the SNE interaction energy should have a strong effect upon the ferroelectricity. In the Slater-Devonshir model for the ferroelectricity of the displacive-type ferroelectric crystals, the effect of the charge-transfer energy has been completely ignored. Accompanying the displacement of the ions in crystals having some covalency, the change of the SNE energy should always appear. In $AB\text{O}_3$ crystals, if the SNE interaction energy gives a lower energy with the displacement of the ions from the ideal perovskite structure, we will expect, at lower temperature, that the crystal has the stable state with the distortion the same as the ZnO crystals.

APPENDIX

The interaction length of SNE is given. From Fig. 10, l_e is directly obtained as

$$l_e^2 = (\tfrac{1}{2}c)^2 + (x_e)^2 ,$$

$$x_e^2 = \left(\frac{a}{2\sqrt{3}}\right)^2 (1-\alpha f_i)^2 + \left(\frac{a}{2\sqrt{3}}\right)^2 (1+\alpha f_i)^2 + 2\left(\frac{a}{2\sqrt{3}}\right)^2 (1-\alpha f_i)(1+\alpha f_i)\cos\theta , \qquad \text{(A1)}$$

where a and c are the lattice constants. For Wu, $\theta = 0$, and $\frac{2}{3}\pi$, and for ZB, $\theta = \frac{1}{3}\pi$.

The strain $\delta_{\parallel}$ parallel to the z axis is introduced; then

$$c \rightarrow c_0(1-\delta_{\parallel}), \quad a \rightarrow a_0(1+\tfrac{1}{2}\delta_{\parallel}) , \qquad \text{(A2)}$$

where the Poisson ratio is assumed to be 2:1. f_i under the stress is

$$f_i = f_{i0} + \Delta f_i . \qquad \text{(A3)}$$

Using (A1)–(A3), in

$$l_e = l_{e0} + \frac{g}{2 l_{e0}} \delta_{\parallel} + \frac{h}{2 l_{e0}} \Delta f_i ,$$

the following relations are obtained: for V_π in ZB,

$$l_{e0} = \left[\left(\frac{c_0}{2}\right)^2 + \left(\frac{a_0}{2\sqrt{3}}\right)^2 (1 + 3\alpha^2 f_{i0}^2)\right]^{1/2} ,$$

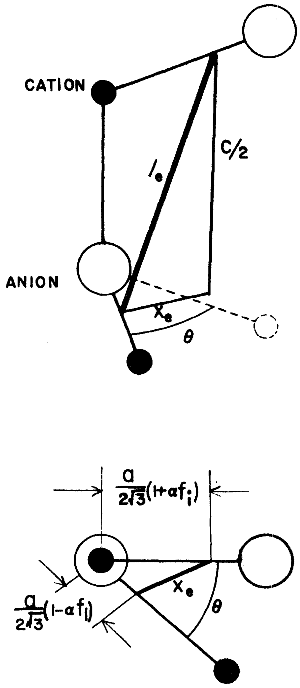

FIG. 10. Interaction length of the second-nearest-neighbor electron (π-electronic) interaction.

$$g = -2\left(\frac{c_0}{2}\right)^2 + \left(\frac{a_0}{2\sqrt{3}}\right)^2 (1 + 3\alpha^2 f_{i0}^2) ,$$

$$h = 6\left(\frac{a_0}{2\sqrt{3}}\right)^2 \alpha^2 f_{i0} ;$$

for V_π' in Wu,

$$l_{e0} = \left[\left(\frac{c_0}{2}\right)^2 + 4\left(\frac{a_0}{2\sqrt{3}}\right)^2 (\alpha f_{i0})^2\right]^{1/2} ,$$

$$g = -2\left(\frac{c_0}{2}\right)^2 + 4\left(\frac{a_0}{2\sqrt{3}}\right)^2 (\alpha f_{i0})^2 ,$$

$$h = 8\left(\frac{a_0}{2\sqrt{3}}\right)^2 \alpha^2 f_{i0};$$

for V_π'' in Wu

$$l_{e0} = \left[\left(\frac{c_0}{2}\right)^2 + \left(\frac{a_0}{2\sqrt{3}}\right)^2 (3 + \alpha^2 f_{i0}^2)\right]^{1/2} ,$$

$$g = -2\left(\frac{c_0}{2}\right)^2 + \left(\frac{a_0}{2\sqrt{3}}\right)^2 (3 + \alpha^2 f_{i0}^2) ,$$

$$h = 2\left(\frac{a_0}{2\sqrt{3}}\right)^2 \alpha^2 f_{i0} . \tag{A4}$$

In V_π'' for Wu, since g and h are small compared to the corresponding values in V_π for ZB or V_π' for Wu, we ignore the effect of V_π'' in Wu. For l_{e0}, we will have the more simplified forms. f_{i0} is in the neighborhood of 0.5 ± 0.25 for all ZB and Wu crystals. Then $f_{i0} = 0.5 + \epsilon f_{i0}$, where ϵf_{i0} is a small value. Using this relation,

$$l_{e0} = \left[\left(\frac{c_0}{2}\right)^2 + \left(\frac{a_0}{2\sqrt{3}}\right)^2\right]^{1/2} \times \{1 + \tau + \tfrac{1}{6}\alpha^2 \epsilon f_{i0}\} \tag{A5}$$

for ZB, and for Wu

$$l_{e0}' = \tfrac{1}{2} c_0 \{1 + \tau' + \tfrac{1}{4}\alpha^2 \epsilon f_{i0}\} .$$

If $f_{i0} = 0$, l_{e0} equals $[(\frac{1}{2}c_0)^2 + (a_0/2\sqrt{3})]^{1/2}$ for ZB and $\frac{1}{2}c_0$ for Wu, respectively. Substituting $f_{i0} \rightarrow \epsilon f_{i0}$ and determining τ and τ' to satisfy this initial condition, we get

$$\begin{aligned} l_{e0}' &= \tfrac{4}{3} d_0 (1 + \tfrac{1}{4}\alpha^2 f_{i0}) \quad \text{for Wu,} \\ l_{e0} &= \sqrt{2}\, d_0 (1 + \tfrac{1}{6}\alpha^2 f_{i0}) \quad \text{for ZB} , \end{aligned} \tag{A6}$$

where $c_0 = \frac{8}{3} d_0$ and $a_0 = (\frac{8}{3})^{1/2} d_0$ are used. d_0 is the bond length from anion to cation. In g in Eq. (A4), small $\alpha^2 f_{i0}^2$ terms can be neglected. Then, $g/(2l_{e0}) = -(5/3\sqrt{2})\, d_0$ for ZB and $-\frac{4}{3} d_0$ for Wu, which are equal to A and A' in Eq. (6).

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