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The Piezoelectric Constant of Zinc-Sulfide[*]

B. D. Saksena[†]
Pennsylvania State College, State College, Pennsylvania
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The piezoelectric constant of zinc-sulfide has been calculated in two ways. First, by regarding it as a purely ionic crystal and considering that all of the atoms are equally effective in producing the moment, and second, by regarding it as a purely covalent crystal and considering only the nearest neighbors. In the former case, the result agrees completely with that obtained by Born and Bormann.

The moment produced in an homogeneous elastic deformation is considered to be $ze\Delta r$, where Δr is the variation of the distance between the sulfur and zinc atoms on deformation and ze is the charge on the ions. We first find the moments due to all the sulfur atoms at a given distance from a zinc atom in the crystal. Resolving these along the axes and summing, we get the piezoelectric equations of the crystal. Next, the moments due to various sets of sulfur atoms are summed so as to obtain a quickly converging result, and from this the piezoelectric constant can be obtained. The piezoelectric constant for a purely covalent crystal (formal charge on Zn atom 2−, and on S atom 2+) is found to be 5.4×10^4 and that for a purely ionic crystal (formal charge on Zn 2+ and on S atom 2−) -15.8×10^4. Since the observed value of the piezoelectric constant (-4.20×10^4) lies between these two extremes, it is seen that the crystal has 67 percent ionic character and a formal charge of 0.68 unit on zinc and −0.68 unit on sulfur.

THE piezoelectric constant of zinc-sulfide has been calculated by Born and Bormann[1] on the basis of the lattice theory. It is proposed to calculate it here by an alternative method used by the author[2] for α-quartz, which enables us to calculate the piezoelectric constant directly from the structure of the crystal.

The Si−O bonds in α-quartz were considered to be largely covalent because of the large value of the Si−O force-constant,[3–5] namely, 5.0×10^5 dynes/cm and the high values of dissociation energy[6] (184 kcal) and the hardness (7.0) of the crystal. The forces between the silicon and oxygen atoms are therefore of a short range character; i.e., the forces between the nearest neighbors are large in comparison with those between the next nearest ones. It was therefore supposed that in the case of α-quartz the nearest neighbors alone would be effective in determining the moment, and the polarization was computed on this basis. The supposition appears to be well justified, since there is good agreement between the observed and calculated values.[2,7] For a purely ionic crystal, since the forces between the neighbors are weak and those between the next nearest are not negligible, the piezoelectric moment would have to be computed by considering all of the atoms.

Zinc-sulfide is considered to be partly homopolar and partly ionic.[8] It may be expected that the force per unit displacement between the zinc and sulfur atoms is much smaller than that between the silicon and oxygen atoms in quartz; and this is, indeed, indicated by its smaller hardness (4.0) and dissociation energy[9] (97 kcal) and greater compressibility (-38×10^{-12} cm^2/dyne). We have, therefore, computed its moment in two ways: firstly, by considering it as a purely ionic crystal, and secondly, by regarding it as a purely covalent crystal and considering only the nearest neighbors. The results obtained in the first case are identical with those obtained by Born.

Zinc-sulfide is a cubic crystal, the side of the unit cell, a, being 5.427A, and the closest distance between the zinc and sulfur atoms equal to 2.35A. There are four zinc and four sulfur atoms in the unit cell, the zinc atoms being at the corners and face-centers of the unit cell, and the sulfur atoms at points $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$, $(\frac{1}{4}, \frac{3}{4}, \frac{3}{4})$, $(\frac{3}{4}, \frac{1}{4}, \frac{3}{4})$, and $(\frac{3}{4}, \frac{3}{4}, \frac{1}{4})$. There is only one piezoelectric constant, e_{14}, given by the equations:

$$p_x=e_{14}u_{yz},\quad p_y=e_{14}u_{xz},\quad p_z=e_{14}u_{xy}, \tag{1}$$

where p_x, p_y, p_z are the components of the electric moments along the axes, and u_{yz}, u_{xz}, and u_{xy} are the strain components.

For finding the moments we suppose that a homogeneous elastic deformation acts on the crystal, and that the axes of the crystal are also the axes of the strain so that they remain unchanged after the strain. In an elastic deformation, the distances between the zinc and sulfur atoms would be altered. For a purely ionic crystal, we can assume that each zinc atom carries a charge of +2 units, and a sulfur atom a charge of −2 units. The electrical moment produced by a change in the distance, r, between a zinc and a sulfur atom would be $2e\Delta r$. If Δr is considered to be positive, there would be a motion of the positive charge away from the negative charge, so that the moment would be directed from the sulfur to the zinc atom along the line joining them. The direction cosines of the moment can be obtained by subtracting the coordinates of the

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[†] Visiting Research Associate. Now at the National Research Council, Ottawa, Canada.

[1] M. Born and E. Bormann, Ann. phys. **62**, 218 (1920).

[2] B. D. Saksena, Proc. Indian Acad. Sci. **28**, 423 (1948).

[3] B. D. Saksena, Proc. Indian Acad. Sci. **16**, 270 (1942).

[4] J. Barriol, J. phys. radium **7**, 209 (1946).

[5] Matossi, J. Chem. Phys. **17**, 679 (1949).

[6] Alfred G. Gaydon, *Dissociation Energies and Spectra of Diatomic Molecules* (Chapman and Hall, Ltd., London, 1947), p. 214.

[7] B. D. Saksena, Proc. Indian Acad. Sci. **A. 28**, 437 (1948).

[8] L. Pauling, *Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1940), pp. 6, 178.

[9] Reference 6, p. 216.

sulfur atom from those of the zinc atom. The moments can then be resolved along the axes.

In a homogeneous elastic deformation, the change in the distance, r, between two points P and Q caused by the strain can be expressed in terms of the strain components. Love[10] has shown that the change in the length of a line PQ after strain is given by the expression:

$$\Delta r = r(l^2 u_{xx} + m^2 u_{yy} + n^2 u_{zz} + lm u_{xy} + mn u_{yz} + ln u_{zx}), \quad (2)$$

where r is the length of a line PQ before strain, l, m, n are its direction cosines, and u_{xx}, u_{xy}, etc., are the strain components. If we associate P with a zinc atom and Q with a sulfur atom, the resolved parts of the moments along the axes due to the elastic deformation would be given by the expressions:

$$p_x = 2e\Delta r \cdot l, \quad p_y = 2e\Delta r \cdot m, \quad p_z = 2e\Delta r \cdot n. \quad (3)$$

In order to obtain the piezoelectric moment for the crystal, we should first find the moments due to all the sulfur atoms at a given zinc atom. We consider the zinc atom P which lies at the origin (0, 0, 0) of our unit cell, and find the moments $2e\Delta r$ due to all the sulfur atoms at the same distance r from P in the crystal. These can be resolved along the axes as indicated in Eqs. (3) and summed. In this way we obtain the piezoelectric equations as given in Eqs. (1). The next step is to add the moments due to various sets of sulfur atoms at different distances from P so as to obtain a quickly converging result. This has been possible by using a method similar to that described by Slater[11] for finding the Madelung constant for NaCl. Knowing the moment due to all of the sulfur atoms at any zinc atom, we can easily determine the piezoelectric moment for the unit-cell; and from this we can obtain the value of the piezoelectric constant by dividing by the volume of the unit cell.

We must first find all the sulfur atoms which surround the zinc atom (0, 0, 0). It is easy to show that these are situated at points $(n_1 a/4; n_2 a/4; n_3 a/4)$, where n_1, n_2, n_3 are any three numbers selected from the set 1, −3, 5, −7, 9, −11, 13, −15, etc. The distance from the origin to any point is $(n_1^2+n_2^2+n_3^2)^{\frac{1}{2}}\cdot a/4$. The number of sulfur atoms at this distance can be determined easily. If n_1, n_2, n_3 are all different, there are six ways of arranging them, and since each can be positive or negative, there are eight possible combinations of signs giving 48 terms. But, since the product of n_1, n_2, n_3 must be either positive or negative, we have only 24 points. If two indices are equal, we have 12 points; and if all are equal, we have only 4 points.

If, therefore, we have a group of four points for which the moments act along the directions whose direction-cosines are $(-l, -m, -n)$, $(-l, m, n)$, $(l, -m, n)$, and $(l, m, -n)$, the resolved parts of moments along the axes will be given by

$$p_x = -(2e)(4rlmn)u_{yz},$$

with similar terms for p_y and p_z. (4)

TABLE I. Values of the moments resulting from neighboring groups of sulfur atoms at any zinc atom.

Values of			Distance r from the zinc atom at the origin	Number s of sulfur atoms at distance r	$-\frac{1}{4}s\frac{(n_1n_2n_3)}{(n_1^2+n_2^2+n_3^2)}$
n_1	n_2	n_3			
1	1	1	$(3)^{\frac{1}{2}}\cdot a/4$	4	−1/3
−3	1	1	$(11)^{\frac{1}{2}}\cdot a/4$	12	9/11
−3	−3	1	$(19)^{\frac{1}{2}}\cdot a/4$	12	−27/19
−3	−3	−3	$(27)^{\frac{1}{2}}\cdot a/4$	4	1
1	5	1	$(27)^{\frac{1}{2}}\cdot a/4$	12	−15/27
1	5	−3	$(35)^{\frac{1}{2}}\cdot a/4$	24	18/7
1	5	5	$(51)^{\frac{1}{2}}\cdot a/4$	12	−25/17
−3	5	−3	$(43)^{\frac{1}{2}}\cdot a/4$	12	−135/43
−3	5	5	$(59)^{\frac{1}{2}}\cdot a/4$	12	225/59
5	5	5	$(75)^{\frac{1}{2}}\cdot a/4$	4	−5/3

Relation (4) can be easily verified with the help of relations (2) and (3). Since we are finding the moments at the zinc atom at the origin (0, 0, 0), we can express the values of l, m, and n in terms of n_1, n_2, and n_3. These are, without regard to their signs,

$$l = n_1/(n_1^2+n_2^2+n_3^2)^{\frac{1}{2}}, \quad m = n_2/(n_1^2+n_2^2+n_3^2)^{\frac{1}{2}},$$
$$n = n_3/(n_1^2+n_2^2+n_3^2)^{\frac{1}{2}}.$$

Since $r = (n_1^2+n_2^2+n_3^2)^{\frac{1}{2}}\cdot a/4$, expression (4) now becomes

$$p_x = -4n_1n_2n_3(2ea)u_{yz}/4(n_1^2+n_2^2+n_3^2) \quad (5)$$

with similar terms for p_y and p_z.

Let us now consider s sulfur atoms (where s is a multiple of four) at distance r from the zinc atom at the origin. Since the direction cosines of the moments due to these atoms can be arranged in groups of four of the type considered above, the moments along the axes due to the s sulfur atoms at distance r from the origin is given by

$$p_x = -sn_1n_2n_3(2ea)u_{yz}/4(n_1^2+n_2^2+n_3^2) \quad (6)$$

with similar terms for p_y and p_z. The values of the quantity g given by the expression $-\frac{1}{4}s(n_1n_2n_3)/(n_1^2+n_2^2+n_3^2)$ are tabulated in Table I for different values of n_1, n_2, n_3. It may be seen that the sign of the moment changes for different values of n_1, n_2, and n_3, since the sign of the product $n_1n_2n_3$ also changes. Table I can be extended to include higher values of n_1, n_2, and n_3.

To find the resolved parts of the moments along the axes resulting from all of the sulfur atoms at different distances from the zinc atom at the origin, or in other words, to obtain the value of the quantity, g, for the crystal, we adopt the following procedure which gives a quickly converging result. We consider the zinc atom $P(0, 0, 0)$ inside a cube whose side extends from $-\frac{1}{4}na$ to $\frac{1}{4}na$ along the three axes of the crystal. All points with all three indices (n_1, n_2, n_3) equal to n lie at the

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[10] A. E. H. Love, *Mathematical Theory of Elasticity* (Dover Publications, New York, 1944), pp. 38, 39.

[11] John C. Slater, *Introduction of Chemical Physics* (McGraw-Hill Book Company, Inc., London and New York, 1939), p. 229.

TABLE II. Variation of moment with cell dimensions.

n	Total number of sulfur atoms	Total moment
1	4	−0.0416666
3	32	−0.1545964
5	108	−0.1206254
7	256	−0.1217672
9	500	−0.1215307
11	864	−0.1216475

corners of the cube, those with two indices equal to n lie at the edges of this cube, and those with one index equal to n lie in the faces of this cube, while the remaining points, with indices all different from n, are wholly within the cube. Their contributions are therefore $\frac{1}{8}$, $\frac{1}{4}$, $\frac{1}{2}$, and 1, respectively.

In this way we have calculated moments for all values of n up to 11. The results are given in Table II. It is thus seen that the result rapidly converges to -0.1216. This quantity multiplied by $(2ea)$ gives the resolved part of the moment from all the sulfur atoms in the crystal at any zinc atom.

Similarly, the resolved part of the moment arising from all of the zinc atoms at any sulfur atom would be the same. The total moment is, however, not doubled and remains the same, since each ion is counted twice, once when the zinc atom was at the origin and secondly when the sulfur atom was at the origin. Since there are four zinc and four sulfur atoms in the unit-cell, the piezoelectric moment along the axes would be multiplied by four; i.e., $-4(0.1216)2ea$. The piezoelectric constant e_{14}, being equal to the moment per unit volume, is given by $e_{14}=-0.9728ea/a^3=-0.9728e/a^2$. Since $e=4.77\times10^{-10}$, and $a=5.427\times10^{-8}$ cm, we get $e_{14}=-15.8\times10^4$. If, however, the charge on the ion is ze instead of $2e$ we have

$$e_{14}=-7.9z\times10^4. \tag{7}$$

We can now consider the moments arising from the nearest neighbors only. If ze is the charge on the ion, then from Table I, the resolved part of the moment from four sulfur atoms at any zinc atom is $-\frac{1}{3}\times\frac{1}{8}(zea)$, and proceeding in the manner described in the previous previous paragraph we get

$$e_{14}=-2.7z\times10^4. \tag{8}$$

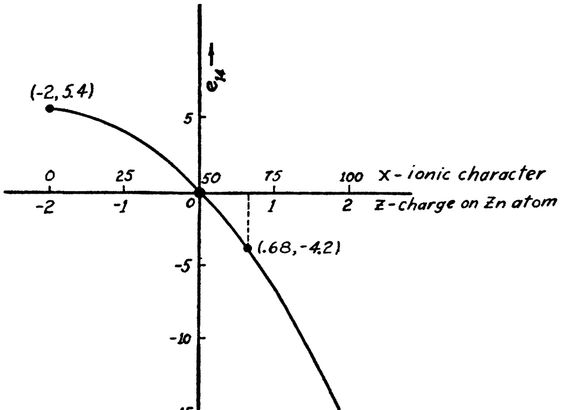

FIG. 1. Dependence of the piezoelectric constant on the ionic character.

If zinc-sulfide were perfectly covalent, there would be a formal charge of 2− on zinc and 2+ on sulfur.[8] The value of e_{14} for a purely covalent crystal is therefore $+5.4\times10^4$, while that for a purely ionic crystal has been shown to be -15.8×10^4. According to Cady[12] the best experimental value of e_{14} is -4.2×10^4, which lies between the two extremes.

We can, therefore, roughly estimate the proportion of the ionic to the covalent character in the following manner. The charge on a zinc atom for a 100 percent ionic crystal is $+2$ units and for a 100 percent covalent character it is -2 units. If, therefore, the crystal has x percent ionic and $100-x$ percent covalent character, the formal charge may be assumed to be

$$z=4a-2, \quad \text{where} \quad a=x/100. \tag{9}$$

Similarly the value of e_{14} for a 100 percent ionic character $(a=1)$ is -15.8×10^4 and for a 100 percent covalent character $(a=0)+5.4\times10^4$. Therefore, for a crystal which is x percent ionic and $100-x$ percent covalent, and has a formal charge of z units, the piezoelectric constant e_{14} is given by

$$e_{14}=-7.9az-2.7(1-a)z. \tag{10}$$

Using Eqs. (9) and (10) it is possible to obtain z for any value of e_{14}. Since the observed value of the latter is -4.2×10^4, we get $a=0.67$ and $z=0.68$. This shows that the atoms have 67 percent ionic character, and that the formal charge on zinc is 0.68 unit. This appears to be a quite reasonable conclusion for, according to Pauling, also, the bonds have enough ionic character. Relation (10) has been plotted graphically in Fig. 1. It appears that the piezoelectric constant is zero when the ionic character is 50 percent and then diminishes rapidly towards -15.8 as the ionic character increases. Since the ionic character may be supposed to increase with the increase of temperature, the value of e_{14} would diminish (towards higher negative value) on heating the crystal. Further, if the crystal be considered to be 100 percent ionic at its melting point (1020°C), it can be seen by a linear intrapolation that even at the absolute zero of temperature the value of e_{14} would have an appreciable negative value (about -0.7).

The results obtained for the purely ionic crystal are identical with those of Born. The second relation in expressions (5) of Born and Bormann reduces to $e_{14}=-7.6z\times10^4$, which is identical with our expression (7). Expression (3) of their paper, which has been quoted in later literature also,[13] does not contain z, the

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[12] Walter G. Cady, *Piezo-Electricity* (McGraw-Hill Book Company, Inc., London and New York, 1946), p. 229.

[13] Reference 12, p. 743.

charge on the ion. The value of e_{14} calculated from this expression[14] is -23×10^4. From relation (7) derived in the present paper we find that for a purely ionic crystal $z=2$, and $e_{14}=-15.8\times 10^4$. This at first sight appears to be a discrepancy; but since the second relation in expressions (5) of Born is identical with our expression (7), it only means that the value 6.5 of $k-k_0$, which has been used to calculate e_{14} from expression (3) of Born, would give a value of z which is 23/15.8 (or 1.5) times 2. This is also verified with the help of the first relation in expressions (5) of Born which gives a relation between z and $k-k_0$, and we find $z=3.03$. The value of $k-k_0$ (6.5) needs to be revised.

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[14] Herzfeld, *Handbuch der Experimental Physik* (VII), Teil 2, p. 341.

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A Note on the Ground State in Antiferromagnetics

J. M. Luttinger
Department of Physics, University of Wisconsin, Madison, Wisconsin

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The lowest state of an antiferromagnetic substance is investigated by using the Ising model for the spins. By means of a method of Luttinger and Tisza it is found possible to derive earlier results of Anderson very simply.

I. INTRODUCTION

Recent neutron diffraction experiments of Shull on antiferromagnetics have been interpreted by Anderson[1] in terms of a model in which spins interact with not only their nearest neighbors, but also with their next-nearest neighbors. Néel[2] had already introduced such a model to explain the large ratios of the "paramagnetic" Curie temperature θ to the actual transition temperature T_c. The basic point of improvement in Anderson's version is the finding of configurations of the spins which give lower energies than the ones which were used by Néel. The existence of these configurations has two effects: (1) the θ/T_c ratios are increased, and are more in conformity with experiment; (2) the configurations predicted seem to be just those found by Shull in his neutron diffraction experiments. Anderson chose the configurations he did largely on the basis of plausibility and intuition, and the question arises as to whether or not these are really the configurations of lowest energy. It is the purpose of this paper to show in a systematic and rigorous manner that this is indeed the case. The technique used is a generalization of a method developed by Luttinger and Tisza,[3] and applied by them to the case of dipole interactions in crystals. The present problem is simpler, however, and allows of a much more complete solution.

II. GENERAL METHOD

The model used is essentially that of Ising,[4] in which each quantum mechanical spin is replaced by a scalar "spin" which can take the values ±1. It is assumed that there is an interaction energy $\gamma(\geq 0)$ between nearest neighbors (NN) and interaction energy $\alpha(\geq 0)$ between next-nearest neighbors (NNN). In this case the energy may be written

$$E=\tfrac{1}{2}\Big[\gamma\sum_j \mu_j \sum_{i=NN\text{ of }j} \mu_i+\alpha\sum_j \mu_j \sum_{i=NNN\text{ of }j} \mu_i\Big], \quad (1)$$

where $\mu_j=\pm 1$ (or $\mu_j^2=1$). For a given arrangement of spins (i.e., a given set of values of μ_j) it is very easy to calculate the energy of the array. One can also ask what the arrangement of spins on the lattice points must be so that E is a minimum. Now the expression for E is a quadratic form in the spins μ_j, and were it not for the complexity of the constraining conditions $\mu_j^2=1$, it would be a simple matter to find its minimum. We can replace (just as in reference 3) the "strong conditions" $\mu_j^2=1$ by the "weak" conditions

$$\textstyle\sum_j \mu_j^2=N, \quad (2a)$$

where N is the number of spins present. This equation follows (by addition) from the strong conditions, but is, of course, considerably less stringent. If we minimize E under the condition (2a) and find that our solution also satisfies the strong condition, then we will have solved the problem. The essence of our method is that this proves to be the case. The minimization of Eq. (1) under the condition (2a) is, of course, a standard problem in the theory of quadratic forms. The solution is given by the lowest eigenvalue of the matrix of the quadratic form.[5] Our problem is then to find the smallest eigenvalue of Eq. (1) for the case of simple cubic (S.C.), body centered cubic (B.C.) and face centered cubic

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[1] P. W. Anderson, Phys. Rev. **79**, 705 (1950). The reference to Shull's work is also to be found in this paper. A very clear summary of Anderson's work is to be found in J. H. Van Vleck, Report to the Grenoble Conference, Grenoble, 1950.

[2] L. Néel, Ann. physique 3, 137 (1948).

[3] J. M. Luttinger and L. Tisza, Phys. Rev. **70**, 954 (1946).

[4] G. Ising, Z. Physik **31**, 253 (1925).

[5] Courant-Hilbert, *Methoden der Mathematischen Physik* (Verlag J. Springer, Berlin, 1931), Vol. I, p. 26.