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COMMENTS AND ADDENDA

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Comment on "Piezoelectricity under Hydrostatic Pressure"

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It is shown that the special termination of the atoms on (111) surfaces of zinc-blende crystals cannot lead to the "hydrostatic piezoelectric effect" proposed by Woo. The present results are a special case of a more general proof given elsewhere and agree with the traditional bulk theory of piezoelectricity.

In a recent paper[1] Woo has given quantitative estimates of "piezoelectricity under hydrostatic pressure," an effect discussed previously on theoretical grounds by several authors[1,2] but never identified experimentally. The effect under discussion is the possible production by surface effects of a piezoelectric polarization which is comparable in magnitude to the usual bulk piezoelectricity. If such an effect exists it would be observable through modifications of bulk symmetry requirements which would depend upon sample shape and detailed surface characteristics.

Conventional treatments[3,4] of piezoelectricity tacitly assume that the polarization produced by strain is purely a bulk effect whose symmetry properties are determined solely by the symmetry of the environment of the atoms in an infinite crystal. However, Woo[1] and others[1,2] have correctly pointed out that a complete description of the polarization produced by a strain in a finite crystal must include possible effects of the surfaces, i.e., effects of the specific termination of the infinite crystal to produce the given finite sample.

The purpose of this comment is to show that the manner of termination of the infinite crystal does *not* affect the piezoelectric polarization. Here also is adopted the point of view of Woo that the conventional derivations of the piezoelectric effect are not sufficient and that consequences of the surface must be critically analyzed. However, we shall see that a consistent treatment of the charge displacement near the surface of a strained insulator must lead to cancellation of surface effects; i.e., the conventional macroscopic bulk results are regained. We start with an analysis of the specific model considered by Woo, after which the relevant physical arguments are placed in perspective as a special case of the general theory of the piezoelectric effect presented in Ref. 5.

Following Woo we consider an isolated zinc-blende crystal with (111) faces and thickness l. As shown in Fig. 1, the crystal may be described as an A-B layer structure. In terms of the lattice constant a, the spacing between like planes is $d = \sqrt{3}a$ and the smallest separation between unlike planes is $\frac{1}{4}d$. Energetic considerations favor cleavage so that one (111) face is terminated on A atoms, the other on B atoms. The asymmetry between A and B atoms determines a direction for the [111] axis and makes [111] and $[\bar{1}\bar{1}\bar{1}]$ inequivalent. The conclusion of Woo is that this asymmetry allows a hydrostatic piezoelectric effect, in contradiction to the macroscopic bulk theory[3,4] of piezoelectricity, which precludes the production of polarization under hydrostatic pressure irrespective of the manner in which the crystal is cut or the type of atoms which terminate the surfaces.

To follow the argument further, assume all charge is restricted to the A and B planes. (It is only in this model that Woo's procedure of calculating macroscopic polarizations from charge flow across microscopic boundaries is viable.) Now, suppose that under pressure charge is transferred from A atoms to B atoms. If the charge of each A

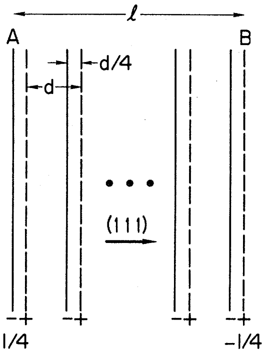

FIG. 1. Idealized zinc-blende (AB) crystal cut with (111) faces. Stress-induced polarization charges are indicated at the bottom: The bulk charges $\pm\delta Q$ are those considered in Ref. 1; the surface charges $\pm\frac{1}{4}\delta Q$ must also be taken into account. The total polarization is zero.

plane decreases by δQ, a moment $\delta Q(\frac{1}{4}l)$ is produced in the +[111] direction. This is the moment considered by Woo in his estimate of the hydrostatic piezoelectric effect. Note, however, that this value of the moment was arrived at assuming that the change of charge on each plane is the same independent of whether the plane is near the surface or deep inside the bulk. We are therefore justified only in concluding that this is an estimate of the moment of a portion of a perfect infinite crystal; here we term this a "cellular" polarization which obviously depends upon the precise boundaries of the cells which define the finite part. (The consequent nonuniqueness of this polarization was noted by Woo.) We shall find, however, that this picture alone is not a sufficient description for a finite crystal with real surfaces.

Let us examine more closely the charge displacement in the vicinity of a surface. The assumption that the surface atoms can become charged equally with the atoms in the bulk ignores essential properties of a real physical surface. Consider the special model where surface effects are restricted to the end layers and all interior atoms are assumed to have bulk tetrahedral character. The relevant observation is that the end layers *cannot* become charged $\pm\delta Q$. Tetrahedral symmetry of all atoms in the interior guarantees that the charge transferred to the end B layer *only from the atomic planes to its left* (Fig. 1) must be $\frac{3}{4}\delta Q = \delta Q - \frac{1}{4}\delta Q$. The result is easily visualized in terms of bonds—surface atoms have only $\frac{3}{4}$ of their bonds completed with the remaining $\frac{1}{4}$ not involved in charge transfer from A to B atoms. The effect of the physical surface is therefore to produce a *surface charge* $-\frac{1}{4}\delta Q$ on the B surface, $+\frac{1}{4}\delta Q$ on the A surface, which gives rise to a moment $-(\frac{1}{4}\delta Q)l$ along the +[111] direction. The total moment of the finite crystal is the sum of cellular and surface-charge moments, which vanishes,

$$\tfrac{1}{4}\delta Q l - \tfrac{1}{4}\delta Q l = 0 \ . \qquad (1)$$

The above model can be readily extended to more general surface configurations with the same conclusion. The only requirements are that (i) all atoms have perfect bulk symmetry except those in some surface regions, and (ii) the volume of the surface regions is assumed to be negligible compared to the total volume. Within the surface regions one can allow arbitrary nonperiodic variations in the strain, atom positions, and electronic charge density. In that case one also arrives at Eq. (1), where the surface charge is the total charge of the surface region.

In Ref. 5 a formal theory of piezoelectricity is presented which is valid for any crystal symmetry and which makes no assumption about the microscopic charge distribution. There the piezoelectric polarization is derived in terms of the charge redistribution produced by displacements of individual atoms. The crux of the proof of the bulk nature of the piezoelectric effect is the requirement that in an insulator one can choose regions of the crystal such that the displacements of atoms within the region produce no change in the crystal charge distribution at long range. The present model invokes a special case of this general argument in that we assume atoms in the bulk can be considered to have perfect bulk symmetry. This assumption is justified if long-range effects must vanish so that only the local (on an atomic scale of length) symmetry of each atom is relevant.

To show explicitly that long-range effects vanish in the present model, we can choose to consider the polarization produced by the simultaneous displacement of all atoms in a given plane. In general, very involved polarization of the charge density is induced in the immediate neighborhood of the plane. At large distances, however, the response of the medium to the atomic displacement is just that of a dielectric medium to the induced dipolar electric fields. We arrive at the desired conclusion that the long-range polarization vanishes since the sum of the fields generated by a plane of dipoles is zero.

Therefore we have shown that the piezoelectric effect is determined by the local environment of the atoms in the bulk; the specific details of the surface can only lead to charge redistribution within each surface region. Thus dipole and higher-multipole layers may be formed in the surface regions having symmetry requirements differing from those of the bulk. One interesting result is that the dipole layers would lead to a change in work function under pressure—increase at one surface and decrease at the other in the present example. The only situation in which the surface-charge redistribution is a true piezoelectric effect is one in which the surface region is in fact the entire sample. Then the local symmetry of atoms throughout the material differs from the symmetry of the ideal infinite lattice. However, a wealth of experimental data sets very small bounds on deviations from bulk symmetry in macroscopic samples. For example, a very sensitive test of the deviation from cubic symmetry in the (111)-cut zinc-blende crystal would be an attempt to measure birefringence for light propagating parallel to the (111) faces.

Arlt and Quadflieg[6] have also arrived at the same conclusion concerning the bulk nature of piezoelectricity. In fact, the present arguments on the charge redistribution in an insulator may be viewed as a more complete and precise analysis of their requirement that no charge flow can occur across real crystal boundaries.

It is relevant to note that different conclusions are found if one allows metallic conduction in all or part of the medium. Then polarization involving charge displacement over arbitrarily long distances can occur with no increase in the internal energy. This allows the metal to maintain zero internal electric field. As an example of the basic difference, we have precluded a hydrostatic piezoelectric effect in a cubic insulator; nevertheless, an analogous charge flow can occur between two dissimilar cubic metals under pressure (hydroelectricity?). As a second example, consider placing the insulating zinc-blende slab between shorted capacitor plates. Now displacement of a plane of atoms produces a long-range displacement of charge in the metal plates to maintain zero voltage difference. Our previous analysis must be modified, but it is only a trivial problem in macroscopic physics to derive the polarization in the shorted sample given the polarization in the isolated sample discussed above.

Finally, the present treatment goes beyond Ref. 5 in one respect: All arguments apply equally well to pyroelectricity. Thus, at least in the point-charge model, we conclude that pyroelectricity is a bulk phenomenon, contrary to Landauer's suggestion.[2]

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[1] J. W. F. Woo, Phys. Rev. B 4, 1218 (1971), and references given there.

[2] R. Landauer, J. Chem. Phys. 32, 1784 (1960).

[3] W. F. Cady, *Piezoelectricity* (McGraw-Hill, New York, 1946).

[4] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford U. P., Oxford, England, 1954), Chap. 5.

[5] R. M. Martin, Phys. Rev. 5, 1607 (1972).

[6] G. Arlt and P. Quadflieg, Phys. Status Solidi 25, 323 (1968).

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Reply to "Comment on 'Piezoelectricity under Hydrostatic Pressure'"

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In a set of two papers[1,2] we put forth the opinion that the classical view relating the occurrence of pyroelectricity and piezoelectricity to the symmetry of the unit cell is invalid, and that it is the symmetry of the actual crystal under consideration, including its surfaces, which is the determining factor. Martin,[3] in the preceding note, as well as in a more detailed paper,[4] disagrees with our conclusions, and argues for the validity of the classically accepted results. Martin, however, agrees with us and departs from the classical treatments to the extent that he does not consider these results an obvious consequence of crystal symmetry. He follows charge displacements in the crystal, and specifically includes consideration of the surface events.

Our basic point is as follows: If the structure shown in Martin's[3] Fig. 1 contains *A* atoms with one sign of charge and *B* atoms with the opposite charge, then it clearly consists of a series of layers with a dipole moment for each *AB* layer. These are layers in which the *A* and *B* planes are separated by $\frac{1}{4}d$. If each such layer has a dipole moment then the over-all structure also has a dipole moment. If now, through temperature changes or hydrostatic pressure, the effective charges change, then we have a resulting change in the dipole moment. Therefore pyroelectricity or piezoelectricity can be observed. (As in any other piezoelectric or pyroelectric system no static polarization can be maintained. Such a polarization would be neutralized through internal or external conductivity.) Each pair of *immediately adjacent AB* planes remains neutral, and the charge exchange, which Martin calls δQ, occurs only between adjacent planes separated by $\frac{1}{4}d$. No charge exchange need take place along the bonds parallel to the (111) direction between planes $\frac{3}{4}d$ apart.