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 $\delta Q$, 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.

We have taken the change in effective atomic charge as the basic quantity and assumed that the charge flux along the bonds must adjust to account for these charge changes and also must satisfy the boundary condition requiring no flow across the crystal surfaces. Martin has instead taken the view that it is the charge flux along each bond that is fundamental, and that the incompletely bonded atoms at the surfaces suffer an accordingly lower charge change. The physical truth is likely to be somewhere between these extreme assumptions; certainly we cannot expect the terminating planes to have exactly the same value of charge change as the corresponding interior planes. If the actual situation, however, is intermediate between the two extreme assumptions then the answer will be correspondingly intermediate. This means that our picture[1,2] overestimates the magnitude of the effect but that the classically accepted vanishing of pyroelectricity and hydrostatic piezoelectricity in the zinc-blende structure is also incorrect.

The differing views between Martin and us can perhaps best be exemplified by considering the one-dimensional charge chain shown in Fig. 1(a), which can be considered to be a schematic representation of a succession of (111) planes in the NaCl structure. Martin will then consider this chain as composed of a series of unit cells, each with the maximal potential symmetry [Fig. 1(b)]. The total chain then has additional left-over material at the end. (The left-over material can be wider than shown as long as it remains a small fraction of the total volume.) Martin now assumes a pattern of charge changes and fluxes within each symmetric cell which is the same as in an infinite symmetric nonpolar chain. He furthermore assumes that the left-over end segments, while polarizable, cannot change their charge. This latter assumption must be *strictly* satisfied to yield the confirmation of the classical results. In our view the many possible choices of unit cell are on an equal physical footing and the splitting of this degeneracy, through the choice of surfaces, should be respected. Thus we view the chain as a sequence of identical cells, as shown in Fig. 1(c), in each of which the same dipole moment change takes place.

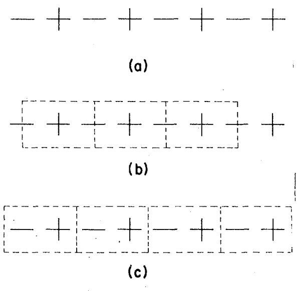

FIG. 1. Periodic chain of equidistant charges with a net dipole moment. In (b) the unit cell is chosen with the maximum potential symmetry, whereas in (c) the unit cell is chosen so that the entire crystal can be included in an integral number of cells.

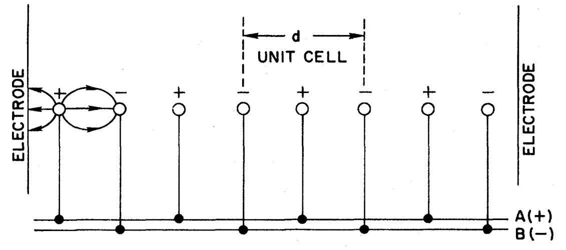

FIG. 2. Macroscopic capacitor array with a symmetrical unit cell exhibiting polarization changes under symmetry-preserving perturbations.

The classically accepted theorems stating the symmetry conditions for pyroelectricity and piezoelectricity are not based on the detailed microscopic physics of the atomic lattice. As a result, if correct, these theorems should apply equally to other periodic arrangements of charges, even though the charge pattern may be the result of macroscopic machinery. Consider a linear periodic array of charged spheres, as shown in Fig. 2. The dotted lines exhibit a unit cell and show that it is symmetrical and nonpolar. *A* and *B* can be considered to be battery electrodes, or, alternatively, electrodes of a very large capacitor. The spheres are taken to have a capacitance large compared to that of the wires leading into them. The separation between *A* and *B* can be taken to be perpendicular to the plane of the paper. Clearly the linear array of charged spheres for the particular crystal shown in Fig. 2 has a net dipole moment. Let the charges on the spheres be $\pm q$. There are electrodes at each end of the chain, and we will assume that the two end electrodes are shorted to each other. If these electrodes are one-quarter cell length, $\frac{1}{4}d$, from the last sphere, then the image charge on these end electrodes will be $\pm\frac{1}{2}q$. This follows from the fact that an end electrode intercepts half the lines of force emanating from a sphere.

Now let us modulate the voltage applied to the spheres. This change will not break the symmetry of the chosen unit cell; it is therefore analogous to a temperature change or hydrostatic pressure applied to a crystal lattice. In fact, we can imagine the voltage change arising from a temperature sensitivity in the battery, or alternatively we can imagine a strain-induced change in the spacing of the capacitor plates *A* and *B* which changes their capacitance, relative to that of the spheres. Clearly then $q$ will change, and with it the image charge in the end electrodes. Thus we will measure a change in polarization!

Martin's discussion of metals[3] is essentially a response to this macroscopic example, and serves to emphasize that the microscopic physics of charge-transfer mechanisms cannot be ignored in the theory of polarization changes.

[1]R. Landauer, J. Chem. Phys. 32, 1784 (1960).
[2]James W. F. Woo, Phys. Rev. B 4, 1218 (1971).
[3]Richard M. Martin, preceding paper, Phys. Rev. B 6, 4874 (1972).
[4]Richard M. Martin, Phys. Rev. B 5, 1607 (1972).

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# Assignments of Optical Phonon Modes in $LiNbO_3$

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In a paper on the quantitative determination of sources of the electro-optic effect in $LiNbO_3$ and $LiTaO_3$ by Kaminow and Johnston,[1] a complete assignment of all optical phonon modes in $LiNbO_3$ has been given. Assignments have earlier also been given by Schaufele and Weber,[2] and Barker and Loudon.[3] Because of important technical applications of the material in nonlinear optical experiments, as for instance second-harmonic generation and parametric oscillators, $LiNbO_3$ has frequently been used as a model crystal for calculations of different optical properties. In most papers of this kind the assignments given by Ref. 1 have been used as a fundamental set of parameters.[4–8] Recent measurements concerning the directional dispersion of the extraordinary polaritons, however, showed that this set predicted dispersion branches which could not be experimentally verified.[9] In extending this work, the directional dispersion branches of all optical phonons have been carefully measured by Raman scattering in steps of 5° from $\theta = 0$ to $\theta = \frac{1}{2}\pi$, where $\theta$ denotes the angle between the phonon wave vector and the optic axis of the crystal. Spectral series have been recorded in backward as well as right-angle scattering for different polarizations of the incident and scattered radiation, and at room temperature as well as at liquid-nitrogen temperature. Furthermore, Raman spectra of the polariton region have been recorded in order to check the data.[10] These experiments formed a firm basis for a new complete assignment. Our new assignments which fit the right-angle scattering and angular dispersion are reproduced in Table I, where the data can be compared with those given in Refs. 1–3. A detailed discussion of the experiments will be given.[11]

We want to thank the Deutsche Forschungsgemeiuschaft for financial support.

TABLE I. Assignments of the optical phonon modes in $LiNbO_3$. Frequencies are given in $cm^{-1}$ with an accuracy of $\pm 2$ $cm^{-1}$ for the present work. Reference 10 has reported Raman as well as ir data. Modes indicated by an asteriskwere assumed to be of second order. The most important changes to the earlier assignments (interchanges of the succession of phonon frequencies) are indicated by arrows at the right-hand side of the table.

| Present work | | Ref. 1 | | Ref. 3 | | | Ref. 2 | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | Raman | IR | | | |
| | | $E(T)$ | 92 | | | | | | ← |
| | | $E(L)$ | 117; 95 | | | | | | ← |
| $E(T)$ | 155 | $E(T)$ | 152 | $E(T)$ | 152 | 152 | $E(T)$ | 152 | |
| $E(L)$ | 198 | $E(L)$ | 198 | $E(L)$ | | 198 | | | |
| $E(T)$ | 238 | $E(T)$ | 238 | $E(T)$ | 238 | 236 | $E(T)$ | 239 | |
| $E(L)$ | 243 | $E(L)$ | 243 | $E(L)$ | | 238 | | | |
| $A_1(T)$ | 255 | $A_1(T)$ | 253 | $A_1(T)$ | 252 | 248 | $A_1(T)$ | 255 | |
| $E(T)$ | 265 | $E(T)$ | 262 | $E(T)$ | 264 | 265 | $E(T)$ | 266 | |
| $A_1(L)$ | 275 | $A_1(L)$ | 273 | $A_1(L)$ | | 273 | | | |
| $A_1(T)$ | 276 | $A_1(T)$ | 275 | $A_1(T)$ | 276 | 274 | $A_1(T)$ | 277 | |
| $E(L)$ | 295 | $E(L)$ | 298 | $E(L)$ | 299 | 296 | | | |
| $E(T)$ | 325 | $E(T)$ | 322 | $A_1(L)$ | | 306 | $E(T)$ | 321 | ← |
| $A_1(L)$ | 333 | $A_1(L)$ | 331 | $E(T)$ | 321 | 322 | | | ← |
| $A_1(T)$ | 334 | $A_1(T)$ | 334 | $A_1(T)$ | 333 | 307 | | | |
| $E(L)$ | 371 | $E(L)$ | 345 | $E(L)$ | 333 | 342 | | | |
| $E(T)$ | 371 | $E(T)$ | 368 | $E(T)$ | 367 | 363 | $E(T)$ | 369 | |
| $E(L)$ | 428 | $E(L)$ | 428 | $E(L)$ | | 418 | | | |
| $E(T)$ | 431 | $A_1(L)$ | 428 | $A_1(L)$ | | 423 | $E(T)$ | 430 | ← |
| $A_1(L)$ | 436 | $E(T)$ | 436 | $E(T)$ | 434 | 431 | | | ← |
| $E(L)$ | 454 | $E(L)$ | 448 | $E(L)$ | | 450 | | | |
| $E(T)$ | 582 | $E(T)$ | 582 | $E(T)$ | 579 | 586 | $E(T)$ | 580 | |
| $A_1(T)$ | 633 | $E(L)$ | 621 | $A_1(T)$ | 634 | 628 | $A_1(T)$ | 632 | ← |
| $E(L)$ | 668 | $E(T)$ | 630 | $^*E(L)$ | | 660 | | | ← |
| $E(T)$ | 668 | $A_1(T)$ | 637 | $^*E(T)$ | | 670 | | | |
| $E(L)$ | 739 | | | $^*A_1(L)$ | | 686 | | | ← |
| $E(T)$ | 743 | | | $^*A_1(T)$ | | 692 | | | ← |
| $A_1(L)$ | 876 | $A_1(L)$ | 874 | $A_1(L)$ | 873 | 869 | | | |
| $E(L)$ | 880 | $E(L)$ | 881 | $E(L)$ | 880 | 878 | $E(L)$ | 883 | |