

### Antiferroelectric Structure of Lead Zirconate

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 (Received June 25, 1951)

A CLOSE resemblance between  $\text{PbZrO}_3$  and ferroelectric  $\text{BaTiO}_3$  has been reported<sup>1</sup> with respect to the variation of the dielectric constant with temperature. However, any decisive evidence supporting exclusively the ferroelectricity of  $\text{PbZrO}_3$ , for example spontaneous polarization, has not yet been observed, for both ferroelectrics and antiferroelectrics may reveal a similar temperature dependence of the dielectric constant. On the other hand, all the phenomenological facts recently observed,<sup>2</sup> especially those concerning the response of this material to a biasing dc field, cannot be understood unless we assume that  $\text{PbZrO}_3$  is antiferroelectric. Of course, the more direct and ultimate proof for its antiferroelectricity can be provided by the x-ray analysis of the superstructure<sup>3</sup> of this crystal.

The structure has been examined by oscillation and powder photographs. We found lattice repetitions with periods of  $4a_0$ ,  $4b_0$ , and  $2c_0$  in the three directions of cubic edges in the perovskite lattice, respectively ( $a_0=4.15\text{\AA}$ ,  $b_0=4.15\text{\AA}$ ,  $c_0=4.10\text{\AA}$ ). Hitherto, the crystal of this substance has been reported to be seemingly tetragonal<sup>4</sup> or monoclinic,<sup>5</sup> but the present x-ray pattern and detailed optical observations on a very minute untwinned crystal by means of a polarization microscope have revealed that it is orthorhombic. The orthorhombic unit cell has spacings  $a=5.87\text{\AA}$ ,  $b=11.74\text{\AA}$ , and  $c=8.20\text{\AA}$ , and contains eight molecules. The main characteristic spots corresponding to the superstructure have indices ( $h \neq 0$ ,  $k=2n+1$ ,  $l=2p$ ). The other spots, with odd  $l$ , are so faint that they are hardly noticeable except on oscillation photographs of small oscillation angle ( $<5$  degrees), so that  $4.10\text{\AA}$ , half of the  $c$  spacing, may be adopted as the approximate value of the  $c$  translation. It also turns out that the crystal has two glide reflection planes, and the space group may be either  $D_{2h}(9)$  or  $C_{2v}(8)$ .

In the case of  $D_{2h}$ , each Pb ion is supposed to be displaced along the orthorhombic  $+a$  or  $-a$  axis as shown exaggerated in Fig. 1. The displacement is calculated to be about  $0.2\text{\AA}$ . If, on the other hand, the symmetry is  $C_{2v}$ , all the Pb ions can make a certain shift along the  $c$  axis in addition to the antiparallel displacement described above. If this common shift along the  $c$  axis is of con-

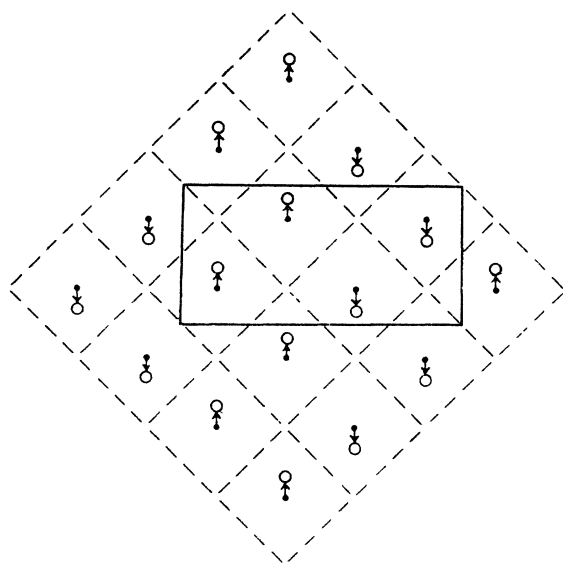


FIG. 1. Antiferroelectric structure of  $\text{PbZrO}_3$ ; arrows represent the direction of shifts of Pb ions; the solid line shows an orthorhombic unit cell.

siderable magnitude, the crystal may be ferroelectric in the  $c$  direction. In fact, however, the relative spot intensities show that the  $c$  shift must be negligibly small, so that the main part of the dipole moment must lie in the  $a-b$  plane bearing an antiferroelectric arrangement. This conclusion suggests a reason for the fact that in  $\text{PbZrO}_3$  the ratio  $c_0/a_0$  is less than 1, in contrast to the situation in  $\text{BaTiO}_3$ .

We wish to thank Professors Y. Takagi and S. Miyake for valuable advice and discussions, and Dr. G. Shirane for helpful discussions and for kindly lending us his powder photograph.

- <sup>1</sup> S. Roberts, *J. Am. Ceram. Soc.* **33**, 63 (1950).  
<sup>2</sup> Shirane, Sawaguchi, and Takagi, *J. Phys. Soc. Japan* **6**, 208 (1951); Sawaguchi, Shirane, and Takagi, *J. Phys. Soc. Japan* (to be published).  
<sup>3</sup> A. Hoffmann, *Z. physik. Chem.* **B28**, 65 (1935).  
<sup>4</sup> H. D. Megaw, *Proc. Phys. Soc. (London)* **58**, 133 (1946); R. Ueda and G. Shirane, *J. Phys. Soc. Japan* **6**, 209 (1951).  
<sup>5</sup> Naray-Szabo, *Naturwiss.* **31**, 203 (1943).

### Piezoelectric Effect in Lead Zirconate

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 (Received July 13, 1951)

CERAMIC disks of pure lead zirconate prepared as formerly described by the author<sup>1</sup> were polarized by applying an electric field while cooling from  $250^\circ\text{C}$  to  $100^\circ\text{C}$ . One disk was polarized with a dc field of about  $250\text{ v/mm}$ , while a second disk was polarized with unidirectional pulses  $800\text{ v/mm}$  in amplitude. The values for  $d_{33}$  measured in both disks under static compression at ambient temperature were approximately  $10^{-13}$  coulomb per newton. This value is just barely detectable in our apparatus, although the results were definitely reproducible and the observed effect reversed when the disk was turned over. The polarity of the field induced by compression is the same as that of the original polarizing field in lead zirconate just as in barium titanate.

The smallness of the effect was at first puzzling, but can now be understood in reference to the structure analysis of Sawaguchi, Maniwa, and Hoshino.<sup>2</sup> Of the two allowable symmetry classes, the choice  $C_{2v}$  is consistent with the observed piezoelectric effect.

- <sup>1</sup> S. Roberts, *J. Am. Ceram. Soc.* **33**, 63 (1950).  
<sup>2</sup> Sawaguchi, Maniwa, and Hoshino, *Phys. Rev.* **83**, 1078 (1951).

### Erratum: Low States of $\text{Li}^7$ in Intermediate Coupling

[*Phys. Rev.* **81**, 910 (1951)]  
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WE are grateful to Igal Talmi of Zürich for pointing out errors in the  $\pi-\nu$ -Majorana interaction listed in Table I. The total Majorana interactions in that table should read, respectively,  $L+K$ ,  $(2L/9)+10K/3$ ,  $-\frac{1}{3}L+5K$ ,  $-\frac{2}{3}L+6K$ ,  $L+11K/3$ ,  $(-2L+16K)/3$  (for  $\tau=3/2$ ),  $(4L+10K)/3$  (for  $\tau=1/2$ ), the last value being calculable from trace invariance with isotopic spin. The consequent changes in the asymptotes on the right side of Fig. 3 are small and the general conclusions of the paper remain unaltered.

### Concerning the Mechanism of Electron-Ion Recombination. II

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 (Received June 29, 1951)

DURING the past few years, experiments<sup>1,2</sup> on the decay of electron density from an initially ionized gas have revealed a recombination between thermal electrons and positive ions whose