## Antiferroelectric Structure of Lead Zirconate

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A CLOSE resemblance between $PbZrO_3$ and ferroelectric $BaTiO_3$ has been reported[1] with respect to the variation of the dielectric constant with temperature. However, any decisive evidence supporting exclusively the ferroelectricity of $PbZrO_3$, 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,[2] especially those concerning the response of this material to a biasing dc field, cannot be understood unless we assume that $PbZrO_3$ is antiferroelectric. Of course, the more direct and ultimate proof for its antiferroelectricity can be provided by the x-ray analysis of the superstructure[3] 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 ($a_0=4.15$A, $b_0=4.15$A, $c_0=4.10$A). Hitherto, the crystal of this substance has been reported to be seemingly tetragonal[4] or monoclinic;[5] 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 $a=5.87$A, $b=11.74$A, and $c=8.20$A, 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 4.10A, 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 0.2A. 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 considerable 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 $PbZrO_3$ the ratio $c_0/a_0$ is less than 1, in contrast to the situation in $BaTiO_3$.

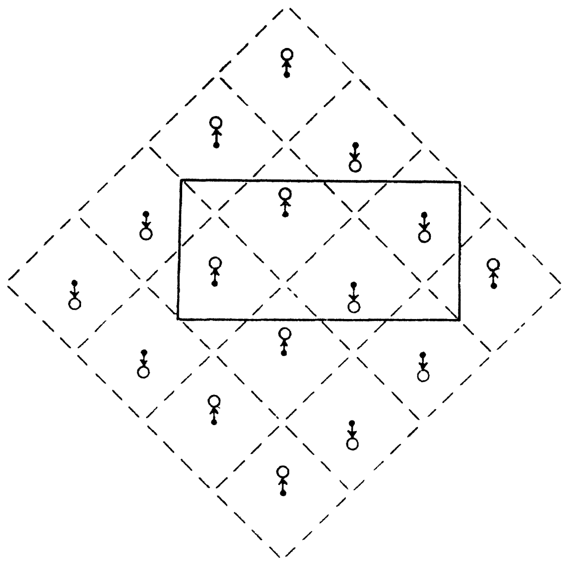

FIG. 1. Antiferroelectric structure of $PbZrO_3$; arrows represent the direction of shifts of Pb ions; the solid line shows an orthorhombic unit cell.

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.

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[4] H. D. Megaw, Proc. Phys. Soc. (London) **58**, 133 (1946); R. Ueda and G. Shirane, J. Phys. Soc. Japan **6**, 209 (1951).
[5] Naray-Szabo, Naturwiss. **31**, 203 (1943).

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## Piezoelectric Effect in Lead Zirconate

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CERAMIC disks of pure lead zirconate prepared as formerly described by the author[1] were polarized by applying an electric field while cooling from 250°C to 100°C. One disk was polarized with a dc field of about 250 v/mm, while a second disk was polarized with unidirectional pulses 800 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.[2] Of the two allowable symmetry classes, the choice $C_{2v}$ is consistent with the observed piezoelectric effect.

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[1] S. Roberts, J. Am. Ceram. Soc. **33**, 63 (1950).
[2] Sawaguchi, Maniwa, and Hoshino, Phys. Rev. **83**, 1078 (1951).

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## Erratum: Low States of $Li^7$ 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.

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

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DURING the past few years, experiments[1,2] on the decay of electron density from an initially ionized gas have revealed a recombination between thermal electrons and positive ions whose rate exceeds the theoretical prediction[3] for radiative recombination by several orders of magnitude. This discrepancy has led to the supposition[4] that the observed recombination involves non-radiative capture of an electron by a molecular ion, followed by dissociation into two (or more) neutral fragments, one of which is in an excited electronic state.

In the first paper of the above title,[5] the hypothesis of dissociative recombination was analyzed from the standpoint of recent data obtained in this laboratory. It was found that our data in helium and neon was consistent with the dissociative scheme provided that helium molecular ions were formed and persisted in high vibration states during our measurements. Qualitative theoretical estimates indicated that the assumption of vibrational persistence, while somewhat extreme, was still conceivable.

In order to demonstrate conclusively the dependence of the observed recombination on the presence of molecular ions, it was proposed to study the decay of electron density in samples of helium and neon containing small admixtures of argon (0.1 percent). The argon atoms would be rapidly ionized by helium or neon metastables, so that the chief positive charge carriers would be atomic argon ions; however, the concentration of argon would be too small to permit appreciable formation of molecular argon ions, $A_2^+$, during our measurements. These experiments are the subject of the present paper.

Previously described[5] microwave and optical techniques were used to measure the electron density and radiation emitted during the afterglow following a discharge. The gas samples were Airco reagent grade helium, neon, and argon. The ultra-high vacuum system[6] used did not contribute significant contamination to the samples.

Typical experimental data for pure argon are presented in Fig. 1. These data fit quite well the relationship

$$1/n_- = (1/n_0) + \alpha t, \tag{1}$$

where $n_-$ is the electron density and $\alpha$ the recombination coefficient. Equation (1) is characteristic of a recombination loss of electrons; the value $\alpha = 8.8 \times 10^{-7}$ cc/sec obtained from the curve is in fair agreement with previous measurements.[1]

Corresponding experimental data for the helium-argon mixture are shown in Fig. 2. In this case the data obey a decay equation of the form

$$n_- = n_0 \exp(-t/T) \tag{2}$$

characteristic of ambipolar diffusion loss of electrons and $A^+$ ions. The decay constant, $T$, is related to the ambipolar diffusion coefficient, $D_a{}^A$, by

$$T = \Lambda^2 / D_a{}^A, \tag{3}$$

where $\Lambda$ is the characteristic diffusion length of the container and has the value 0.735 cm. From our values of $D_a{}^A$, which exhibit the correct pressure dependence as shown by Fig. 3, we compute[1] the mobility of our alleged $A^+$ in helium as $\mu_+ = 22.4$ cm/sec per volt/cm (at 291°K and 760 mm Hg). This value lies within 2 percent (experimental error) of the curve of mobility *versus* mass number for various ions in helium[7] (see Fig. 8 of reference 1), indicating strongly that the ion under observation is indeed $A^+$.

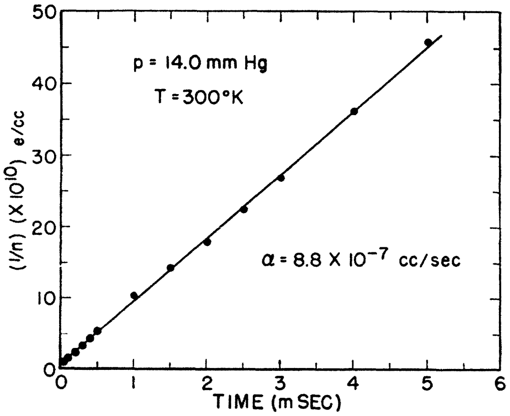

FIG. 1. Decay of electron density in pure argon.

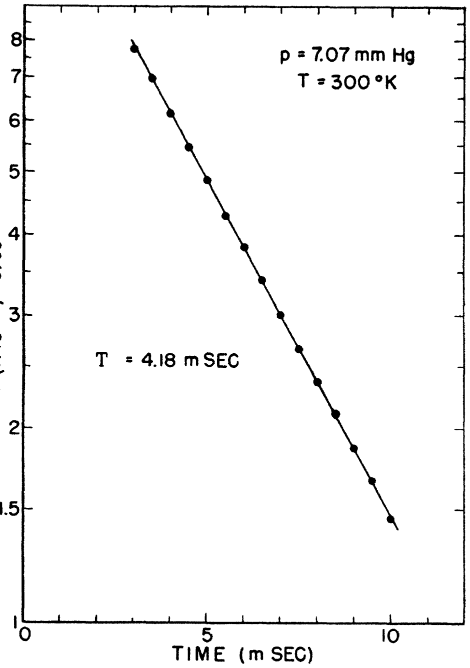

FIG. 2. Decay of electron density in helium-argon mixtures (0.1 percent argon).

Detailed consideration of experimental errors in the data of Fig. 2 permit us to set an upper bound for recombination loss. It is found that the recombination coefficient must be $< 10^{-3}$ times that obtained in pure argon. Data similar to that shown in Fig. 2 were taken over the pressure range 1.6–7.2 mm Hg, and in all cases the above conclusion was substantiated. In addition, radiation measurements, which previously gave a photon yield consistent with a value of $\alpha \sim 10^{-6}$ in pure argon, show a 1000-fold decrease in intensity in the argon admixture experiments. It is not necessary to assign this yield to atomic ion recombination, since it is quite possible that in these admixture experiments the concentration of molecular positive ions $\sim 10^{-3} n_-$. The recombination of these molecular ions with electrons would then explain our radiation yield.

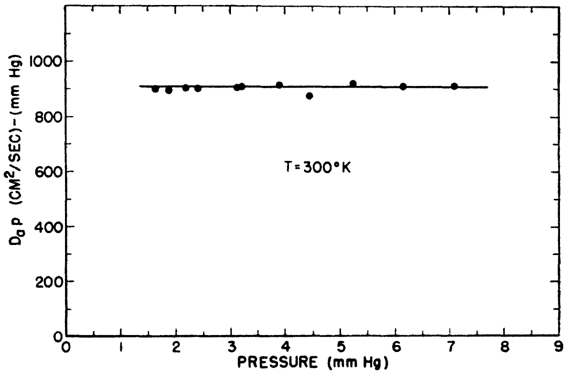

FIG. 3. Ambipolar diffusion coefficient of argon ions in helium at 300°K.

Experiments using 0.1 percent argon in neon were also carried out. These experiments gave identical results to the helium-argon studies, again showing the absence of large recombination under conditions in which molecular ions are absent.

Following the initial report of the large recombination coefficients, a variety of processes were considered as possible recombination mechanisms. For example, in addition to the previously mentioned radiative capture and dissociative capture of electrons by molecular ions, three-body processes involving two electrons and an ion, various plasma effects (e.g., cut-off of coulomb potential in an ionized medium), and negative ion formation in noble gases were all considered in an effort to find the source of the large recombination. These considerations, which were necessitated by the difficulty in finding an electron capture mechanism efficient enough to yield the observed recombination coefficients, may now be discarded. All available evidence indicates that the recombination is a two-body process involving an electron and a molecular ion and that the mechanism is probably dissociative recombination.

The author is greatly indebted to T. Holstein for suggesting these admixture experiments as a conclusive demonstration of the role of molecular ions in the observed recombination.

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[6] The system and techniques are based on material described by D. Alpert, Rev. Sci. Instr., to be published.

[7] R. J. Munson and A. M. Tyndall, Proc. Roy. Soc. (London) **A172**, 33 (1939).

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## Measurement of the Elastic Constants of Silicon Single Crystals and Their Thermal Coefficients

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Interest in the properties of silicon single crystals arising from their use as semiconductors has led us to make measurements of the elastic constants of two single crystals. Measurements of velocities of propagation for both shear and longitudinal waves were made in the crystals as described in a recent paper by McSkimin.[1] Frequencies in the range 8–12 Mc/sec were used.

The three independent elastic constants were evaluated, a density of 2.331 (measured by pycrometer) being used. Data and formulas used are summarized in Table I. Two crystals were measured—as indicated—with data obtained from the larger one being used to determine the elastic constants. Check measurements were made for the smaller crystal; and despite the less accurate "pulse overlap" technique used for two of the measurements, velocity agreement to within 0.15 percent was obtained.

Both crystals were of a high degree of crystalline perfection as shown by etching and x-ray tests.

[1] H. J. McSkimin, J. Acoust. Soc. Am. **22**, 413 (1950).

TABLE I. Data for silicon single crystals ($\rho = 2.331$; $\alpha = 7.63 \times 10^{-6}$).

| Direction of propagation | Direction of particle motion | Type of mode | Equation for velocity | Velocity at 25°C in cm/sec | Velocity temp. coeff. |
|---|---|---|---|---|---|
| | | | (Crystal 1) | | |
| 110<br>$t = 9.0140$ mm | $1\bar{1}0$ | Shear | $V_1 = \left(\frac{0.5C_{11} - 0.5C_{12}}{\rho}\right)^{\frac{1}{2}}$ | $4.682 \times 10^5$ | — |
| 001<br>$t = 5.9746$ mm | 110 | Shear | $V_2 = (C_{44}/\rho)^{\frac{1}{2}}$ | $5.843 \times 10^5$ | $-16.3 \times 10^{-6}$ |
| 001 | 001 | Long. | $V_3 = (C_{11}/\rho)^{\frac{1}{2}}$ | $8.474 \times 10^5$ | $-26.2 \times 10^{-6}$ |
| 110 | 110 | Long. | $V_4 = \left(\frac{0.5C_{11} + 0.5C_{12} + C_{44}}{\rho}\right)$ | $9.167 \times 10^5$<br>(calculated) | — |
| | | | (Check crystal 2) | | |
| 110<br>$t = 3.2215$ mm | $1\bar{1}0$ | Shear | $V_1$ | $4.682 \times 10^5$ | $-42.3 \times 10^{-6}$ |
| 110 | 001 | Shear | $V_2$ | $5.834 \times 10^5$<br>(29°) | — |
| 110 | 110 | Long. | $V_4$ | $9.152 \times 10^5$<br>(30°) | — |

Elastic constants (25°C)
$C_{11} = 1.6740 \times 10^{12}$ dynes/cm$^2$
$C_{12} = 0.6523 \times 10^{12}$
$C_{44} = 0.7957 \times 10^{12}$

Elasticity-temp. coeff.
$K_{C_{11}} = -75.3 \times 10^{-6}$ parts per °C
$K_{C_{12}} = -24.5 \times 10^{-6}$
$K_{C_{44}} = -55.5 \times 10^{-6}$

Uncertainties for crystal 1
$l$—0.02%; freq.—0.01%; elastic constants—0.26%; $\rho$—0.10%; velocities—0.08%