

FIG. 2. Field-induced electron conducting channel on germanium p - n junction. A thin piece of mica separates the electrode and the germanium surface. Current is assumed to flow along channel and then through spots of low resistance as shown by arrow.

ionic which we conclude from the fact that the water-induced and field-induced curves have the same shape when compared, as shown, separated by a factor of four in magnitude of current. The factor of four results from the following considerations. There are two surfaces involved in the water-vapor-induced current, whereas only one surface is used in the field-induced current as shown in Fig. 2. The current induced by water vapor should therefore be at least twice as large as that induced by the external field. In addition, we wish to compare the two curves under conditions in which there are equal electron concentrations in the water-induced and field-induced layers. Hence, we must introduce a second factor of two in order to account for the difference in electron mobilities at room temperature (H_2O vapor experiment) and at $207^\circ K$ (field experiment).

A model can be formulated to explain the shape of the observed current-voltage curves as follows: (1) It is necessary to assume a smaller voltage dependence of channel resistance than has been used in the simple theory (direct proportionality). Thus, we will assume that

$$R_{\text{channel}} \propto V^m. \quad (0 \leq m < 1)$$

(2) It is also necessary to postulate that current flow is not uniform over the channel, but that the current flows through the conducting layer and then through a spot (or line, or many such spots along the junction) into the bulk of the crystal as shown by the arrow in Fig. 2. Such spots might be regions of low resistance. With such a model it is easy to show that excess current

$$I \propto V_A^{1-m}$$

if it is assumed that most of the voltage drop occurs in the conducting surface layer rather than through the conducting spot. For the curves shown in Fig. 1, $m \approx 0$ over a wide range of voltages. At voltages above 4 or 5 volts, m appears to become an increasing function of applied voltage, a result to be expected if an appreciable number of conducting electrons are removed from the channel which at lower voltage is known to contain

about 10^{12} conducting electrons per cm^2 of surface. The above expression for excess current is then not valid at the higher voltages.

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X-Ray Study of Phase Transition of Ferroelectric $PbTiO_3$ at Low Temperature

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LEAD titanate, $PbTiO_3$, is a ferroelectric of particular interest in two respects. Firstly, $PbTiO_3$ has polar symmetry based on a monomolecular unit cell in the ferroelectric region. By contrast, other perovskite-type $PbMe^{+4}O_3$ crystals have nonpolar puckered structures with multiplications of perovskite cell sides in their room temperature modifications; $PbZrO_3$,¹ $PbHfO_3$,² and $PbSnO_3$ ³ are cases in point. Secondly, structural evidence of markedly large spontaneous polarization in the tetragonal modification has recently been discovered by Shirane, Pepinsky, and Frazer⁴ and by the present authors⁵: metal ions undergo large shifts with respect to the oxygen framework. This cannot be understood on the basis of ionic radii, since Zachariasen's tolerance factor is nearly unity. The similar compound $SrTiO_3$, where the radius of Sr^{+2} (1.13 Å) lies near that of Pb^{+2} , remains cubic down to absolute zero. It

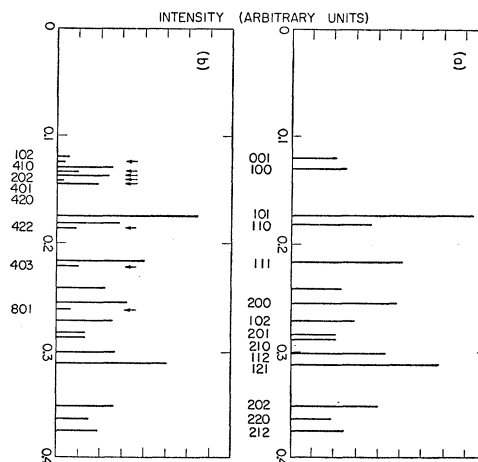


FIG. 1. Schematic representations of powder patterns. Abscissas indicate $\sin\theta/\lambda$; ordinates indicate uncorrected intensities. (a) Original perovskite structure. (b) Superstructure, where large arrows indicate the superstructure lines.

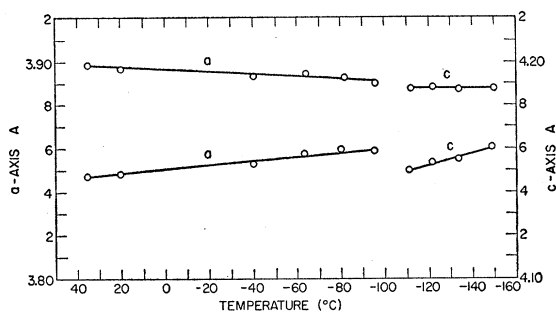


FIG. 2. Lattice spacing as a function of temperature.

appeared worthwhile to re-examine the structure of PbTiO_3 at lower temperature, although no phase transition has been found heretofore except for the ferroelectric one at the Curie point, 490°C .⁶

We have carried out an x-ray study of a powder specimen cooled by liquid air. PbTiO_3 crystals were grown from the melt, using stoichiometric mixtures of PbO and TiO_2 and PbCl_2 as flux; the powder specimen was prepared from this material.

Thermal hysteresis of the substance was found to be very large, and we found no evidence of a low-temperature phase change in a specimen cooled suddenly to -150°C . However, the specimen under gradual cooling showed a definite transition at about -100°C . X-ray powder photographs of an hour exposure were taken at steps of 30°C down from room temperature. We repeated the above procedures and found that the transitions were reproducible except for a slight scattering of transition temperatures for different samples and cooling rates.

At about -100°C , extra lines appear. An important feature is that the extra lines appear only within the region of small values of $\sin\theta/\lambda$, i.e., $0.26 \times 10^8 \text{ \AA}^{-1}$; and no change in intensity of diffraction could be observed in high-angle spectra before and after the transition. Furthermore, the new lines appear not as splitting due to lowering of crystal symmetry, but rather as superlattice lines, indices being assignable by assuming that $a' = 4a$ and $c' = 2c$, where a and c are the former perovskite axes. The observed spectra are indicated in Fig. 1, where ordinates show uncorrected intensities.

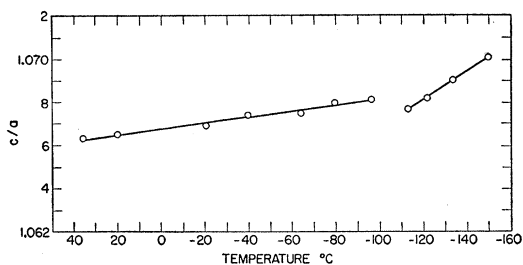


FIG. 3. Axial ratio as a function of temperature.

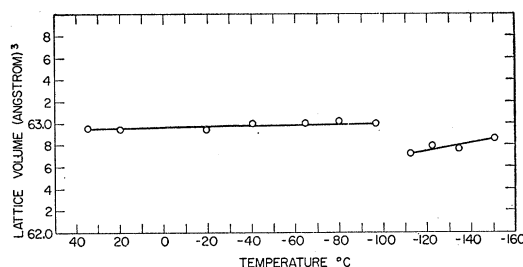


FIG. 4. Unit cell volume as a function of temperature.

The plotting of lattice constants and axial ratio *vs* temperature are shown in Figs. 2–4. The temperature dependence of the *c*-axial length is notable. Its expansion coefficient is negative, and the behavior is more remarkable after the transition in which a volume contraction occurs. It is to be stressed that the steep rise in axial ratio is observed with decreasing temperature between the transition point and -150°C .

It is possible that ferroelectric PbTiO_3 transforms into an antiferroelectric structure at about -100°C . However, other measurements and a detailed investigation of the crystal structure are needed to determine whether this is the case. Observations to these ends are in progress.

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Theory of the Infrared Absorption by Carriers in Semiconductors

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IN a recent paper Kahn¹ has shown that the observed magnitudes of infrared absorption by *n*-type germanium and *p*-type silicon are approximately those calculated from the Drude-Kronig-Zener (DKZ) formula when the effective carrier masses inserted in the theory are those obtained from diamagnetic ("cyclotron") resonance experiments.

It should be noted, however, that the DKZ absorption should be supplemented by a term arising from the anomalous nature of the skin effect.^{2–5} It is not possible to express this correction in the form of a modification to the "absorption coefficient" quoted by Kahn¹ from Seitz,⁶ since the definition of this quantity presupposes that the electric field decays precisely