

anomaly resulting from the distributed nuclear magnetic moment over the finite nuclear volume to be quite small.⁶ Another electron-nuclear interaction which would affect the magnetic-dipole coupling constants is the perturbation of levels with the same value of F in the $P_{3/2}-P_{1/2}$ fine structure doublet, in this case the $F=2$ and $F=1$ levels. An estimate of the order of magnitude of this interaction reveals that both hfs ratios would be changed by less than one part in 100,000.

We wish to thank Professors B. T. Feld and J. R. Zacharias for their counsel.

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¹ Davis, Feld, Zabel, and Zacharias, *Phys. Rev.* **76**, 1076 (1949). (A review of the hfs interaction and the observable transitions in this atomic beam apparatus is given in this article.)

² V. Jaccarino and J. G. King, *Phys. Rev.* **83**, 471 (1951).

³ H. B. G. Casimir, *On the Interaction Between Atomic Nuclei and Electrons*, (DeErven F. Bohn N. V., Haarlem, 1936).

⁴ V. Jaccarino and J. King, *Phys. Rev.* **83**, 209 (1951). (A preliminary report of this work was presented at the Washington meeting, 1951. Failure to consider the anomalous spin gyromagnetic ratio of the electron in $gJ(^2P_{3/2})$ and $gJ(^2P_{1/2})$ results in the large value of $\Delta\nu$ reported.)

⁵ We wish to thank Mr. Henry Argento of the Raytheon Manufacturing Company for the OK-174A magnetron.

⁶ A. Bohr and V. Weisskopf, *Phys. Rev.* **77**, 94 (1950).

Phase Transitions in Solid Solutions Containing PbZrO_3

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RECENT investigations on the dielectric^{1,2} and structural³ properties of lead zirconate have shown that this crystal is not a ferroelectric but an antiferroelectric. At the same time, the study⁴ of solid solutions of PbZrO_3 and PbTiO_3 has revealed that when some of the Zr ions in PbZrO_3 are replaced by Ti ions, a ferroelectric intermediate phase can be observed between the paraelectric and antiferroelectric phases. The $(\text{Pb}-\text{Ba})\text{ZrO}_3$ ⁵ and $(\text{Pb}-\text{Sr})\text{ZrO}_3$ systems have now been investigated to determine whether such an intermediate phase can be observed also in these systems.

Specimens were made from PbO , BaCO_3 , SrCO_3 , and high purity ZrO_2 which are the same chemicals as used for the previous study.² These ingredients were mixed in the desired compositions

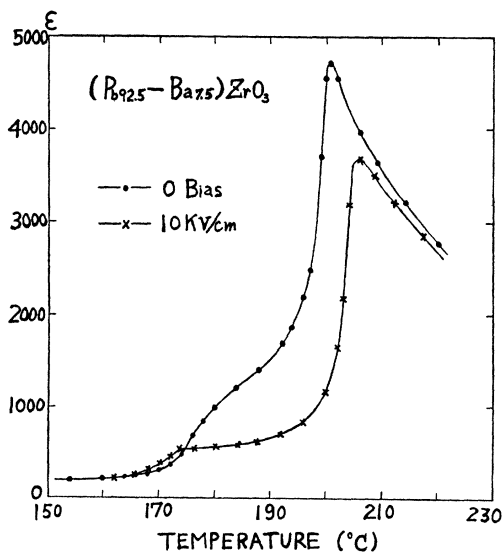


FIG. 1. Effect of a dc biasing field of 10 kv/cm on the permittivity of $(\text{Pb}92.5-\text{Ba}7.5)\text{ZrO}_3$ at 1 Mc/sec.

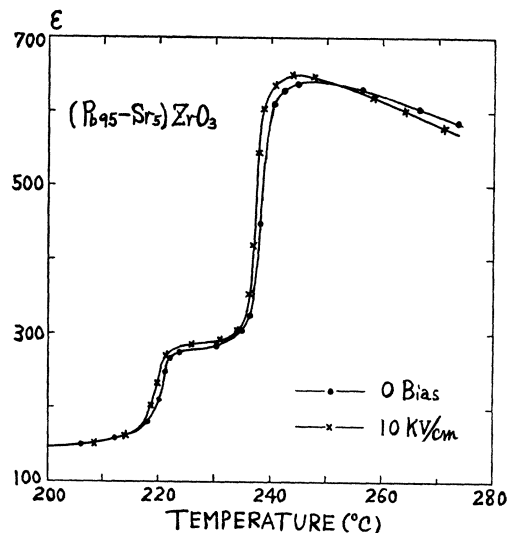


FIG. 2. Effect of a dc biasing field of 10 kv/cm on the permittivity of $(\text{Pb}95-\text{Sr}5)\text{ZrO}_3$ at 1 Mc/sec.

and then sintered at temperatures between 1200° and 1300°C after preliminary calcination.

Curves of permittivity vs rising temperature for $(\text{Pb}92.5-\text{Ba}7.5)-\text{ZrO}_3$ and $(\text{Pb}95-\text{Sr}5)\text{ZrO}_3$ are shown in Figs. 1 and 2. Besides the remarkable maximum at the ordinary Curie point, another small anomaly can be perceived in these two curves.⁶ It is to be noticed here that the anomaly at the lower transition in $(\text{Pb}95-\text{Sr}5)\text{ZrO}_3$ is more pronounced than that of $(\text{Pb}92.5-\text{Ba}7.5)\text{ZrO}_3$, whereas the peak value at the Curie point of the former is smaller than that of the latter.

To confirm whether the properties of these intermediate phases are both ferroelectric, as in the case of $\text{Pb}(\text{Zr}-\text{Ti})\text{O}_3$, we have carried out the study of the $D-E$ characteristics of the present solid solutions under an ac field of 20 kv/cm. The curve for $(\text{Pb}92.5-\text{Ba}7.5)\text{ZrO}_3$ shows typical hysteresis loops in the intermediate phase between 175° and 200°C, insuring the ferroelectricity of this phase. On the other hand, the curve for $(\text{Pb}95-\text{Sr}5)\text{ZrO}_3$ shows no hysteresis loops and is almost linear, not only in the lowest phase but also in the intermediate phase, except at temperatures just below the upper transition point in which a slight upward curvature was observed. This result seems to suggest that the intermediate phase in this specimen is not ferro-

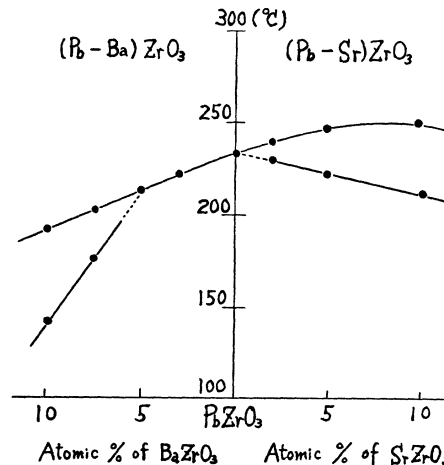


FIG. 3. Phase diagram of the $(\text{Pb}-\text{Ba})\text{ZrO}_3$ and $(\text{Pb}-\text{Sr})\text{ZrO}_3$ systems.

electric but antiferroelectric, being different from the phase of pure PbZrO_3 .

The effect of a dc biasing field of 10 kv/cm upon the permittivity of these two solid solutions was studied, with the results shown in Figs. 1 and 2. In $(\text{Pb}92.5\text{--Ba}7.5)\text{ZrO}_3$, the permittivity value in the ferroelectric phase is lowered considerably by the biasing field as in the case of barium titanate.⁷ The situation is very different for $(\text{Pb}95\text{--Sr}5)\text{ZrO}_3$. Below the upper transition temperature, the permittivity of this specimen is slightly increased by a dc field. A comparison of this result with that² of pure PbZrO_3 gives further support for the above assumption of the antiferroelectricity of the intermediate phase in this specimen. The atomic arrangement of this antiferroelectric phase must of course be different from that of pure PbZrO_3 . An x-ray study is now in progress.

The phase diagram of the $(\text{Pb--Ba})\text{ZrO}_3$ and $(\text{Pb--Sr})\text{ZrO}_3$ systems is shown in Fig. 3. The situation is to be summarized as follows:

(1) When some of the Pb ions in PbZrO_3 are replaced by other suitable ions, an intermediate phase can be observed between antiferroelectric and paraelectric phases. The temperature range of this intermediate phase increases with the concentration of substituted ions.

(2) In the $(\text{Pb--Ba})\text{ZrO}_3$ system, this intermediate phase is clearly ferroelectric, just as in the case of $\text{Pb}(\text{Zr--Ti})\text{O}_3$ system.

(3) In the $(\text{Pb--Sr})\text{ZrO}_3$ system, the intermediate phase seems to be another antiferroelectric phase which is different from the phase of pure PbZrO_3 .

These facts show that the antiferroelectric phase in pure PbZrO_3 is very critical in nature; namely, the free energy of this phase is very closely adjacent to those of a ferroelectric phase and another antiferroelectric phase, especially near the Curie point. This peculiar situation indicates that a ferroelectric state and an antiferroelectric state can be realized by only a small change in the polarizabilities of constituent ions. Detailed results will be reported shortly.

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¹ Sawaguchi, Shirane, and Takagi, *J. Phys. Soc. Japan* (to be published).

² Shirane, Sawaguchi, and Takagi, *J. Phys. Soc. Japan* **6**, 208 (1951); *Phys. Rev.* **84**, 476 (1951).

³ Sawaguchi, Maniwa, and Hoshino, *Phys. Rev.* **83**, 1078 (1951).

⁴ G. Shirane and A. Takeda, *J. Phys. Soc. Japan* (to be published).

⁵ S. Roberts, *J. Am. Ceram. Soc.* **33**, 63 (1950).

⁶ The permittivity anomaly at the lower transition in $(\text{Pb}90\text{--Ba}10)\text{ZrO}_3$ was also observed by Dr. S. Roberts (private communication to the author, January, 1951).

⁷ S. Roberts, *Phys. Rev.* **71**, 890 (1947).

The Change in Electrical Resistance of Magnesium on Melting

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THE change in the electrical resistance of magnesium was determined using Johnson, Matthey and Company, Ltd., spectrographically pure metal (99.95 percent) and two commercially pure magnesium samples (99.52 and 98.67 percent with small amounts of Al, Fe, Mn, Cu, Si, and Cr). The resistivity-temperature data are shown plotted in Fig. 1.

There are three interesting features of the data. First, the ratio of the resistivity of liquid, ρ_l , to that of the solid, ρ_s , is 1.63 for the spectrographic material (1.56 for the commercially pure metal). This value is considerably less than the value 2.1 calculated from the equation of Mott and Wills¹ relating the ratio ρ_l/ρ_s to the latent heat of fusion. The value is also less than that observed for cadmium and zinc with which it may be compared structurally. The low value of ρ_l/ρ_s suggests that there are a larger number of

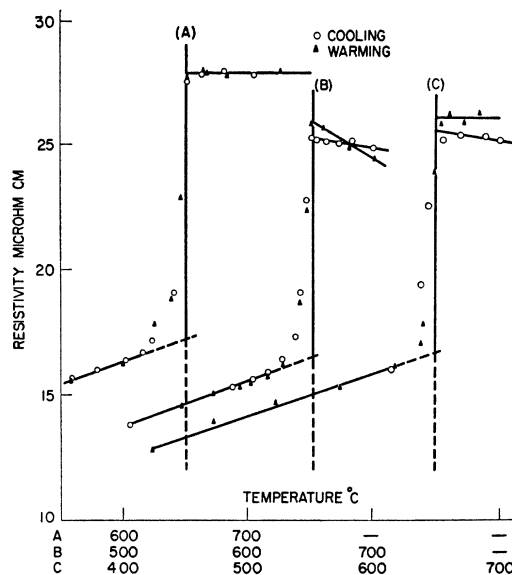


FIG. 1. Magnesium metal resistivity vs temperature. (A) Spectroscopically pure; (B) commercially pure, 98.7 percent; (C) commercially pure, 99.5 percent.

effective free electrons in the liquid than in the solid—a suggestion consistent with the brillouin-zone picture. Second, the temperature coefficient of resistivity for molten magnesium is extremely small (negative in the case of the commercially pure samples). In the case of zinc, in which a marked negative temperature coefficient of resistivity is observed, Mott and Jones² have suggested that in the liquid a further distortion of the lattice increases the number of free electrons. Third, for each of the materials studied, the resistivity departs from a linear temperature dependence some 20–30° before the melting point is reached at 651°. This anticipation of melting is evidenced whether the cell is warming or cooling and is therefore not readily explained by a hysteresis effect. The effect may be of an undetermined experimental origin. Such an anticipation of melting has been observed for antimony³ which, however, has a lower resistance in the liquid than solid phase, thus making direct comparison tenuous. The nonlinear change in resistance at a temperature considerably below that required for melting in the case of magnesium may be real. It would be of interest to clarify this effect through the use of other techniques, such as possibly x-ray diffraction.

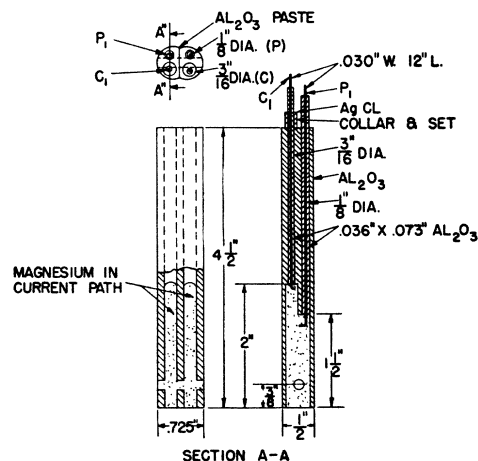


FIG. 2. Ceramic cell for electrical resistance measurement.