Electron Paramagnetic Resonance of Fe^{3+} in the Strong Axial Field of $PbTiO_3$ Host

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An electron paramagnetic resonance investigation has been made of single crystals of tetragonal $PbTiO_3$. A spectrum attributed to Fe^{3+} was found which can be described by the spin Hamiltonain: $\mathcal{H} = g_{||}\beta H_z S_z + g_\perp\beta(H_x S_x + H_y S_y)$ with $S=\frac{1}{2}$, $g_{||}=2.009\pm0.005$ and $g_\perp=5.97\pm0.02$ at room temperature. These values are explained in terms of a strong tetragonal component of the crystalline field.

INTRODUCTION

LEAD titanate is a ferroelectric which is isomorphous at room temperature with tetragonal barium titanate and possesses a Curie point at 490°C, where the structure changes to cubic symmetry. The cell dimensions are $a=3.904$ Å and $c=4.150$ Å at 20°C. Small single crystals can be grown, but ceramics of $PbTiO_3$ tend to fracture when cooled through the Curie point. The purpose of this work has been to study the paramagnetic resonance spectrum of $PbTiO_3$ and to correlate the results with the known properties of this substance.

MEASUREMENTS AND RESULTS

Single crystals of $PbTiO_3$, grown from a KF flux melt in platinum crucibles, occur in the form of small plates or cubes up to several millimeters which can be yellow, green, or black. It is not at present possible to grow large single domain crystals.

Measurements were made primarily at room temperature[1] using a Varian V-4502 spectrometer working at about 8.8 Gc/sec with a magnetic field modulation frequency of 400 cps.

All the crystals studied show the same spectrum, which is essentially composed of three resonance lines. The lines are relatively broad; the absorption derivative peak-to-peak value is about 50 G. Variation of the orientation of the magnetic field relative to the crystallographic axes shows that each of the lines belongs to a paramagnetic impurity of effective spin $S=\frac{1}{2}$ and follows the spin-Hamiltonian

$$\mathcal{H} = g_{||}\beta H_z S_z + g_\perp\beta(H_x S_x + H_y S_y),$$

with

$$g_{||} = 2.009\pm0.005,$$

$$g_\perp = 5.97\pm0.02.$$

The only difference between the three lines is the orientation of the Z axis which, for each line, corresponds to one of the crystal axes. It is therefore natural to conclude that the spectrum is produced by the same impurity in the three possible orientations of domains (twinning of 180° being magnetically unobservable). This is confirmed by the fact that the relative intensity of the lines is strongly variable from one crystal to another, showing a different distribution of the domains. The three lines can be roughly equal; but also one or two of them can be of weaker intensity or unobserved, particularly in the crystals occurring in the form of plates. Among the cubes, the most extreme departure from random distribution was found in a crystal possessing about 80% of the domains in the same orientation.

The identification of $g_\perp$ is given by rotation of the magnetic field around one of the crystal axes. In this case the domains whose Z axes always remain perpendicular to the direction of H correspond to the orientation independent resonance line.

DISCUSSION

The measurements show that the paramagnetic impurity responsible for the spectrum is located in a position of local tetragonal symmetry and therefore probably substituted for an ion in the lattice.

Several considerations allow us to identify this impurity as Fe^{3+}. The signal is relatively strong, and spectrographic analysis of nominally pure samples shows that iron is the impurity present in the highest concentration (between 0.05 and 0.5 at. %). Crystals intentionally iron-doped gave the same spectrum; no additional resonance lines appeared. The resonance of Fe^{3+} is relatively strong in the other titanium compounds of perovskite-type structure, $BaTiO_3$[2] and $SrTiO_3$,[3] which are grown basically by the same method. No trace was found of the five-line spectrum characteristic of Fe^{3+} in tetragonal symmetry in any of the $PbTiO_3$ samples. The iron could possibly be in a reduced state (Fe^{2+} is expected to be unobserved at room temperature). The oxidation of Fe^{2+} to Fe^{3+} was apparently done without difficulty in $BaTiO_3$.[2] In $PbTiO_3$, heating in air for several hours, at temperatures up to 1000°C, then in oxygen (flow of 3.25 l/min for 40 h at 800°C) did not change the spectrum, suggesting that the iron was in the trivalent state prior to the oxidation.

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[1] Investigation of the spectrum up to 300°C and down to −120°C did not produce any fundamental change. In particular, the transition to a multiple cell structure reported at −100°C when cooling slowly (see Ref. 9) did not produce a transformation of the spectrum.

[2] A. W. Hornig, R. C. Rempel, and H. E. Weaver, Phys. Chem. Solids 10, 1 (1959).

[3] K. A. Müller, Helv. Phys. Acta 31, 173 (1958).

Although other ions which may be paramagnetic are present in the crystal, i.e., titanium, platinum,[4] niobium, and copper,[5] they are not expected to have the observed g values and spectral intensity.

Because of size considerations, Fe^{3+} is expected to substitute for Ti^{4+} in the lattice, and its paramagnetic spectrum can be explained in terms of a strong axial field. The problem was theoretically studied by Griffith.[6] Fe^{3+} in its high-spin form is in the $^6S_{5/2}$ state. Under the action of a tetragonal crystalline field, this ground state splits into three twofold degenerate levels and its behavior in the presence of a magnetic field can be described by an adequate spin-Hamiltonian. If, however, the coefficient D of S_z^2 in the spin-Hamiltonian, proportional to the zero-field splitting, is much larger than the magnetic field energy, the lowest doublet is not mixed with the highest ones and the spectrum is described by a new spin-Hamiltonian with $S' = \frac{1}{2}$, $g_{||}' \cong 2$, and $g_\perp' \cong 6$. This effect was observed by Griffith and Bennett et al.,[7] but with relatively low precision in a few organic compounds (haemoglobin derivatives).

Several facts help to explain the large zero-field splitting of Fe^{3+} in $PbTiO_3$. The work of the above authors suggests that a D of at least 1 cm⁻¹ is required to observe a true $g_\perp$ of 6 if the minimum wavelength available is about 3 cm. Although studies at shorter wavelengths would provide further information, a minimum D of 1 cm⁻¹ seems consistent with the crystalline structure of $PbTiO_3$. The relation between D and the coefficient A_2^0 of Y_2^0 in the development of the crystalline field potential is not completely understood, but an extrapolation of the tentative quadratic relation given by Nicholson and Burns[8] leads to an A_2^0 at least two times larger in $PbTiO_3$ than in $BaTiO_3$. This is in accord with the main feature in $PbTiO_3$, which is the large displacement of the Pb and Ti ions, leading to a strong tetragonal component. Pb moves through 0.47 Å (0.05 Å for Ba in $BaTiO_3$) and Ti through 0.30 Å (0.10 Å in $BaTiO_3$) relative to the almost undistorted framework of oxygen ions. The ratio c/a of the cell dimensions is 1.063 in $PbTiO_3$, about six times larger. The spontaneous polarization calculated from ionic
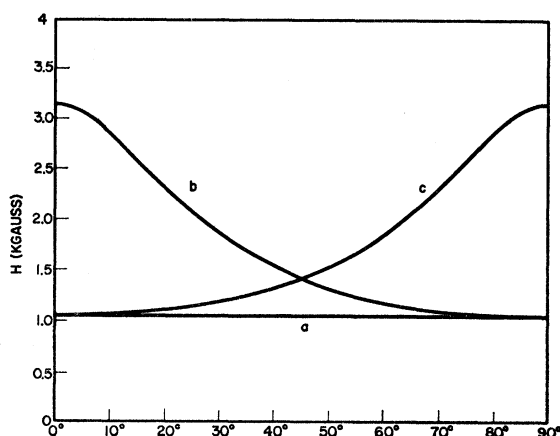

FIG. 1. Angular dependence of the three resonance lines for rotation of the magnetic field around one of the symmetry axes. Curve (a) corresponds to domains whose Z axes always remain perpendicular to the magnetic field. Curves (b) and (c) correspond to domains whose Z axes lie in the plane of rotation of H.

displacements is about three times larger than for $BaTiO_3$.[9] Thus, the observed EPR spectrum of Fe^{3+} appears consistent with the strong tetragonal crystalline field of $PbTiO_3$. It should be noted that possible distortions due to the noncompensated charge of Fe^{3+} may locally modify the crystal field.

After this work was completed we learned from Müller[10] that similar resonances have been observed in cubic $SrTiO_3$ which have an intensity about 0.15 times that of the central transition of the cubic spectrum. Accurate determination of $g_\perp$ at two different frequencies allowed these workers to calculate a value of $|2D| = 2.85 \pm 0.15$ cm⁻¹. They concluded that the only possible explanation for such a large D is that local charge compensation takes place at a nearest oxygen site. An interpretation of the $PbTiO_3$ spectrum in terms of local charge compensation would imply (1) that this charge compensation occurs only along the direction of polarization (since the resonance lines are of unequal intensities) and (2) that all the Fe^{3+} ions are locally compensated in an equivalent manner (since no other spectrum due to Fe^{3+} is detected).

[4] Z. Sroubek, Z. Zdansky, and E. Simanek, Phys. Stat. Solidi 3, 165 (1963), observed in $BaTiO_3$ at 78°K a signal that they attribute to Pt^{3+}. Their crystals, however, were doped with about 0.4 at. % niobium, which acts like a donor, to reduce the valence state of diamagnetic Pt^{4+}. The fact that our samples contained only about 0.03 at. % niobium is additional evidence that the spectrum is not due to Pt^{3+}.

[5] In some crystals a weaker signal is observed, following the same spin-Hamiltonian as the strong one but with $g_{||} = 2.00 \pm 0.01$ and $g_\perp = 2.24 \pm 0.01$. This may be eventually attributed to Cu^{2+}.

[6] J. S. Griffith, The Theory of Transition-Metal Ions (Cambridge University Press, Cambridge, 1961), Chap. 12.

[7] J. E. Bennett, J. F. Gibson, and D. J. E. Ingram, Proc. Roy. Soc. (London) A240, 67 (1957).

[8] W. J. Nicholson and G. Burns, Phys. Rev. 129, 2490 (1963).

[9] F. Jona and G. Shirane, Ferroelectric Crystals (The Macmillan Company, New York, 1962), Chap. 5.

[10] E. S. Kirkpatrick, K. A. Müller, and R. S. Rubins (to be published).