

## Electron Paramagnetic Resonance in SrTiO<sub>3</sub>

W. I. DOBROV, R. F. VIETH, AND M. E. BROWNE  
 Lockheed Research Laboratories, Palo Alto, California

(Received February 13, 1959)

The intensities of paramagnetic resonance lines in SrTiO<sub>3</sub> have been correlated to the iron concentrations. Evidence for attributing the origin of the resonance in titanates to iron impurities (Fe<sup>3+</sup>) rather than to the domain structure was obtained. In SrTiO<sub>3</sub>, resonance experiments over the temperature range 300°K to 1.9°K show a slow continuous increase of the tetragonal component of the crystalline field down to the ferroelectric region. From intensity considerations the absolute signs of the crystalline splitting parameters have been determined.

**E**LECTRON spin resonance has been studied in single crystals of SrTiO<sub>3</sub> at 3-cm wavelength between 1.9°K and 300°K in order to determine the variation of the crystalline field parameters and to study the phase transitions. Mueller<sup>1</sup> observed paramagnetic resonances in SrTiO<sub>3</sub> at 300°K and 80°K. He has shown that the spectrum can be described by the following spin Hamiltonian:

$$\mathcal{H} = g\beta\mathbf{H} \cdot \mathbf{S} + (a/6)(S_x^4 + S_y^4 + S_z^4) + DS_z^2,$$

$$g = 2.004,$$

if one assumes <sup>6</sup>S<sub>5/2</sub> as the ground state of the resonance centers. <sup>6</sup>S<sub>5/2</sub> is the ground state of the trivalent iron which is usually present in SrTiO<sub>3</sub> crystals as an impurity. However, it seemed that a direct proof of the relation between the observed resonances and iron was needed in view of the controversy<sup>2,3</sup> concerning the origin of resonances in BaTiO<sub>3</sub> where an analogous situation exists. We investigated two crystals obtained from the National Lead Company in which the ratio of iron concentration in the melt was approximately 10:1. The intensity of the resonances observed was in the ratio 7.3:1, thereby identifying the paramagnetic species as iron.

Previously two groups, Hornig, Rempel, and Weaver<sup>2</sup> and Low and Shaltiel,<sup>3,4</sup> have published reports concerning the origin of the paramagnetic resonance in single crystals of BaTiO<sub>3</sub>. Low and Shaltiel suggested in one of their papers<sup>3</sup> that the resonances were connected with the ferroelectric state, while Hornig *et al.*<sup>2</sup> deduced that they were due to Fe<sup>3+</sup> impurities. Our results substantiate the results of Hornig, since SrTiO<sub>3</sub>, which is chemically similar to BaTiO<sub>3</sub>, is not ferroelectric at room temperature and yet shows an analogous resonance. We also investigated KNbO<sub>3</sub>, a substance ferroelectrically very similar but chemically dissimilar to BaTiO<sub>3</sub>, and found no trace of a resonance. Hence, there is no indication that the ferroelectric state is responsible for the observed resonances.

The spectrum was studied at 300°K as a function of

crystalline orientation with respect to the applied magnetic field, and the fit of experimental data with theory is shown in Fig. 1. Except for the fact that we found a better agreement with the theory (maximum deviation from the theoretical positions is 1.5% for the  $\pm\frac{3}{2} \leftrightarrow \pm\frac{1}{2}$  lines as compared to 5% in reference 1), our results are in basic agreement with Mueller's. For the  $\pm\frac{5}{2} \leftrightarrow \pm\frac{3}{2}$  lines the deviations are greater (3%). However, contrary to reference 1 we found that the positions of the  $\pm\frac{5}{2} \leftrightarrow \pm\frac{3}{2}$  lines are in sufficiently close agreement with the theory to be clearly resolved from the  $\pm\frac{3}{2} \leftrightarrow \pm\frac{1}{2}$  lines and to be measured accurately (Fig. 2). It is not clear from our measurements that the existence of partial covalent bonding should be inferred from the observed discrepancies.<sup>1</sup>

At 77°K a doubling of the  $\pm\frac{5}{2} \leftrightarrow \pm\frac{3}{2}$  and  $\pm\frac{3}{2} \leftrightarrow \pm\frac{1}{2}$  lines appears for orientations with the magnetic field parallel to the [100] direction. This doubling is attributed<sup>1</sup> to the formation of domains with the tetragonal domain axes parallel to the cubic axes. We observed at 4.2°K an intensity ratio of 2:1 for the components of each line, corresponding to  $\frac{2}{3}$  of the ions in domains oriented perpendicular and  $\frac{1}{3}$  in domains oriented parallel to the magnetic field. The over-all splitting of the spectrum is given by

$$\Delta_{\theta=0^\circ} = 5a - 4D, \quad \Delta_{\theta=90^\circ} = 5a + 2D,$$

where  $\theta$  = angle between the tetragonal axis and the

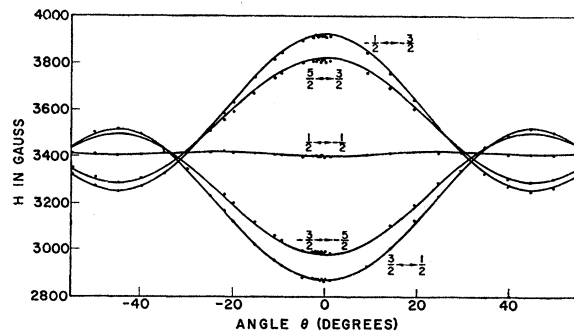


FIG. 1. Paramagnetic spectrum of Fe<sup>3+</sup> in SrTiO<sub>3</sub> at 300°K ( $D=0$ ) vs angle between the magnetic field and crystalline cubic axis. The magnetic field was rotated in the [100] plane. The curves represent the calculated line positions; the points are the experimental data.

<sup>1</sup> K. A. Mueller, *Helv. Phys. Acta* **31**, 173 (1958).

<sup>2</sup> Hornig, Rempel, and Weaver, *Phys. Rev. Letters* **1**, 284 (1958).

<sup>3</sup> W. Low and D. Shaltiel, *Phys. Rev. Letters* **1**, 51 (1958).

<sup>4</sup> W. Low and D. Shaltiel, *Phys. Rev. Letters* **1**, 286 (1958).

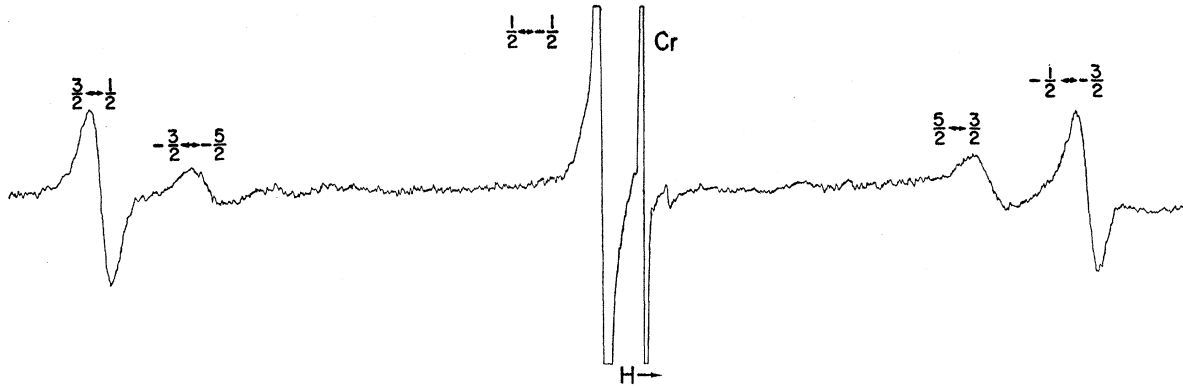


FIG. 2. Derivatives of absorption lines of  $\text{Fe}^{+++}$  and  $\text{Cr}^{+++}$  (line Cr) vs magnetic field at  $300^\circ\text{K}$ . The magnetic field is in the  $[100]$  direction.

magnetic field. Since the component of the doublet nearest the center of the spectrum is strongest, we deduce that  $D$  and  $a$  have opposite signs. The sign of  $a$  may be determined by a method suggested by Low.<sup>5</sup> By varying the temperature down to  $1.9^\circ\text{K}$  and observing the intensity change for the  $+\frac{3}{2} \leftrightarrow +\frac{1}{2}$  and  $-\frac{1}{2} \leftrightarrow -\frac{3}{2}$  lines, it was found that the intensity of the high field line increased more rapidly than the low field line. Thus, the sign of  $a$  was determined to be negative.

TABLE I. Magnitude and sign of  $a$  and  $D$  for  $\text{Fe}^{+++}$  in  $\text{SrTiO}_3$ .

$T$ ( $^\circ\text{K}$ )	$a$ ( $\text{cm}^{-1}$ )	$D$ ( $\text{cm}^{-1}$ )
300	$(-1.977 \pm 0.007) \times 10^{-2}$	0 ( $< 1.0 \times 10^{-4}$ )
77	$(-2.208 \pm 0.011) \times 10^{-2}$	$(+7.3 \pm 0.3) \times 10^{-4}$
4.2	$(-2.256 \pm 0.019) \times 10^{-2}$	$(+16.1 \pm 0.7) \times 10^{-4}$
1.9	$(-2.3 \pm 0.1) \times 10^{-2}$	$(+17.9 \pm 1.0) \times 10^{-4}$

<sup>5</sup> W. Low, Phys. Rev. **105**, 793 (1956).

The values of the crystalline parameters at various temperatures are given in Table I. From the (Ba-Sr) $\text{TiO}_3$  phase diagram<sup>6</sup> one should expect a ferroelectric phase transition for  $\text{SrTiO}_3$  at about  $40^\circ\text{K}$ . Also, the dielectric constant of  $\text{SrTiO}_3$  follows closely the Curie-Weiss law,

$$\epsilon = C/(T - \theta),$$

between  $100^\circ\text{K}$  and  $240^\circ\text{K}$ , with  $C = 83 \times 10^3$  and  $\theta = 38^\circ\text{K}$ .

Comparison of our values of  $D$  (Table I) at  $1.9^\circ\text{K}$ ,  $4.2^\circ\text{K}$ , and  $77^\circ\text{K}$  shows that no sharp phase transition occurs between  $77^\circ\text{K}$  and  $1.9^\circ\text{K}$ . These data also indicate that the transition from the nonferroelectric to the ferroelectric state is much more gradual in  $\text{SrTiO}_3$  than in  $\text{BaTiO}_3$ .

Work is continuing on the effects of electric fields on the spectrum of  $\text{SrTiO}_3$  at temperatures down to  $2^\circ\text{K}$ . Certain anomalies in the line shapes at low temperatures will be discussed in a future publication.

<sup>6</sup> H. Graenicher, Helv. Phys. Acta **29**, 210 (1956).