

## Electron Paramagnetic Resonance of Trivalent Gadolinium Ions in Strontium and Barium Titanates

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This paper reports electron paramagnetic resonance data of substitutional  $Gd^{3+}$  impurities in the cubic and tetragonal phases of barium and strontium titanates. The pertinent spin Hamiltonian parameters are determined as a function of temperature in these two mentioned phases of both crystals. The temperature for the cubic-to-tetragonal phase transition in  $SrTiO_3$  is determined from these data to be  $110 \pm 2.5^\circ K$ , a result that has been checked by the observation of the temperature dependence of the birefringence pattern of pure (undoped) crystals. This experiment is also briefly described. In the latter crystal we find a smooth transition, contrary to the corresponding case in  $BaTiO_3$ . The  $Gd^{3+}$  resonance results are compared with previous data on electron paramagnetic resonance of iron-group impurities, and some comments and conjectures are offered as to possible correlation of these results with the temperature dependence of certain properties of the host crystals in the neighborhood of the phase transition.

### INTRODUCTION

THE purpose of this paper is to present and discuss results obtained by examining the electron paramagnetic resonance (EPR) of  $Gd^{3+}$  occurring as a substitutional impurity in the barium and strontium titanates. A number of publications<sup>1-6</sup> have dealt with the EPR of iron group impurities in these crystals. Size considerations indicate that such ions would preferentially substitute at the  $Ti^{4+}$  site whereas larger ions, e.g., the rare earths, would probably substitute for the alkaline earth. We decided, therefore, that a study of a rare-earth impurity would be useful.<sup>7</sup> Among the rare earths, only the *S*-state ions  $Gd^{3+}$  and  $Eu^{2+}$  are susceptible to investigation over a wide range of temperatures.

It is well established<sup>8</sup> that  $BaTiO_3$  exhibits an abrupt phase change in the neighborhood of  $120^\circ C$  from the high-temperature cubic, unpolarized phase to a tetragonal, ferroelectric phase which is the stable phase at room temperature. This transition shows its effect quite obviously on the temperature dependence of the EPR of the  $Fe^{3+}$  impurities.<sup>2</sup> Our results show a similar effect in the EPR of  $Gd^{3+}$ . A sharp change is observed at the transition temperature.

For a long time,  $SrTiO_3$  was considered to be cubic at all temperatures.<sup>9</sup> EPR studies of Mn impurities<sup>3</sup>

indicated, however, the presence of a phase change in the neighborhood of the temperature of liquid air. One cannot be sure in this case that the  $Mn^{IV}$  ion is perfectly substitutional in either phase. This makes the analysis of these results insofar as the characterization of a transition in the host somewhat difficult. The most reasonable interpretation indicates, however, that there is a structural change from a cubic phase stable at the higher temperatures to a tetragonal phase stable below the boiling point of  $N_2$ .

EPR studies of  $Fe^{3+}$  in  $SrTiO_3$  also show that it is a substitutional impurity with cubic site symmetry at room temperature, but with a small tetragonal distortion present at  $77^\circ K$  and below.<sup>4,5</sup> A more detailed temperature dependence of the spectrum in this case could presumably have characterized the phase transition in more detail.

The results to be presented in this paper, in particular the detailed temperature dependence of the  $Gd^{3+}$  spectrum in  $SrTiO_3$  indicate the existence of a cubic to tetragonal phase transition close to  $110^\circ K$ . Within the limits of experimental accuracy, this transition is smooth in contrast to the sharp one found in  $BaTiO_3$ . In order to obtain definite evidence that this transition is not a property of the neighborhood of the impurity alone, we have examined the temperature dependence of the birefringence pattern of single crystals of pure  $SrTiO_3$  and determined that a phase change in these crystals does indeed occur near  $110^\circ K$ . More recently, further confirmation for this finding has been obtained.<sup>10,11</sup> Actually, the fact that the EPR lines remain narrow when the temperature is varied through  $110^\circ K$  is in itself evidence that this transition is brought about by a cooperative phenomenon in the host crystal.

Some comment on the birefringence experiments will

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

<sup>2</sup> A. W. Honing, P. C. Rempel, and H. E. Weaver, J. Phys. Chem. Solids **10**, 1 (1959).

<sup>3</sup> K. A. Müller, Phys. Rev. Letters **2**, 341 (1959).

<sup>4</sup> K. A. Müller, Helv. Phys. Acta **31**, 173 (1958).

<sup>5</sup> W. I. Dobrov, R. F. Vieth, and M. E. Browne, Phys. Rev. **115**, 79 (1959).

<sup>6</sup> K. A. Müller, Arch. Sci. (Geneva) **11**, 150 (1958).

<sup>7</sup> While this paper was in preparation, a communication to the spring meeting of the *Société Suisse de Physique* by J. Sierro describing EPR results on  $Gd^{3+}$  in  $SrTiO_3$  at room temperature came to our attention.

<sup>8</sup> W. Känzig, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1957), Vol. 4. See also the comprehensive set of references in W. Känzig's article.

<sup>9</sup> Evidence for a low temperature phase transition in  $SrTiO_3$  from dielectric studies has been presented earlier. This, however, gave rise to some controversy. See references to work by Gränicher as mentioned in references 4 and 8.

<sup>10</sup> R. O. Bell and G. Rupprecht (to be published). These authors have discovered a marked change in the elastic properties of  $SrTiO_3$  in the neighborhood of  $112^\circ K$ . See also G. Rupprecht and R. O. Bell, Phys. Rev. **125**, 1915 (1962).

<sup>11</sup> O. Guentert has privately communicated to the authors as a preliminary result of neutron diffraction studies in  $SrTiO_3$  single crystals, the discovery of a change in intensities of the diffraction pattern, as the temperature is varied through  $110^\circ K$ .

be given in Sec. II, together with a discussion of the experimental techniques involved in the EPR spectroscopy. The results of the EPR measurements will be presented in detail in Sec. III. Section IV is devoted to a discussion of our results in light of present theories of ferroelectrics of the  $BaTiO_3$  type.

We feel that these comparative studies of the tetragonal-cubic transition in the two crystals considered should be of help in bringing about a more complete understanding of the properties of either.

## II. EXPERIMENTAL TECHNIQUES

### A. Samples and Crystallographic Considerations

The  $SrTiO_3$  samples were purchased from the National Lead Company and contained about 0.1 at. % Gd. The  $BaTiO_3$  crystals were grown in this laboratory by B. diBenedetto using flux techniques. Crystals containing atomic concentrations of  $Gd^{3+}$  from 0.2 to 0.01% were examined. The less concentrated crystals were slightly colored plates with their larger faces along (100) planes, although (110) faces were also present on some. The crystals with higher  $Gd^{3+}$  concentrations generally exhibited the same geometry as the others; however, they contained, in most cases, dark occlusions of unreacted flux material and were appreciably lossier. Nevertheless, the same spectrum was encountered in all the samples examined aside, of course, from intensity variations due to concentration differences. Our temperature resolution ( $\pm 1.5^\circ C$ ) in the region above room temperature was not sufficient to measure the slight impurity concentration dependence of the transition temperature which may be observed by other means.<sup>12</sup>

In the high-temperature phase, both crystals have the cubic perovskite structure,<sup>8</sup> in which there is only one metal ion of each kind per unit cell. Thus, the metallic sites have cubic point symmetry, and for substitutional  $Gd^{3+}$  the spectrum exhibits this symmetry with axes parallel to edges of the unit cell. A number of subsidiary weak lines are observed in the spectrum of  $Gd^{3+}$  in  $SrTiO_3$ . These lines may be attributed to a small fraction of  $Gd^{3+}$  ions which do not enter as perfect substitutional ions, conceivably due to some axial symmetry in the mechanism of charge compensation for the valance unbalance.<sup>7</sup> We shall not be concerned with such spectra in the present paper.

In the tetragonal phase, twinning of the crystal takes place resulting in the formation of domains.<sup>13</sup> There are three equivalent types of domains according to which of the three [100] directions is parallel to the direction of tetragonal distortion. Thus, with an arbitrary orientation of the magnetic field  $H$  with respect

to the crystal axes, three different spectra should be observed. However, if  $H$  is confined to a (110) plane, two of these coincide. Our angular dependence data were taken in this situation.

Since the  $BaTiO_3$  crystals exhibited natural (100) faces, these planes were used to obtain rotation patterns. In this case there was a strong preferential orientation of the domains such that the axis of tetragonal distortion (or "c" axis) was normal to a particular face. Thus, rotation in a natural (001) face parallel to the direction of preferential orientation yielded the best signal-to-noise ratio. Lines due to the other domains were observed also.

### B. Remarks on EPR Experiments

The EPR data were taken using a spectrometer built to cover the  $K_u$  microwave band (12–18 kMc/sec). The system was of fairly standard design using a balanced bolometer detection scheme with 25-cps field modulation and phase-sensitive narrow banding.<sup>14</sup> The klystron was frequency stabilized to the sample cavity resonance. This was quite necessary in view of the high and appreciably temperature-dependent dielectric constant of the samples. In the temperature range from 300 to 77°K a platinum thermometer imbedded in the cavity wall was used. The accuracy in sample temperature determination thereby achieved was  $\pm 0.5^\circ K$ .<sup>15</sup> In the range above 300°C the temperature was measured by means of a thermocouple.

An interesting effect appears in the neighborhood of the transition for  $BaTiO_3$ . When the transition temperature is approached from below, the tetragonal spectrum disappears and the cubic spectrum appears. There is a small hysteresis region in which the two spectra should exist simultaneously. This temperature interval is very small (about  $2^\circ C$ )<sup>8</sup> and we have not observed it, due to lack of resolution. We observed, however, that as the transition was approached there was a marked loss in the intensity of the tetragonal spectrum and, also, that the cubic spectrum when it first appeared was quite weak increasing in intensity with  $T$  right above the transition. There was definitely a large loss of total intensity near the transition temperature. There was, however, no observable increase of the losses in the sample as shown by the fact that the coupling and  $Q$  of the cavity did not change. This effect seems to indicate a strong increase in the line widths of all but the central ( $1/2, -1/2$ ) EPR lines when the transition temperature is approached. This in turn might be a consequence of ionic motion in the sample of frequency not too far removed from that corresponding to the tetragonal microwave splitting.

<sup>12</sup> B. diBenedetto (to be published).

<sup>13</sup> By the term "domains" we simply mean, in this case, regions of uniform tetragonal distortion. Their boundaries are not necessarily determined by the long range dipolar interaction. They are more probably related to the distribution of strains in the crystal.

<sup>14</sup> G. Feher, Bell System Tech. J. **36**, 449 (1957).

<sup>15</sup> The accuracy with which we are able to state the temperature for the phase transition in  $SrTiO_3$  is less, however. This is due to the limitation imposed on spectral resolution by the width of the absorption lines.

### C. The Birefringence Experiment

When viewed between crossed polaroids, pure  $\text{SrTiO}_3$  crystals exhibit a complex birefringence pattern even at room temperature. When a plate (about 1-mm thickness) is examined with monochromatic light it exhibits distinct regions, each with the characteristic  $45^\circ$  angular separation between directions of light polarization for maximum and minimum transmission.<sup>16</sup> These regions are separated by lines that are always opaque (nonbirefringent). Such a pattern may be explained by the existence of uniformly strained regions in the initially cubic crystal. All crystals examined exhibited such patterns and annealing for a few hours at  $1600^\circ\text{C}$  was not effective in altering them.

These strain patterns were examined as a function of the temperature between 300 and  $77^\circ\text{K}$  with the crystal mounted in an optical Dewar. No noticeable changes occurred in the pattern between 300 and  $130^\circ\text{K}$ . Below  $100^\circ\text{K}$  a temperature-independent pattern was observed again, markedly different, however, from the room temperature pattern. As the sample was slowly warmed up from  $100^\circ\text{K}$  the dark boundaries between the birefringent regions started to move and broaden until in the neighborhood of  $110^\circ\text{K}$ , the crystal was opaque. At this temperature, rotation of the polaroids showed the crystal to be essentially optically isotropic.<sup>17</sup> As the temperature continued to rise new transparent regions started to appear and grow until at about  $130^\circ\text{K}$ , a pattern appeared which was identical to what was observed at room temperature.

Even if the birefringence pattern in the crystal above and below  $110^\circ$  is ascribed to strains, the rearrangement

in this pattern that occurs at this temperature definitely indicates a structural modification in the crystal. This result gives us confidence in interpreting the transition of the EPR spectrum as a result of a structural change in the host crystal. Thus, the information obtained from the EPR may be used as a description in some detail of the nature of this transition.

### III. EPR RESULTS

The ground state of the free  $\text{Gd}^{3+}$  ion is  $4f^7 {}^8S$ .<sup>18</sup> To describe the energy levels resulting from the splitting of this degenerate state by the combined effect of the crystalline electrostatic field and the external magnetic field  $H$ , we write a spin Hamiltonian<sup>19</sup>

$$\mathcal{H} = g\beta\mathbf{H} \cdot \mathbf{S} + b_{2,0}Y_{2,0} + b_{4,0}Y_{4,0} + b_{4,4}(Y_{4,4} + Y_{4,-4}) + b_{6,0}Y_{6,0} + b_{6,4}(Y_{6,4} + Y_{6,-4}). \quad (1)$$

The first term is the Zeeman energy with an isotropic splitting factor  $g$ .  $\mathbf{S}$  is the spin vector;  $S = 7/2$  for the free ion ground state. Crystalline anisotropy of  $g$  is usually negligible for  $S$  ground states.<sup>18</sup> The other terms represent the interaction of the spin  $\mathbf{S}$  with the electrostatic field at the site that the ion occupies in the crystal unit cell. We have assumed tetragonal point symmetry at the ion site and have chosen axes along the three  $[100]$  directions with  $z$  the fourfold axis. The spin-dependent operators  $Y_{l,m}(\mathbf{S})$  have the property that under rotation they transform as the  $(l,m)$ th spherical harmonic.<sup>20</sup> Their matrix elements between eigenstates of  $S_z = M_S$  may be readily obtained from

TABLE I. Spin Hamiltonian parameters of  $\text{Gd}^{3+}$  in the titanates.

Ion	Host	$T$ ( $^\circ\text{K}$ )	$g$	$b_{20}$	$b_{40}$
$\text{Gd}^{3+}$	$\text{SrTiO}_3$	300	$1.992 \pm 0.002$	...	$(-5.7 \pm 0.2) \times 10^{-4}$
$\text{Gd}^{3+}$	$\text{SrTiO}_3$	77	$1.992 \pm 0.002$	$(-233.6 \pm 0.5) \times 10^{-4}$	$(-4.8 \pm 0.5) \times 10^{-4}$
$\text{Gd}^{3+}$	$\text{SrTiO}_3$	4.2	$1.992 \pm 0.002$	$(-362.5 \pm 0.5) \times 10^{-4}$	$(-3.24 \pm 0.5) \times 10^{-4}$
$\text{Gd}^{3+}$	$\text{BaTiO}_3$	300	$1.995 \pm 0.003$	$(-293.6 \pm 1.0) \times 10^{-4}$	$(+4.0 \pm 1.0) \times 10^{-4}$
$\text{Gd}^{3+}$	$\text{BaTiO}_3$	425	$1.995 \pm 0.003$	...	$\sim 6 \times 10^{-4}$
$\text{Fe}^{3+}$	$\text{BaTiO}_3$	425 <sup>a</sup>	...	...	$17.0 \times 10^{-4}$
$\text{Fe}^{3+}$	$\text{BaTiO}_3$	300 <sup>a</sup>	...	$b_{20} = 930 \times 10^{-4}$	$17.0 \times 10^{-4}$
$\text{Fe}^{3+}$	$\text{SrTiO}_3$	300 <sup>b</sup>	...	...	$-33 \times 10^{-4}$
$\text{Fe}^{3+}$	$\text{SrTiO}_3$	77 <sup>b</sup>	...	$b_{20} = 7.3 \times 10^{-4}$	$-37 \times 10^{-4}$
$\text{Fe}^{3+}$	$\text{SrTiO}_3$	4.2 <sup>b</sup>	...	$b_{20} = 16.1 \times 10^{-4}$	$-38 \times 10^{-4}$
Ion	Host	$T$ ( $^\circ\text{K}$ )	$b_{44}$	$b_{60}$	$b_{64}$
$\text{Gd}^{3+}$	$\text{SrTiO}_3$	300	...	$(0.5 \pm 0.3) \times 10^{-4}$	...
$\text{Gd}^{3+}$	$\text{SrTiO}_3$	77	$(-2.5 \pm 0.3) \times 10^{-4}$	$(-0.25 \pm 0.5) \times 10^{-4}$	$(0.1 \pm 0.5) \times 10^{-4}$
$\text{Gd}^{3+}$	$\text{SrTiO}_3$	4.2	$(-4.2 \pm 0.5) \times 10^{-4}$	$(+1.4 \pm 0.5) \times 10^{-4}$	$(-0.69 \pm 0.5) \times 10^{-4}$
$\text{Gd}^{3+}$	$\text{BaTiO}_3$	300	$(-2.0 \pm 1.0) \times 10^{-4}$	$(1.6 \pm 1.0) \times 10^{-4}$	$(\sim 0)$

<sup>a</sup> See reference 2.

<sup>b</sup> See reference 5.

<sup>16</sup> A. Sommerfeld, *Optics* (Academic Press Inc., New York, 1949), Vol. 4.

<sup>17</sup> We do not propose to explain this particular effect here. It is tempting, however, to conjecture that at this temperature the domain size in the crystal becomes relatively small, say, of the order of the optical wavelength, and the crystal appears to be isotropic as would any polycrystalline material.

<sup>18</sup> W. Low, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1960), Suppl. 2.

<sup>19</sup> B. Bleaney and K. W. H. Stevens, *Reports on Progress in Physics* (The Physical Society, London, 1953), Vol. 16, p. 108.

<sup>20</sup> M. E. Rose, *Elementary Theory of Angular Momentum* (John Wiley & Sons, New York, 1957).

tables of  $3j$  symbols,<sup>21</sup> since the reduced matrix elements which are in this case diagonal with  $S=7/2$  may be incorporated in the constants  $b_{l,m}$ . We normalize the  $Y_{l,m}(\mathbf{S})$  in such a way that the diagonal matrix elements become the smallest possible integers. This is achieved by incorporating into the  $b_{l,m}$  factors depending only on  $l$ . Using this recipe to write the matrix elements, the coefficients  $b_{l,0}$  that we determine from our data are in the same convention as those for which the same notation has been used.<sup>18,22,23</sup>

We have restricted Eq. (1) to terms with  $l \leq 6$ , since higher  $l$  terms yield vanishing matrix elements with  $S=7/2$ . In the particular case of cubic symmetry the number of independent coefficients is decreased since the following relations hold<sup>18</sup>:

$$\begin{aligned} b_{2,0} &= 0, \\ b_{4,4} &= [(70)^{1/2}/14]b_{4,0}, \\ b_{6,4} &= -[(14)^{1/2}/2]b_{6,0}. \end{aligned} \quad (2)$$

If the magnetic field is parallel to  $z$ , and if we choose a representation for which  $S_z$  is diagonal, (1) will be diagonal except for the  $M=4$  terms. It turns out fortunately, however, that the frequency at which these experiments were performed ( $\omega/2\pi = 16$  kMc/sec) is sufficiently high so as to permit the treatment of the crystal field interaction by perturbation theory; first order for terms in  $l=4$  and 6, second order at the lower temperatures for  $l=2$ .

Thus, from data obtained with  $\mathbf{H}$  parallel to the tetragonal axis, the three constants  $b_{2,0}$ ,  $b_{4,0}$ , and  $b_{6,0}$  may be determined from first-order formulas alone. The  $g$  value is determined from the position of the  $(-1/2, 1/2)$  transition also from these data.

For a tetragonal spectrum,  $b_{4,4}$  and  $b_{6,4}$  are obtained from data taken when  $\mathbf{H}$  is in a plane normal to the tetragonal axis, either parallel to a  $[100]$  or to a  $[110]$ .

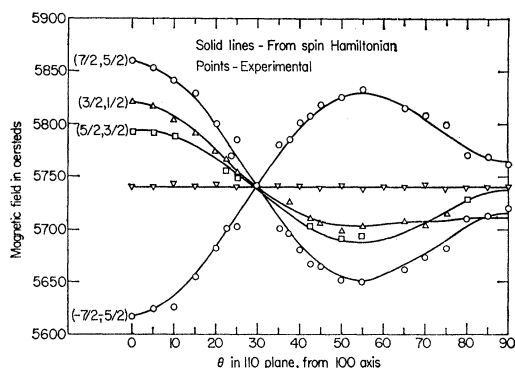


FIG. 1. Angular dependence of some of the EPR transitions for  $Gd^{3+}$  in  $SrTiO_3$ , at room temperature at a frequency of 16 kMc/sec.  $\theta=0$  corresponds to  $\mathbf{H}$  parallel to the  $[100]$  direction.

<sup>21</sup> M. Rotenberg, R. Bivins, N. Metropolis, and J. K. Wooten, *Table of 3j Symbols and 6j Symbols* (Technology Press, Cambridge, Massachusetts, 1959).

<sup>22</sup> C. A. Hutchison, Jr., B. R. Judd, and D. F. D. Pope, *Proc. Phys. Soc. (London)* **70**, 514 (1957).

<sup>23</sup> S. Geschwind and J. P. Remeika, *Phys. Rev.* **122**, 757 (1961).

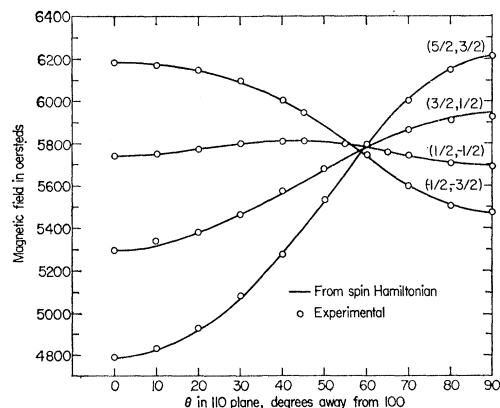


FIG. 2. Angular dependence of some of the EPR transitions for  $Gd^{3+}$  in  $SrTiO_3$  at 77°K at a frequency of 16 kMc/sec.  $\theta=0$  corresponds to  $\mathbf{H}$  parallel to the tetragonal axis.

Table I contains a collection of values of these parameters obtained at a few selected temperatures. Using these parameters, we have calculated by perturbation theory as outlined above the angular dependence of some of the transitions and obtained satisfactory agreement with experimental results as shown in Figs. 1, 2, and 3. The verification of the angular dependence serves the purpose of excluding the presence of extra terms in the spin Hamiltonian, e.g.,  $Y_{2,2} + Y_{2,-2}$ , due to a rhombic distortion or of a tetragonal term  $Y_{2,0}$  in the cubic phase which would mean that the impurity is not substitutional.

The comparison of the values in Table I among themselves and to the Zeeman energy for 16 kMc/sec justifies the use of perturbation theory as outlined. As a consequence, we do not have appreciable mixing of

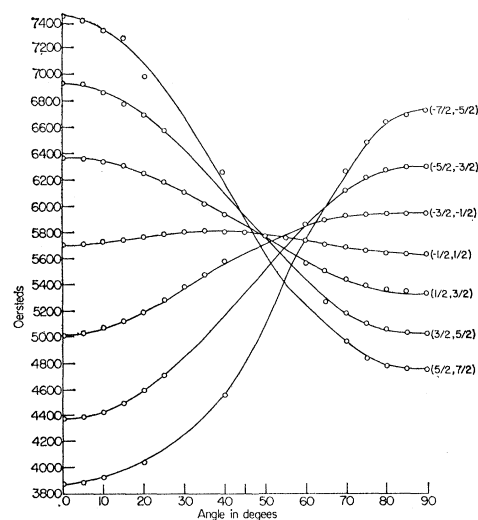


FIG. 3. Angular dependence of the EPR spectrum of  $Gd^{3+}$  in tetragonal  $BaTiO_3$  at room temperature, with the magnetic field in a  $(100)$  plane. The origin for the angles is the  $[100]$  tetragonal axis. The frequency is 16 kMc/sec.

different  $|M_s\rangle$  states and thus relative line intensities serve to identify the various transitions. To obtain good agreement with ratios of rf transition probabilities for the  $\text{BaTiO}_3$  data, integrated intensities had to be used since there is noticeable broadening of these lines. This broadening increases as we move away from the central  $(1/2, -1/2)$  line, presumably due to fluctuations in the crystal field parameters throughout the imperfect crystal. For  $\text{BaTiO}_3$  we determined only the relative signs of the parameters.

For  $\text{SrTiO}_3$ , however, the signs given are absolute since the fact that the tetragonal spectrum was observable down to  $1.5^\circ\text{K}$  permitted the direct determination of the sign of  $b_{2,0}$  relative to which we have taken the signs of the other parameters. We observed that in cooling to  $1.5^\circ\text{K}$  the intensity of the outermost high field  $(7/2-5/2)$  transition decreased relative to the corresponding low field transition. Thus,  $b_{2,0} < 0$ . The assignment of absolute signs to  $b_{4,0}$ ,  $b_{6,0}$  in the cubic phase rests on the assumption that  $b_{4,0}$  is a smooth function of the temperature in the neighborhood of the transition. This is reasonable since its absolute value is certainly so and a reversal in sign at the transition without change in absolute value seems unlikely.

The above discussion has dealt with the determination of the values of the parameters in the spin Hamiltonian. The most interesting results of the present work are the temperature dependence of the EPR spectrum and the temperature dependence of the parameters, especially that of  $b_{2,0}$ .

Figure 4 shows the temperature dependence of the observed spectrum in  $\text{SrTiO}_3$  when  $\mathbf{H}$  is parallel to the tetragonal axis of certain domains. We see below  $110^\circ\text{K}$  two spectra due to the presence of ions with tetragonal axes along the other two  $[100]$  directions. We also

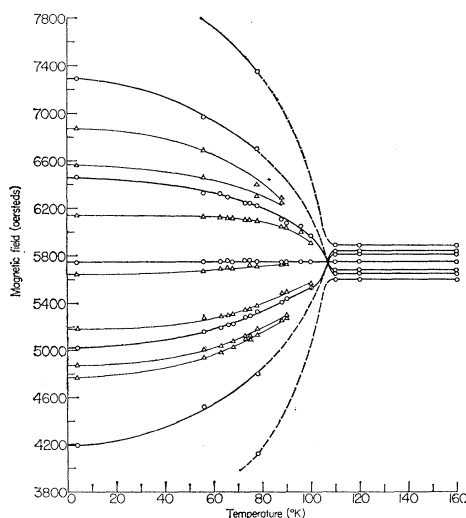


FIG. 4. Temperature dependence of the  $\text{Gd}^{3+}$  EPR spectrum in  $\text{SrTiO}_3$ , with the magnetic field parallel to a  $[100]$  direction and at a frequency of  $16 \text{ kMc/sec}$ . The circles correspond to lines due to the ions whose tetragonal axis is parallel to the field.

observe the seven transitions of a practically temperature independent spectrum above  $110^\circ\text{K}$ , corresponding to one type of ion only.

Figure 5 shows the temperature dependence of the spectrum in  $\text{BaTiO}_3$  with  $\mathbf{H}$  parallel to the preferred tetragonal axis. In the cubic phase, due to the large line widths, the various transitions could not be resolved. From latent structure in the lines, the value for  $b_{4,0}$  shown on Table I is deduced. The abrupt nature of the transition is clearly observable.

The parameter with the strongest temperature dependence is  $b_{2,0}$ . This is shown in Fig. 6 for  $\text{SrTiO}_3$ . Possible implications of this result will be discussed in the next section. Included in Fig. 6 is the temperature dependence of  $b_{4,0}$  which is much slower than that of  $b_{2,0}$ .

The values of  $b_{6,0}$  in most cases are very small, bordering experimental error limits, and will not be discussed further.

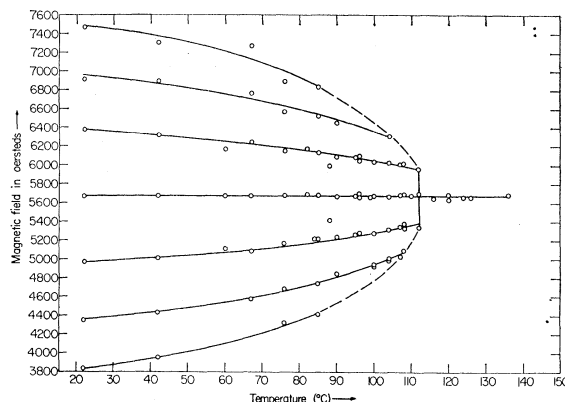


FIG. 5. Temperature dependence of the EPR spectrum of  $\text{Gd}^{3+}$  ions in  $\text{BaTiO}_3$ , in the neighborhood of the tetragonal to cubic phase transition, with the magnetic field parallel to the tetragonal axis. The frequency is again  $16 \text{ kMc/sec}$ .

#### IV. DISCUSSION

Certain aspects of the above results are of interest in their relation to the properties of the host in the vicinity of the phase transition. In what follows we discuss some of these points.

(a) The existence of the cubic-tetragonal phase transition in  $\text{BaTiO}_3$  has been established and studied by many techniques previous to the first EPR investigations. In the case of  $\text{SrTiO}_3$ , however, the initial evidence for the existence of such a transition in the neighborhood of  $110^\circ\text{K}$  has been obtained from EPR results.<sup>3,4</sup> In spite of the fact that in such experiments one is dealing with properties of impurity ions included dilutely in the host, these results alone permit us to conclude the existence of such a phase change.

If one had assumed the crystal to be cubic at all temperatures, the tetragonal symmetry of the spectra at low temperatures could be explained by saying that the impurity is not perfectly substitutional. The

impurity ion would be displaced from the substitutional position of cubic symmetry, say by a small amount parallel to the  $[100]$  direction. Since there are three equivalent such directions, one would obtain in general three inequivalent spectra.<sup>24</sup> With increasing temperature a thermally activated motion characterized by a correlation time  $\tau = \tau_0 \exp(-\Delta/kT)$  would enable the ion to jump between the equivalent positions with distortions along the three  $[100]$  directions.<sup>25</sup> Such a motion would, upon heating, progressively average out the noncubic component  $b_{2,0}$  of the spectral splitting, resulting in a cubic spectrum at the higher temperatures. Complete averaging would be expected at temperatures sufficiently high so that  $(b_{2,0}/h)\tau \ll 1$ ,<sup>26</sup> where  $b_{2,0}$  is the noncubic splitting. This mechanism, however, would cause a temperature-dependent broadening of the EPR lines to a width of the order of  $b_{2,0}/g\beta$ ,<sup>27</sup> which would mean that between  $T=0$  and  $T$  such that  $b_{2,0}\tau/h \approx 1$  the linewidth would increase appreciably. At the latter temperature one would observe, at the most, one very broad line centered at the position of the  $(-1/2, 1/2)$  transition with a width in field  $\Delta H = b_{2,0}/g\beta$ . No increase in the linewidths and no corresponding loss in intensity is observed in  $\text{SrTiO}_3$ . Thus, such a random rotation is not present. All the  $\text{Gd}^{3+}$  ions (and thus the whole lattice) move coherently from positions of tetragonal to positions of cubic symmetry. This can only be a consequence of a cooperative phenomenon due to which sizeable regions (containing many unit cells) of the crystal change structure in an ordered fashion.

(b) In this, as in other similar situations, we are faced with the problem of deciding in which site of the host lattice the impurity substitution takes place. For both  $\text{Fe}^{3+}$  and  $\text{Gd}^{3+}$  there is a valence difference of one unit from either metallic constituent of the host. From the EPR data in the cubic phase, we deduce for both impurities that the mechanism responsible for the charge compensation does not distort the cubic site symmetry. In the  $\text{Gd}^{3+}$  spectrum, a set of low intensity lines was observed indicating that for about 2% of the  $\text{Gd}^{3+}$  ions in these dilute crystals there are deviations from cubic symmetry even at room temperature. It was suggested that the lack of cubic symmetry in such a spectrum was due to association of the Gd ions with  $\text{Al}^{3+}$  impurities. Analyses of these crystals indicate the Al concentration to be far too low to explain the intensity of these lines. It seems more probable that

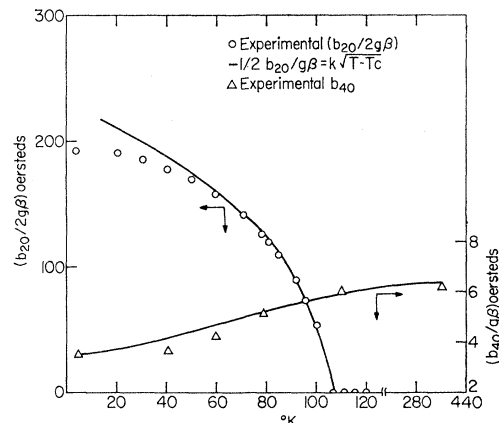


FIG. 6. Temperature dependence of two of the parameters in the spin Hamiltonian for  $\text{Gd}^{3+}$  in  $\text{SrTiO}_3$ .

one is dealing with charge compensation by a combination of  $\text{O}^{2-}$  interstitials and vacancies.<sup>28</sup>

The  $\text{Mn}^{IV}$  spectrum,<sup>3</sup> which is the one that should not exhibit the effects of any charge compensation if we assume that it substitutes for  $\text{Ti}^{4+}$ , does have an axial field splitting in cubic  $\text{SrTiO}_3$ . The reasons for this are not completely understood. We shall base further discussions on the assumption that the size consideration determines in what site the substitution takes place. Comparison of ionic radii<sup>29,30</sup> indicates that  $\text{Gd}^{3+}$  substitutes for the divalent alkaline-earth, whereas  $\text{Fe}^{3+}$  substitutes for  $\text{Ti}^{4+}$ .

(c) The temperature dependence of the  $\text{Gd}^{3+}$  spectrum indicates that of the parameters in the spin Hamiltonian only  $b_{2,0}$  changes appreciably with temperature below the phase transition. This suggests that the mechanism responsible for the  $b_{2,0}$  term is independent of the mechanism responsible for the other terms. Furthermore, this mechanism is only present in the tetragonal phase. The expansion of the crystalline potential in spherical harmonics around the alkaline earth site (or, also, the Ti site) has no  $V_{2,0} = A_{2,0}r^2(\theta, \phi)$  (axial) component in the cubic phase.<sup>31</sup> Such a component will appear, however, with the tetragonal distortion. Let us assume that we have a purely ionic crystal. Let us also assume that the tetragonal distortion is such that the various inequivalent sublattices move rigidly in the  $z$  direction and contract uniformly in the transverse plane. These are the only possible displacements that will conserve one molecule per unit cell of the crystal. Diffraction studies in  $\text{BaTiO}_3$  indicate this to be the case in the tetragonal phase.<sup>32</sup> Following Känzig<sup>8</sup>

<sup>28</sup> G. Rupprecht (private communication) has shown that such vacancies do exist in  $\text{Gd}^{3+}$ -doped  $\text{SrTiO}_3$ .

<sup>29</sup> L. Pauling, *Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1960), 3rd ed.

<sup>30</sup> *Handbook of Physics and Chemistry* (Chemical Rubber Publishing Company, Cleveland, Ohio, 1956), 38th ed.

<sup>31</sup> R. J. Elliott and K. W. H. Stevens, *Proc. Roy. Soc. (London)* **A215**, 437 (1952).

<sup>32</sup> B. C. Frazer, B. C. Danner, and R. Pepinsky, *Phys. Rev.* **100**, 745 (1955).

<sup>24</sup> For trivalent impurities, this tetragonal symmetry could be ascribed to a suitable distribution of localized charges (e.g., cation vacancies, extra anions) in the neighborhood of the impurity. The following discussion would then apply to a thermally activated motion of such charges.

<sup>25</sup> H. S. Gutowsky and G. E. Pake, *J. Chem. Phys.* **18**, 97 (1950).

<sup>26</sup> N. Bloembergen, E. M. Purcell, and R. V. Pound, *Phys. Rev.* **73**, 27 (1948).

<sup>27</sup> R. Kubo and K. Tomita, *J. Phys. Soc. Japan* **9**, 45 (1954).

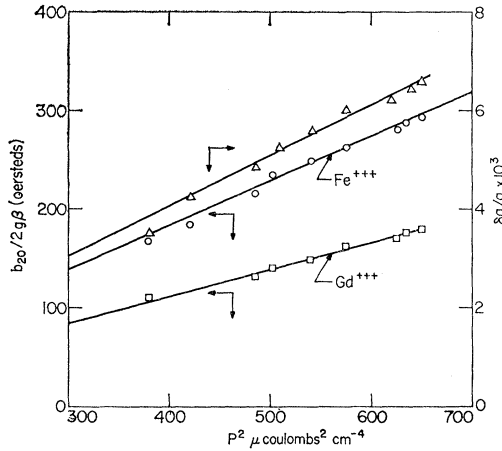


FIG. 7. Dependence on the polarization of the piezoelectric strain and the second-order spin Hamiltonian parameter of  $Gd^{3+}$  in tetragonal  $BaTiO_3$ .

we call these various tetragonal displacements  $\delta z_{Ti}$ ,  $\delta z_{OI}$ ,  $\delta z_{OII}$ , and  $\delta a$  the change in the transverse dimension. Then, a point-charge calculation shows that at the alkaline earth site<sup>33</sup>

$$\delta V_{2,0} = \frac{\pi}{\sqrt{10}} \sigma \langle r^2 \rangle \frac{e}{a^3} \left[ -27.27 \left( \frac{\delta a}{a} \right) + 20.5 \left( \frac{\delta a}{a} \right)^2 + 0.68 \left( \frac{\delta z_{Ti}}{a} \right)^2 - 3.18 \left( \frac{\delta z_{OI}}{a} \right)^2 - 6.36 \left( \frac{\delta z_{OII}}{a} \right)^2 \right], \quad (3)$$

where  $r$  is the electronic radius vector and the average  $\langle r^2 \rangle$  has to be taken over the unfilled shell radial electron wave function ( $4f$  or  $3d$ ) of the magnetic ions.  $\sigma$  is a shielding parameter which should account for the screening of the potential by outer electron shells,  $e$  is the electronic charge, and  $a$  is the edge of the initial cubic unit cell in the undistorted phase. Various perturbation schemes that permit calculation of the  $b_{l,m}$  parameters for the ground state of  $Gd^{3+}$  have been discussed.<sup>22</sup> They involve, in addition to the crystalline field, the spin-orbit or the spin-spin interactions of the  $4f$  shell. Such mechanisms may involve  $\delta V_{2,0}$  either quadratically or linearly.

Since in  $BaTiO_3$  the polarized phase may be considered as resulting from a small distortion of a cubic structure with a center of inversion, the piezoelectric strain  $\delta a/a$  should depend quadratically on the permanent moment  $P$ . For small displacements one may neglect the second-order terms in (3). Then with the assumption  $b_{2,0} \propto \delta V_{2,0}$  one is led to expect  $b_{2,0} \propto P^2$ . The proportionality  $b_{2,0} \propto P^2$  is indeed verified, at least with the same degree of accuracy as that of  $\delta a/a \propto P^2$ , as is seen in Fig. 7.<sup>34</sup> This fact seems to support the

assumption of a dominant mechanism for  $b_{2,0}$  linear in  $\delta V_{2,0}$ .<sup>35</sup> Here  $a = V^{1/3}$ , where  $V$  is the volume of the unit cell.

Incidentally, for rigid sublattice displacements we see in (3) that  $\delta V_{2,0}$  depends quadratically on  $\delta z$ . This is due to the fact that  $\delta V_{2,0} = 0$  in the cubic structure is an extremum for such rigid sublattice displacements, and it is true for both the Ti and the alkaline earth site. Since the permanent moment is parallel to  $z$ , it should depend linearly on  $\delta z$  and thus even with these second order terms included,  $b_{2,0} \propto P^2$ .

(d) Let us now turn to the  $SrTiO_3$  data. Assuming similar mechanisms for  $b_{2,0}$  in both crystals, one may estimate the tetragonal strain in  $SrTiO_3$ . Using Eq. (3), measured strain data for  $BaTiO_3$ ,<sup>8</sup> one obtains for  $SrTiO_3$   $\delta a \sim 0.019 \text{ \AA}$  at  $4^\circ K$  at  $\delta a \sim 0.012 \text{ \AA}$  at  $77^\circ K$ . No evidence for such a large strain is found in this case.<sup>36</sup> There is an interesting point, however. In Fig. 6 we show the temperature dependence of  $b_{2,0}$  for  $Gd^{3+}$  in this crystal. There is no measurable discontinuity in  $b_{2,0}$  or, for that matter, in the value of the other parameters at the transition. Such would be the situation for a transition of order  $n > 1$ . How smooth a transition looks depends to some extent on the range of the microscopic interactions involved in the phenomenon under observation. Other properties involving interactions of range shorter than the electrostatic potential might conceivably exhibit much faster changes than  $b_{2,0}$ . It is a straightforward consequence of the "local field catastrophe" theory of transitions between a polarized and an unpolarized phase that if  $n = 2$ , the dependence of the permanent moment on temperature below the transition is  $P \propto (T_{tr} - T)^{1/2}$ .<sup>37,38</sup> This is true at temperatures sufficiently high so that quantum effects may be neglected. The data in Fig. 7 seem to fit down to  $50^\circ K$  such a law quite well with  $T_{tr} = 107.5^\circ K$ . This, however, according to our assumed mechanism for  $b_{2,0}$ , contrary to what happens in  $BaTiO_3$ , would mean a proportionality between  $b_{2,0}$  and  $P$ . As a consequence, linear terms in  $\delta z$  should be present in (3), which will only be the case if it is assumed that the various inequivalent sublattices do not displace rigidly in the  $z$  direction when the cubic phase distorts into the tetragonal phase. This in turn would mean that in the tetragonal phase we have a larger than minimum unit cell. The implication would then be that we are dealing in  $SrTiO_3$  with a structural phase change of different nature than that in  $BaTiO_3$  at  $120^\circ C$  and, since we do have a high and  $T$ -dependent dielectric constant, the conjecture of an antiferroelectric phase

<sup>35</sup> A calculation of the contribution to the  $b_{2,0}$  of  $Gd^{3+}$  in  $BaTiO_3$  for the second of the linear mechanisms proposed by Hutchison *et al.*, reference 22, with experimental  $\delta a$  and  $\delta z$  in Eq. (3), indicates that with  $\langle r^2 \rangle^{1/2} = 0.5 \times 10^{-8} \text{ \AA}$  we obtain the observed magnitude of  $b_{2,0}$ . This compares favorably with  $\langle r^2 \rangle^{1/2} = 0.53 \times 10^{-8} \text{ \AA}$  as obtained by Fermi-Thomas calculations [G. F. Koster and H. Statz (unpublished)].

<sup>36</sup> O. Guentert (private communication).

<sup>37</sup> T. Slater, Phys. Rev. **78**, 748 (1950).

<sup>38</sup> C. Kittel, Phys. Rev. **82**, 729 (1951).

<sup>33</sup> Here we have neglected the contribution to this potential due to the induced polarization on the  $O^{2-}$  ions. This is justifiable in view of the qualitative nature of the argument.

<sup>34</sup> W. Merz, Phys. Rev. **91**, 513 (1953).

might find partial justification. We should stress here that the above discussion is independent of the host cation site at which the substitution takes place.

Using the ratio  $b_{2,0}$  in  $BaTiO_3$  at  $300^\circ K$  to  $b_{2,0}$  in  $SrTiO_3$ , we estimate for the latter, provided there is no accidental cancellation in (3), ionic displacements at  $4^\circ K$  of the order of  $\delta z \sim 0.0014 \text{ \AA}$  and at  $77^\circ K$ ,  $\delta z \sim 0.0006 \text{ \AA}$ . They would be quite small at  $77^\circ K$ . This would explain the difficulty in detecting this phase transition by x-ray diffraction methods. For this mechanism in  $SrTiO_3$ ,  $b_{2,0} < 0$  indicates  $\delta V_{2,0} > 0$ .

(e) It is of interest to compare the relative magnitudes of  $b_{2,0}$  in these crystals for both  $Fe^{3+}$  and  $Gd^{3+}$  (the values of these constants for  $Fe^{3+}$  in  $BaTiO_3$  are less accurate but still seem to exhibit with reasonable accuracy  $b_{2,0} \propto P^2$  as seen in Fig. 7).

$$Fe^{3+}: \quad b_{2,0}(BaTiO_3)/b_{2,0}(SrTiO_3) = 930.1/16.1,$$

$$Gd^{3+}: \quad b_{2,0}(BaTiO_3)/b_{2,0}(SrTiO_3) = 293.6/362.5.$$

The temperatures for comparison were chosen sufficiently below the transition so that  $\partial b_{2,0}/\partial T$  is small and does not affect the order-of-magnitude comparison. Similar ratios for the  $b_{l,m}$ ,  $l > 2$  in corresponding phases for both ions are of the order of 1, independently of temperature. This indicates that, whereas  $Gd^{3+}$  in both crystals sees about the same amount of tetragonal distortion, such distortion at the  $Fe^{3+}$  site is much larger in the barium salt than in the strontium salt. If the site assignment assumed earlier is indeed correct this would mean that the difference in behavior at the cubic-tetragonal phase transition of the crystals is associated with a radical difference in the distortion of the  $Ti-O_6$  octahedra.

(f) There is a fundamental problem with the explanation of the dielectric behavior of  $SrTiO_3$  brought about by the accurate definition of the cubic-tetragonal phase transition. Whereas in  $BaTiO_3$  the actual phase transition temperature  $T_{tr}$  (aside from hysteresis effects) is very close to the Curie temperature  $T_c$  [ $\epsilon \propto 1/(T-T_c)$  for  $T > T_c$ ], the two temperatures are quite different in  $SrTiO_3$ :  $T_c \sim 30^\circ K$ ,<sup>39</sup>  $T_{tr} = 110^\circ K$ . The present results do not clarify this point. Nevertheless, there is one aspect of these results which tempts one to some conjectures in this direction. If these phase transitions are examined from a lattice dynamics point of view,<sup>40</sup> one may describe them by a change in the relative equilibrium position of the ions around which one should expand the lattice potential in order to satisfy the conditions for stable equilibrium. As the transition temperature is approximated, say in the cubic phase, the ionic vibration amplitudes increase to

a point where terms in the Hamiltonian of order higher than two in the deviations from equilibrium become important. The ionic potential which had a minimum for the configuration of cubic symmetry now develops another minimum for the slightly different configuration of the ions, corresponding to a tetragonal unit cell. The transition temperature is the one at which the free energies calculated by expanding the Hamiltonian around both configurations become equal. It is shown by Cochran<sup>40</sup> that transitions such as we have studied may be achieved by assuming that the modes in a certain small range of some optical branch attain large amplitudes and their frequency decreases to an abnormally low value. In particular, such a mode for  $BaTiO_3$  could be an optical mode with vibration along the tetragonal axis and in the neighborhood of wave vectors  $k=0$  in the branch. The temperature dependence of the frequency of such a mode is given by

$$\omega^2 = K_1(T - T_c). \quad (4)$$

This is a consequence of the fact that when the vibration amplitudes are sufficiently large so that higher than second-order terms in the energy become significant, a first-order correction to account for this is the assumption of spring constants  $K$  that depend linearly on  $T$  (as in the theory of thermal expansion)  $K = K_0 + K_1(T)$ . For a ferroelectric transition,  $K$  is more than canceled out by strong, long-range electrostatic interactions. Since  $\omega^2 \propto K$ , a relationship of form (4) is then obtained. The actual phase transition takes place at a temperature slightly above  $T_c$  and thus  $\omega$  never actually becomes zero. Here is where our results might have some significance. If such a lattice vibration frequency would come at all close to the frequency corresponding to the EPR splittings  $E/h$ , it would cause a broadening of the lines to a width of the order of  $(E/h)^2(2\pi/\omega)$ , where  $E$  is of the order of the maximum tetragonal splitting. No temperature-dependent line broadening is observed in  $SrTiO_3$ . This would put  $\omega/2\pi > 10^8 \text{ kMc/sec}$  at all times which in turn indicates a sizeable minimum difference  $T_{tr} - T_c$ . In the case of  $BaTiO_3$  this difference is very small ( $\sim 2^\circ K$ ). The loss of resonance intensity observed around the transition and discussed in Sec. II might be ascribed to this fact. There is about a  $2^\circ K$  hysteresis associated with this transition which means that within this  $2^\circ$  region the two phases exist simultaneously. This might also mean that in the part of the crystal still in the cubic phase very large linewidths could prevail, so large that their contribution to the resonance lines would disappear as  $\omega$  becomes sufficiently low or  $T$  comes sufficiently close to  $T_c$ . If we assume that the lines do reach their maximum width,  $\omega$  could be as low as  $20 \text{ kMc/sec}$ . However, much smaller broadenings might cause disappearance of the lines and thus  $\omega_{\text{minimum}}$  could be larger than this by at least an order of magnitude.

<sup>39</sup> H. E. Weaver, Quarterly Progress Report 6, Varian Associates, October-December, 1958 (unpublished).

<sup>40</sup> W. Cochran, *Advances in Physics*, edited by N. F. Motz (Taylor and Francis, Ltd., London, 1958), Vol. 9, p. 387.



(g) In  $\text{BaTiO}_3$  it is assumed that the unstable modes correspond to wave vectors  $k$  near  $k=0$ . The domain size is determined roughly by  $\lambda=2\pi/k$  for the unstable modes. In addition, modes where  $k=0$  correspond to tetragonal distortions with no change of the number of ions in the unit cell (rigid distortions of the inequivalent sublattices). Distortions that correspond to the increase in the number of ions in the unit cell by a small factor would come from wave vectors  $k$  near the edge of the Brillouin zone. No domain structure should be observed in this case for an unstrained crystal. This, as was said earlier, is a reasonable possibility for  $\text{SrTiO}_3$ . It would mean, however, that the size and shape of the region of uniform birefringence observed in  $\text{SrTiO}_3$  would be determined by the strain field built into the crystal at growth. This strain causes birefringence even in cubic phase. At the phase transition the elastic constants change slightly<sup>10</sup> and thus the strain field changes. The change in birefringence pattern observed at the transition is a reflection of this effect.

## V. CONCLUSION

The  $\text{Gd}^{3+}$  EPR spectrum has been studied in detail in the cubic and tetragonal phase of two isomorphous crystals  $\text{SrTiO}_3$  and  $\text{BaTiO}_3$ . A birefringence experiment is reported that confirms the existence of such transition as a property of pure  $\text{SrTiO}_3$ . This is of some importance since previous evidence of such a transition came from EPR measurements of impurities in the crystal. The temperature of the cubic to tetragonal transition in  $\text{SrTiO}_3$  has been determined to be  $110 \pm 2.5^\circ\text{K}$ . This transition was shown to be of a different nature than that in  $\text{BaTiO}_3$ . It is a transition of the order of  $n>1$  and probably the tetragonal phase has no permanent polarization.

## VI. ACKNOWLEDGMENTS

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# Pulsed Magnetic Field Studies of the Negative Magnetoresistivities of Dilute Ti-Mn and Cu-Mn Alloys at Low Temperatures\*

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Measurements of the low-temperature negative magnetoresistivities of dilute Ti-Mn and Cu-Mn alloys have been extended to higher magnetic fields by means of pulsed magnetic field techniques. At  $4.2^\circ\text{K}$  the observed decreases of resistivity in a transverse magnetic field of 130 kG are approximately 5, 23, and 26% of the zero-field resistivity, respectively, for Ti-0.101 at.% Mn, Ti-1.00 at.% Mn, and Cu-1.00 at.% Mn. Saturation of the negative magnetoresistivity is essentially complete in Ti-0.101 at.% Mn below 100 kG. A trend toward saturation is strongly evident in Ti-1.00 at.% Mn and is less marked in Cu-1.00 at.% Mn. Close agreement between transverse and longitudinal magnetic field measurements is observed in all cases. The Ti-Mn data are in accord with earlier evidence which suggests that in these alloys there exist localized magnetic states which interact with the conduction electrons.

## I. INTRODUCTION

NOBLE metal rich alloys containing dilute additions of first transition group metals have been the subject of intensive study by a number of investigators.<sup>1,2</sup> Perhaps the best known example of such an alloy is Cu containing up to several percent Mn. At low temperatures an alloy of this type might exhibit several (though seldom all) of the characteristic types of electron transport property behavior listed below:

1. A minimum in the resistivity vs temperature (followed in some instances by a maximum at lower temperatures).
2. A decrease of resistivity with applied magnetic field (negative magnetoresistance).
3. A strong temperature dependence of the negative magnetoresistance. (In accord with Kohler's rule<sup>3</sup> normal positive magnetoresistivities are in general temperature independent below  $4^\circ\text{K}$ .)
4. Near equality of transverse and longitudinal negative magnetoresistivities for not too dilute compositions. (In contrast normal positive magnetoresistivities of

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<sup>1</sup> For a tabulation of resistive, magnetic, and thermal property results on fifteen different alloy systems (with references) see A. N. Gerritsen, *Physica* **25**, 489 (1959).

<sup>2</sup> For a recent review, see G. J. van den Berg, in *Proceedings of the Seventh International Conference on Low-Temperature Physics* (University of Toronto Press, Toronto, 1961), p. 246.

<sup>3</sup> J. P. Jan, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1957), Vol. 5, p. 29.