Observation of Paramagnetic Resonances in Single Crystals of Barium Titanate

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PARAMAGNETIC resonances consisting of several components have been observed at microwave frequencies in single crystals of barium titanate,[1] which contain small amounts of iron. Figure 1 illustrates the nature of the observed lines obtained at room temperature from a single crystal polarized in a direction perpendicular to the plane of the crystal, and to the direction of the dc and rf magnetic fields. Approximate g values, at 9.5 kMc/sec and room temperature, of the four observable components were 3.52, 2.72, 2.41, 1.79. Preliminary measurements indicate a variation with temperature in both the amplitudes and positions of the quartet. These approximate measurements are summarized in graph form in Fig. 2. The structure of the resonance changes radically at the Curie temperature (~120°C) indicating the occurrence of the tetragonal-cubic phase transition. Finer details of the growth and decay of the paramagnetic resonances at the region of the Curie temperature (not shown in Fig. 2) suggest that the transition of any domain in the crystal is discontinuous but that the crystal as a whole does not change structure at one temperature. Such effects may be caused by crystal imperfections or the existence of a temperature gradient over the crystal. Quantitative measurements of the resulting signals at the Curie temperature were complicated by the lossy nature of the sample at microwave frequencies.

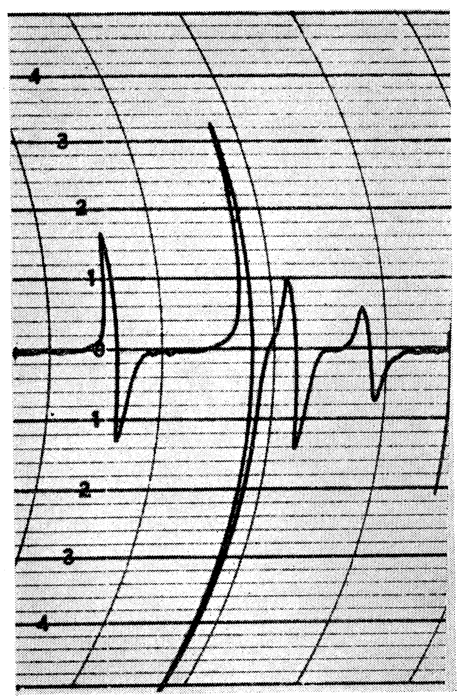

Fig. 1. The above reproduction illustrates typical signals obtained from $BaTiO_3$ crystals, in the ferroelectric state corresponding to room temperature, and polarized perpendicular to the direction of the dc magnetic field produced by the V-4007 Electromagnet and V-2200 Power Supply. The resonant frequency of the V-260 Klystron was set at 9.5 kMc/sec.

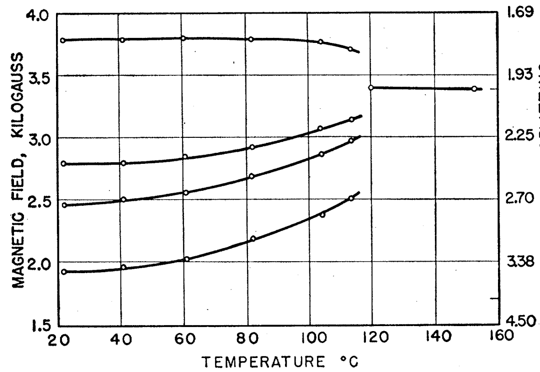

Fig. 2. Graphical representation of the change in the relative positions of the structure with temperature. A single detectable line at $g=2.0$ results from the cubic phase of barium titanate.

As the temperature is lowered below about 0°C, barium titanate crystals undergo a phase transition involving a change in direction of polarization resulting in orthorhombic symmetry. Signals observed below this transition temperature show a marked change from those obtained at room temperature. In particular, they consist of two principal lines easily resolved and located approximately symmetrically about a g value of two, and superimposed upon a background of unresolved information.

It is assumed that the small amount of iron (added to the pre-melt mixture in the form of Fe_2O_3) is acting as the source of the electron resonances, since other crystals of essentially pure $BaTiO_3$ do not yield a detectable electron resonance. The ferric ion, with a $^6S_{5/2}$ basic level, would be expected to give crystalline field splittings much smaller than those observed. It is believed therefore, that the electron resonances result from ferrous ions ($^5D_4$ basic level), probably located at the barium position in the lattice. Further experimental and theoretical work designed to identify the states involved is underway.

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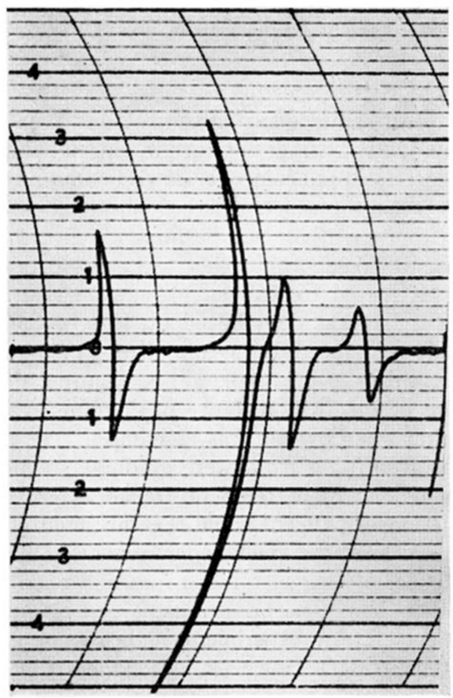
[1] Supplied through the courtesy of Dr. S. O. Morgan at Bell Telephone Laboratories, Murray Hill, New Jersey.



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