Anomalous behavior of the dielectric constant of the system $Fe_{1.6}Cr_{1.4}O_4$

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(Submitted 6 February 1985; resubmitted 23 May 1985)
Pis'ma Zh. Eksp. Teor. Fiz. **42**, No. 1, 37–39 (10 July 1985)

At $T_c = 337$ K the dielectric constant of the system $Fe_{1.6}Cr_{1.4}O_4$ behaves anomalously. This anomalous behavior of the sample is accompanied by a substantial change in its size. It is assumed that at this temperature the compound undergoes a transition to the polar state.

According to Francombe[1] and Robbins *et al.*,[2] chromium-containing ferrite with a cation distribution $Fe^{2+}_{0.4}Fe^{3+}_{0.6}[Fe^{2+}_{0.6}Cr^{3+}_{1.4}]O^{2-}_4$ in the region $T_M \simeq 200$ K undergoes a transition from the paramagnetic state to the ferromagnetic state and at $T_D \lesssim 140$ K its cubic lattice becomes tetragonally distorted, with $c/a > 1$. This struc-

0021-3640/85/130044-04$01.00

tural transition occurs as a result of a cooperative Jahn-Teller effect produced by the Fe_A^{2+} $(3d^6)$ ions which are situated in the tetrahedral sites. Mössbauer measurements[3–5] of the ferrites in the system $Fe_{3-x}Cr_xO_4$ have shown that a quadrupole splitting of the samples with $x \geqslant 1.2$ occurs even at temperatures much higher than those of the structural transitions. Since the quadrupole splitting is highly sensitive to lattice distortions, we can assume that at $T > T_D$ ferrites of this sort do not have an O_h^7 crystal structure, as does an ideal spinel cubic lattice.

Since charge ordering is one of the ways in which ionic compounds become structurally distorted (the ferroelectric transition), we became interested in determining how the dielectric constant and the linear expansion of the system $Fe_{1.6}Cr_{1.4}O_4$ depend on the temperature at $T \gg 200$ K.

A polycrystalline $Fe_{1.6}Cr_{1.4}O_4$ sample was synthesized by a method used in ceramic technology. The first annealing of the sample was carried out in a $CO_2 + H_2$ medium at 1100 °C for two hours. The final baking of it was carried out in the same medium at 1300 °C for four hours. An x-ray structural analysis and x-ray phase analysis have shown that the sample is a single-phase spinel.

The low-frequency (static) dielectric constant ϵ was measured by a digital volt-farad meter P-385. Indium-gallium paste was used to establish electrical contacts. Strain gauges were used to measure the linear expansion $\Delta l/l$ of the sample.

These studies have shown for the first time that the dielectric constant ϵ and the linear expansion $\Delta l/l$ of a $Fe_{1.6}Cr_{1.4}O_4$ sample behave anomalously in the region $T_c \simeq 337$ K and that this anomalous behavior is similar to that generally exhibited by the intrinsic ferroelectrics near the transition from the paraelectric to the ferroelectric state.[6] Figure 1 shows that near $T_c \simeq 337$ K a sharp, λ-type change occurs in the

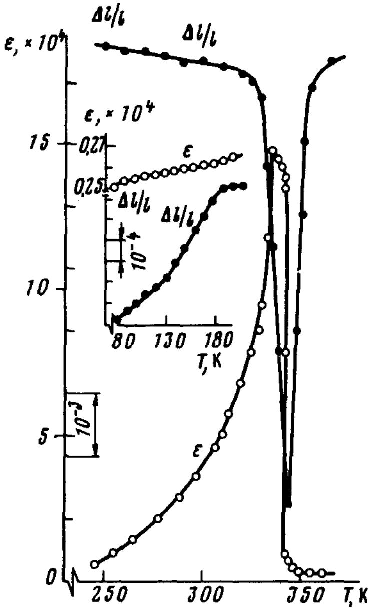

FIG. 1. The dielectric constant ϵ and linear expansion $\Delta l/l$ versus the temperature.

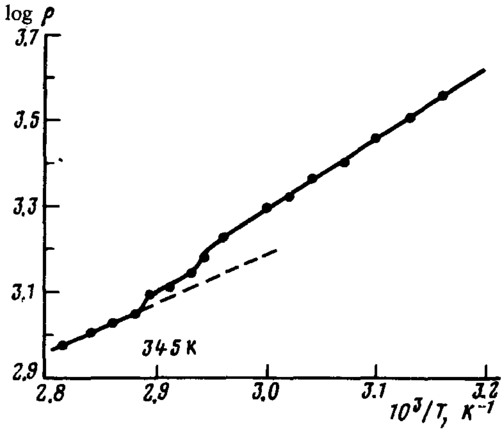

FIG. 2. The logarithm of the electrical resistivity versus the temperature.

behavior of the dielectric constant, whereas the value of ϵ changes smoothly with temperature near the structural transition (according to our data, $T_D \simeq 130$ K).

Since the activation energy E of ferroelectrics-semiconductors generally changes near the phase transition to the polar state,[7] we found it useful to study the behavior of the resistivity of the sample under consideration. Our measurements showed that this sample is a p-type semiconductor with $\rho \simeq 7 \times 10^3$ Ω·cm at $T = 293$ K. From the plot of $\log \rho$ versus the temperature ($10^3/T$) shown in Fig. 2, we find that near $T_c \simeq 337$ K the activation energy changes by the amount $\Delta E \simeq 0.08$ eV. Accordingly, this result is further evidence in favor of our assumption that $Fe_{1.6}Cr_{1.4}O_4$ undergoes a transition to the polar state at $T_c \simeq 337$ K. It is not possible, however, to determine whether the sample under study is a ferroelectric or antiferroelectric at $T \lesssim 337$ K, since the resistance of this material is low near this phase transition, making it impossible to apply a large enough static electric field in order to measure the temperature dependence $\epsilon(T)$ and the electric-polarization hysteresis loop $P(E)$.

In studying the diffraction and optical spectra of chromium-containing spinels $MgCr_{2-x}Al_2O_4$, Grimes and Collet[8] and Ford and Hill[9] have found that in samples with a large concentration of Cr^{3+} ions the octahedral complexes are tetragonally distorted, i.e., they have a local symmetry C_{3v}. The Cr^{3+} ions, which are displaced in this case from the centers of the octahedra, have three identical short bonds and three identical long bonds with the neighboring oxygen ions. A crystal symmetry of this sort is consistent with the presence of charge ordering in ionic compounds. It is quite conceivable that the anomalous behavior of the dielectric constant ϵ of the $Fe_{1.6}Cr_{1.4}O_4$ sample is caused by the displacement of Cr^{3+} ions from the centers of the octahedral complexes.

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Translated by S. J. Amoretty