Thermally excited electric-dipole glass in crystals with Jahn-Teller ions

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A cooperative effect—a change in the polarization properties—has been observed in the $EuCrO_3$ crystal upon the thermal excitation of the Jahn-Teller state of Eu^{3+} ions ($^7F_1$). As the temperature is raised, and the density of excited ions reaches a sufficiently high value, a thermally excited state of an electric-dipole glass arises.

Rare-earth ions in crystals generally have low-lying excited states whose populations can change substantially with the crystal temperature. The properties of the ions in their ground and excited states are generally different. In the case of Jahn-Teller ions, for which the electronic state of the ion is typically closely associated with a local distortion of the lattice, we can expect changes in the polarization properties of the crystal with changing temperature. Compounds with Eu^{3+} ions are interesting in this connection. The ground state of the Eu^{3+} ions is nondegenerate ($^7F_0$), while the lower excited state is a degenerate Jahn-Teller state ($^7F_1$). The $^7F_0$–$^7F_1$ splitting is ~ 300 cm^{-1}, so that changes in the dielectric properties due to changes in the population of the $^7F_1$ level should be observed in an accessible temperature interval. The striking difference between the properties of the ions in the $^7F_0$ and $^7F_1$ states suggests that we should expect large changes in the dielectric properties. In a previous study[1] of $EuCrO_3$ with intense optical pumping, we observed a phase transition at low temperatures: Eu^{3+} ions which are nonmagnetic ($I = 0$) before the pumping become magnetic ($I = 1$) and antiferromagnetically ordered.

In the present letter we report experiments on the dielectric properties of $EuCrO_3$. The measurements were carried out at low frequencies, 30 Hz–20 kHz, and over the temperature range 100–500 K. Near room temperature we observed a sharp increase in the dielectric constant ϵ', accompanied by a maximum in ϵ''. We observed a low-frequency dispersion in the dielectric properties. At low temperatures, ϵ' is essentially independent of the temperature ($\epsilon' \simeq 20$). From Fig. 1 we see that ϵ' and ϵ'' begin to increase with the temperature at $T = 200$ K. The value of ϵ'' goes through a maximum at the temperature where ϵ' changes most rapidly. The temperature of the rapid increase in ϵ' and of the maximum in ϵ'' depends on the frequency: The lower the frequency, the lower the temperature at which the anomalies in ϵ are observed. Figure 2 shows plots of $\ln \epsilon'(T^{-1})$ and $\ln \epsilon''(T^{-1})$ for two frequencies. On the $\ln \epsilon'(T^{-1})$ curves for all frequencies we see two linear regions. In the first, at relatively low temperatures, there is an activation barrier of 317 cm^{-1} at all frequencies, in accordance with the size of the gap before the $^7F_1$ excited level of the Eu^{3+} ion. At $T \simeq T_1$, the slope of the $\ln \epsilon'(T^{-1})$ curve changes sharply. The activation barrier becomes $\sim 10^4$ K and is again approximately the same at all frequencies. The value of the temperature T_1, on the other hand, depends on the frequency. The $\ln \epsilon'(T^{-1})$ curve retains this slope up to a

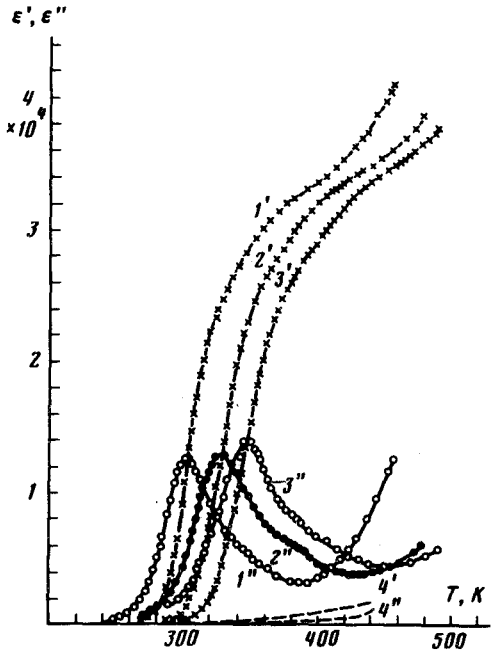

FIG. 1. Temperature dependence of the dielectric constant ϵ' (curves 1', 2', 3') and of ϵ'' (curves 1'', 2'', 3'') at frequencies of 70 Hz, 370 Hz, and 1 kHz, respectively. Curves 4' and 4'' show corresponding results for $YCrO_3$ at 370 Hz.

temperature $T \simeq T_2$, whose value also depends on the frequency. The interval between these two temperatures is T_1-$T_2 \sim 40$–50 K. At $T > T_2$, $\epsilon'(T)$ slows down considerably (Fig. 1), although ϵ' does not reach saturation. The value of ϵ' reaches 4×10^4 at $\tan\delta \sim 5 \times 10^{-2}$. The maximum in ϵ'' in Fig. 1 corresponds to the position $T \simeq T_2$: the end of the sharp increase in $\ln \epsilon'(T^{-1})$. At $T \simeq T_1$, there is no change of any sort in the slope of the $\ln \epsilon''(T^{-1})$ curve. If the increase in ϵ' were due to the conductivity, we would have observed a correlation between the anomalies in $\ln \epsilon'(T^{-1})$ and $\ln \epsilon''(T^{-1})$ at $T \simeq T_1$. As the temperature is increased to $T > T_2$, the losses ϵ'' initially decrease; later, beginning at $T \sim 450$ K, there is a repeated increase in ϵ'', which we attribute to an increase in impurity conductivity. In this temperature interval there is an increase in the dc conductivity of $EuCrO_3$, and the conductivity in $YCrO_3$ is observed to increase. As the temperature is lowered, the state with the larger ϵ' decays. We observe a temperature hysteresis ~ 10 K.

All these facts suggest that the observed effects are of a cooperative nature. These effects can be explained qualitatively as follows.

The $EuCrO_3$ crystal has the structure of an orthorhombically distorted perovskite. The Eu^{3+} ions occupy noncentral positions: C_s. During thermal excitation of the Eu^{3+} ions to the $^7F_1$ state and during the splitting of this state, there is a local distortion of the neighborhood of the Eu^{3+} ($^7F_1$) ion. This distortion is an additional distortion in comparison with the situation at $I = 0$. It apparently leads to a significant

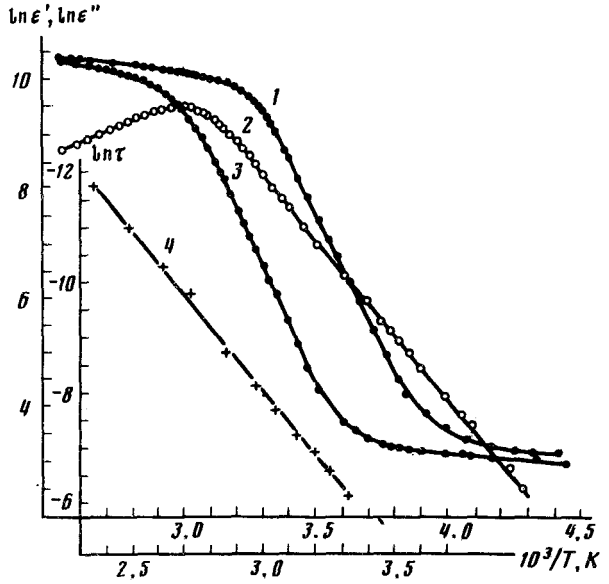

FIG. 2. Temperature dependence of ln ϵ' at frequencies of 70 Hz (1) and 560 Hz (3), of ln ϵ'' at 560 Hz (2), and of ln τ (4).

increase in the electric dipolarity. At a low concentration of thermally excited Eu^{3+} ions (i.e., the electric dipoles), before these ions begin interacting with each other, the value of ϵ' is proportional to the population of the $^7F_1$ level. With increasing temperature and thus with increasing concentration of excited Eu^{3+} ions ($^7F_1$), an interaction sets in between the electric dipoles. At $T \simeq T_1$, where the concentration of electric dipoles reaches ~20–25%, the conditions apparently favor the appearance of clusters of interacting dipoles. The energy decrease caused by the interaction of the dipoles in the clusters makes them metastable. The region of a linear increase in ln $\epsilon'(T^{-1})$ in the interval T_1–T_2 with the barrier $\sim 10^4$ K corresponds to an increase in the concentration of thermally activated metastable clusters. At $T \simeq T_2$, a correlated electric-dipole state is established in a macroscopic part of the crystal (percolation). The height of the thermal-activation barrier of the clusters, $\sim 10^4$ K, and the independence of the barrier from the observation frequency apparently imply that the processes accompanying the clustering are analogous to those which occur in displacive ferroelectric transitions.[2] Because of the interaction between dipoles during the formation of clusters, the displacements of the Eu^{3+} ($^7F_1$) ions are coordinated. The height of the barrier reflects the change in the local field of the dipole and does not depend on the number of dipoles in the cluster (the barrier does not depend on the frequency). The short-range part of the electric-dipole interaction is clearly important for this mechanism for cluster formation. During thermal population of states there is an unavoidable spread in the number of nearest neighbors of excited ions. The short-range interaction between dipoles may vary in magnitude and sign, leading to different relative orientations of the dipoles: ferroelectric and antiferroelectric. The situation is similar to that characteristic of a spin glass. The temperature and frequency dependences observed by us for

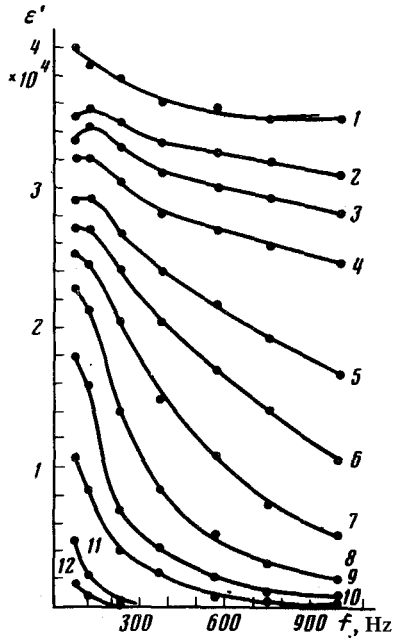

FIG. 3. Frequency dependence of ϵ' at several temperatures: 1—450 K; 2—400 K, 3—380 K, 4—370 K, 5—350 K, 6—340 K, 7—330 K, 8—320 K, 9—310 K, 10—300 K, 11—290 K, 12—280 K.

the dielectric constant are similar to those for the magnetic susceptibility of spin glasses.[3] In our case, however, we are dealing with an excited electric-dipole glass. As in the case of spin glasses, we observe a broad set of relaxation times τ. We see from Fig. 3 that in the temperature interval T_1–T_2 the $\epsilon'(f)$ dependence is sharp, while at $T > T_2$ it is a quasi-Debye dependence. We were not able to describe it with a single value of τ. Calculations of τ from the condition that the maximum of ϵ'' corresponds to $\omega\tau = 1$ yield $\tau \sim 10^{-2}$–10^{-5} s. Curve 4 in Fig. 2 shows a curve of $\ln \tau(T^{-1})$, illustrating the thermal-activation nature of τ with a barrier $\sim 6 \times 10^3$ K. The saturation of $\epsilon'(f)$ at low frequencies at $T > T_2$ (Fig. 3) shows the values $\tau \gg 10^{-2}$ s also prevail in the system.

In summary, during thermal excitation of the Jahn-Teller state of Eu^{3+} ($^7F_1$) ions in $EuCrO_3$ the concentration of Jahn-Teller ions becomes sufficiently high at a certain temperature to give rise to a thermally excited state of an electric-dipole glass.

[1]E. I. Golovenchits, V. A. Sanina, and T. A. Shaplygina, Zh. Eksp. Teor. Fiz. **80**, 1911 (1981) [Sov. Phys. JETP **53**, 992 (1981)].
[2]B. A. Strukov and A. P. Levanyuk, Fizicheskie osnovy segnetoélektricheskikh yavleniĭ v kristallakh (Basic Physics of Ferroelectric Phenomena in Crystals), Nauka, Moscow, 1982, p. 163.
[3]J. A. Mydosh, J. Phys. Soc. Jpn. **52**, 585 (1983); L. Lundgren, P. Svedlindh, and O. Beekman, J. Magn. Mater. **25**, 33 (1981); J. Phys. F **22**, 2663 (1982).

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