Percolation-type phase transitions in lead zinconiobate crystals in an electric field

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(Submitted 22 October 1992)
Pis'ma Zh. Eksp. Teor. Fiz. **56**, No. 10, 532–535 (25 November 1992)

With the help of the small-angle light scattering method, the appearance of a percolation-type phase transition in an electric field has been detected for the first time in the strongly disordered ferroelectric lead zinconiobate. In fields above a critical value, the behavior of anomalous light scattering was found to be in agreement with the conclusions of the phenomenological Andelman–Joanny theory.

At present, the problem of phase transitions in disordered solids remains, as before, at the center of attention. A characteristic feature of a number of segnetoelectrics of complex composition and ferroelectric solid solutions is, as is well known, the presence of a smeared out anomaly in the dielectric constant $\epsilon(T,\omega)$ and the thermal expansion over a wide temperature interval, which has served as a basis for the formation of theories about "smearing" of phase transitions in such compounds.[1] On the other hand, the detection of anomalies in the frequency dispersion of $\epsilon(T,\omega)$ with huge relaxation times of the polarization,[2] and also anomalies in the temperature dependence of the nonlinear susceptibility $\partial^2\epsilon/\partial E^2$ for $T \lesssim T_g$ has provided a basis for drawing a qualitative analogy with the "sudden" transition to a state of spin-glass type. Here T_g is treated as the corresponding freezing temperature.[3]

The indicated measurements of the dielectric constant, however, describe volume-averaged properties of the sample, while the phase transition in a real disordered crystal should inevitably be accompanied by a spatially nonuniform rearrangement of its structure. In particular, it is well known that in a number of models of strongly disordered media there exist critical values of the external fields $E_c(T)$ at which there is a departure from the "many-valleyed' metastable states to the equilibrium regime. Thus, in the model of the Ising ferromagnet with random Sherrington–Kirkpatrick exchange[4] a similar role is played by the Almeida–Thauless line,[5] in a disordered Heisenberg ferromagnet it is played by the Gabay–Toulous line,[6] and in an Ising ferromagnet with random internal field, the Andelman–Joanny line.[7] Near all these lines the corresponding correlation lengths diverge.

Earlier, using arguments for the sudden growth of the dimensions of the clusters of new phase near percolation-type phase transition points, we observed peaks in the temperature dependence of the intensity of small-angle light scattering (SALS) in disordered ferroelectric materials of the type $PbB'_{1/2}B''_{1/2}O_3$ (Refs. 8 and 9). At the same time, in compounds of the type $PbB''_{1/3}B''_{2/3;}O_3$ in the absence of an electric field such peaks were not observed. Taking into account what has been said above about the presence in many disordered systems of critical values $E_c(T)$ at which there takes place a sudden increase in the correlation length, we have attempted to determine the

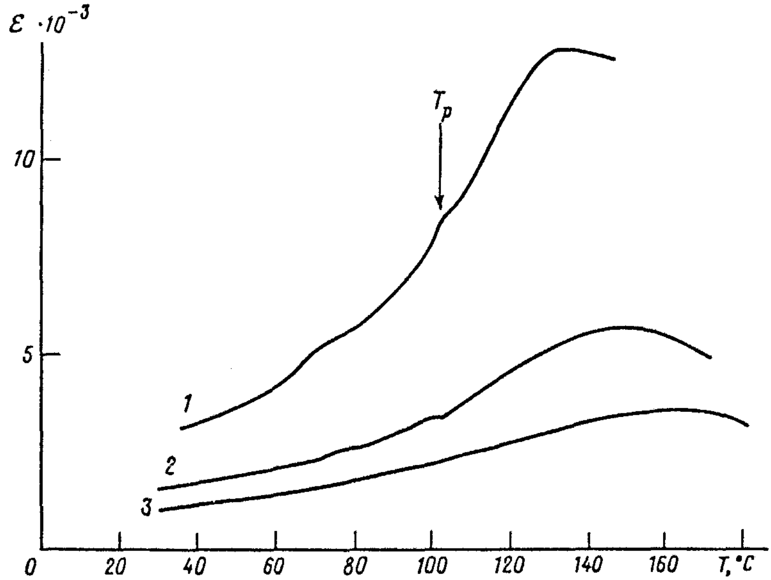

FIG. 1. Temperature dependence of the dielectric constant for a crystal of lead zinconiobate, taken during heating in different electric fields: 1) 0, 2) 4, 3) 8 kV/cm. The crystal was first cooled in a field of 10 kV/cm.

existence of a critical electric field for the strongly disordered ferroelectric $PbZn_{1/3}Nb_{2/3}O_3$ (PZN) with the help of the SALS method.

The crystals of PZN which were used in the present work had a temperature maximum of ϵ, $T_m = 135$ °C. At the temperature $T_p \simeq 103$ °C in the disordered samples we observed a small anomaly of ϵ and a jump in the optical transmission.[10] Similar anomalies of ϵ occur in crystals of lead magnesio-niobate $PbMg_{1/3}Nb_{2/3}O_3$. These anomalies are usually treated as an example of destruction of the macrodomain ferroelectric state.[11,12]

In order to study the nature of the spatial rearrangement of the structure of the PZN crystal, which accounts for the above-indicated anomalies, we measured SALS and the dielectric constant for two different regimes of application of the external constant electric field: 1) cooling in zero electric field and heating in a field, and 2) cooling in a field and heating in a field. The experimental setup is described in Ref. 8.

In the case in which the electric field is applied according to the first regime, no intensity peaks were observed in the SALS temperature dependence. This indicates that due to the presence of strong random fields, which occur as a result of incomplete ordering of the Zn^{+2} and Nb^{+5} ions, no macrodomain ferroelectric state arises in the crystal. The picture changes qualitatively for the second regime, when a sufficiently strong electric field is applied. If the crystal is cooled in fields up to 20 kV/cm, then, as in the first case, no peaks are observed in the SALS temperature dependence measured during the heating of the crystal in fields lower than 20 kV/cm. In the temperature dependence of $\epsilon(T,\omega)$ all that can be seen is a small anomaly at T_p

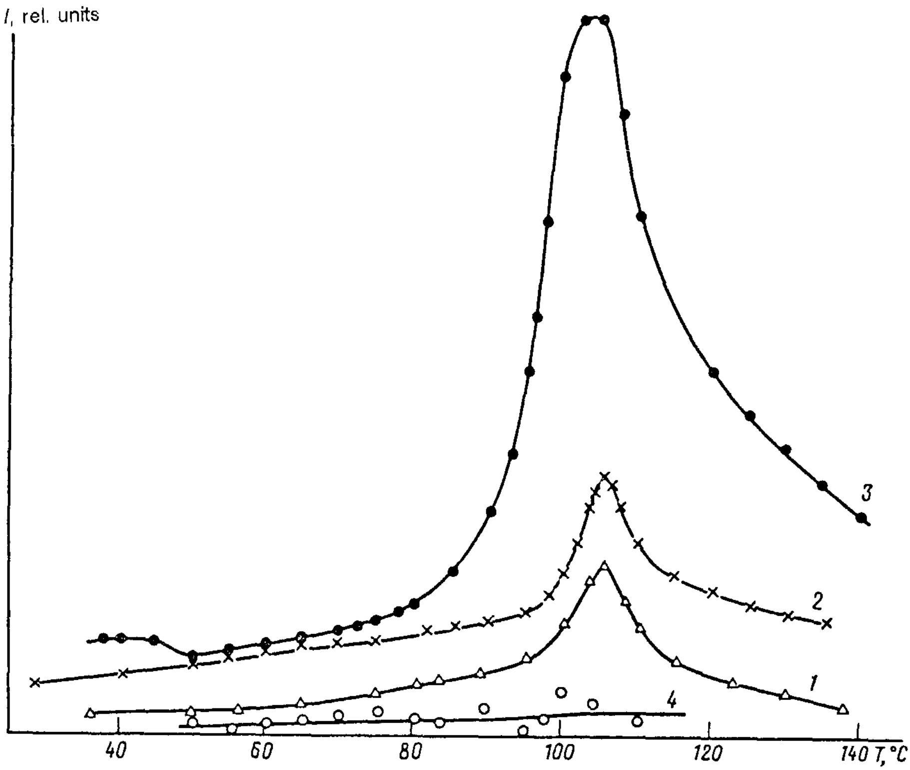

FIG. 2. Temperature dependence of the intensity of small-angle light scattering at an observation angle of 30′ in PZN crystals in different electric fields, *E*, kV/cm. The crystal was first cooled in a field of 20 kV/cm. Curves: *1*—0, *2*—2, *3*—10 kV/cm. Curve *4*—0 kV/cm, with the crystal first cooled in a field of 15 kV/cm.

$\simeq$103 °C (Fig. 1). The absence of a peak in the SALS intensity indicates that the dimensions of the regions of the ferroelectric phase formed in the field are insufficient for the creation of an "infinite" macrodomain cluster. When the crystal is cooled in fields $E \gtrsim 20$ kV/cm, sharp peaks are observed in the temperature dependence of SALS measured during the heating (Fig. 2). As can be seen in Fig. 2, with an increase in the intensity of the electric field applied to the sample during heating, the intensity of SALS at the maximum increase. Correspondingly, a field of 20 kV/cm is apparently the critical field for PZN crystals. For $E \geqslant E_c$ the dimensions of the domains suddenly increase. The homogeneous macrodomain ferroelectric state appears, and destruction of this state upon heating of the sample takes place in the manner of a percolative phase transition with the formation of an "infinite" cluster. In connection with this circumstance, we note that the nature of the high-temperature nonpolar phase requires additional study.

As the electric field approaches its critical value E_c, the correlation scale of the stochastic domain structure increases abruptly and, correspondingly, the SALS intensity is observed to increase (Fig. 2, curves 1–3).

The SALS measurements in crystals of lead zinconiobate which we have carried out indicate the presence of a critical value of the external electric field, starting at which there appears a clearly defined peak in the light scattering intensity. Its presence points unambiguously to the appearance of large-scale inhomogeneous states in the process of polarization of a strongly disordered crystal of PZN. Here the maximum characteristic scale of the emerging superstructure is at least several tens of microns, which makes it possible to use scaling concepts. Consequently, there is a basis for asserting that the phenomenological Andelman–Joanny theory, developed for the Ising model with a random internal field, can be used in a qualitative description of the process of polarization of the strongly disordered ferroelectric PZN in near-critical electric fields.

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Translated by P. F. Schippnick