Anomalous small-angle scattering of light in ferroelectrics with diffuse phase transition

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An anomalous small-angle scattering of light has been observed in crystals of $PbSc_{1/2}Ta_{1/2}O_3$ (PST), which undergo diffuse phase transitions. The experimental data are consistent with the assertion that a diffuse phase transition in disordered PST crystals is accompanied by a percolation phase transition.

Much experimental information has now been accumulated on the unusual ferroelectric properties of several ferroelectric perovskite crystals of the type $AB'B''O_3$ near the average Curie temperature.[1] Despite this information, whether a "genuine" phase transition occurs in these compounds remains an open question, as does the value of the temperature at which it may occur. Furthermore, although it is a solidly established fact that structural defects of a crystal influence the extent to which the transition is diffuse, it is not clear to what extent the processes of evolution from a paraelectric state to a polar state are similar in ferroelectric crystals with diffuse phase transitions with different degrees of structural disorder.

Since there are cations of two types, B′ and B″, in these crystals, there is the possibility of an ordering or disordering of ions in octahedral lattice positions. In the case of a complete ordering, the B′ and B″ cations alternate regularly in neighboring octahedra. The degree of order (long-range order) in the distribution of ions is usually monitored by x-ray diffraction, since the ordering leads to a doubling of the lattice period and to the appearance of a superstructure. The intensities of the superstructural lines reach a maximum in the case of ideal order and decrease with a decrease in the degree of long-range order.

We have suggested that the percolation theory could be used to describe these processes. One consequence of our model is the prediction that peaks will appear in the temperature dependence of the integral intensity of small-angle scattering. In the present letter we are reporting experimental data on an anomalous scattering of light which has been seen for the first time in PST crystals with different degrees of ordering of Sc^{3+} and Ta^{5+} ions in octahedral positions of the crystal lattice.

The presence of a high-temperature phase transition ($T_t = 1470\,^\circ C$) of the order-disorder type in PST crystals makes it possible to vary the degree of order of these ions either by heat treatment or by varying the temperature at which single crystals are grown. It thus becomes possible to alter the extent to which the ferroelectric phase transition is diffuse at temperatures near room temperature.[2] In selecting a crystal for studying the problem of difuse phase transitions, we decided on PST precisely because of this possibility of following the effect of the ordering of ions on small-angle scattering by monitoring the degree of ordering, s, by x-ray diffraction.

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Let us briefly review the arguments which lead to the conclusion that an anomalous small-angle scattering will occur. We know that, depending on the degree of ordering of the ions, the dielectric constant of this crystal will reach a maximum at a temperature between $-5\,^{\circ}\mathrm{C}$ and $+45\,^{\circ}\mathrm{C}$ (Refs. 1–3). It is thus natural to suggest that spatial fluctuations in $c(\mathbf{r})$, the concentration of disordered positions of these ions, will lead to fluctuations in the temperature $T_C(\mathbf{r})$ of the local phase transition to the ferroelectric state. In the case of a slight disorder, we might expect that the distribution function $\Phi(T_C)$ would have a maximum at a temperature close to the Curie temperature $T^0{}_C$ of the transition to the orthorhombic phase for a completely ordered $(s=1)$ PST crystal. Denoting the correlation length of the field $T_C(\mathbf{r})$ by R_0, and assuming that the function $\Phi(T_C)$ does not change qualitatively when the interaction of polar clusters through long-range elastic and electric forces is taken into account, we find the following expression for the average cluster size R as a function of the relative size of the nucleating phase, $x(T)$, according to continuum percolation theory[4]:

$$R = R_0 \left| \frac{x - x_c}{x_c} \right|^{-\nu_p}, \qquad (1)$$

where x_c is the critical value of the relative size of the new phase, which corresponds to the percolation threshold, and ν_p is the index of the percolation theory for the correlation length. The integral intensity of the light scattered by a heterophase crystal near the percolation threshold is (under the condition $qR \ll 1$)

$$I(q) = VQ_s \sum_{i=1}^{3} \{ D_{11}(t_i^l t_i^s)^2 + \sum_{k \neq i} [D_{12} t_i^l t_i^s t_k^l t_k^s + D_{44}(t_i^l t_k^s)^2] \}, \qquad (2)$$

where $\mathbf{t}^l$ and $\mathbf{t}^s$ are the polarization vectors of the incident and scattered light, and the tensor functions $D_{ik}(\mathbf{q})$ are expressed in terms of the components of the Fourier transform of the correlation functions of the dielectric tensor; e.g., $D_{11}(\mathbf{q}) = \langle |\Delta\varepsilon_{xx}(\mathbf{q})|^2 \rangle$. If we assume that polar clusters are single-domain regions of an orthorhombic phase, then all the functions $D_{ik}(\mathbf{q})$ are proportional to the Fourier transform of the Green's function $K(\mathbf{q})$ of percolation theory[5]:

$$D_{11}(\mathbf{q}) = D_{12}(\mathbf{q}) = [{}^1/_3(a_{11} + 2a_{12})P_0^2]^2 K(\mathbf{q}), \qquad D_{44}(\mathbf{q}) = (\frac{1}{3} a_{44} P_0^2)^2 K(\mathbf{q})$$

$$K(\mathbf{q}) = \frac{4\pi R_0}{3(q^2 + R_p^{-2})}, \qquad (3)$$

where $\Delta\varepsilon_{ik} = a_{ikmn} P_m P_n$, and P_0 is the discontinuity in the polarization in a cluster. It can be seen from (3) that for small scattering angles $(qR < 1)$ the intensity has the behavior $I(\mathbf{q}) \sim R_p^2$, and it has a sharp peak near the percolation threshold. At high degrees of disorder of the Sc^{3+} and Ta^{5+} ions, the distribution function $\Phi(T_c)$ may be qualitatively different from that in the case of a slight disorder. In particular, this is the case if the field $c(\mathbf{r})$ has several most probable values. Correspondingly, peaks can appear in the intensity of the small-angle scattering of light at several temperatures.

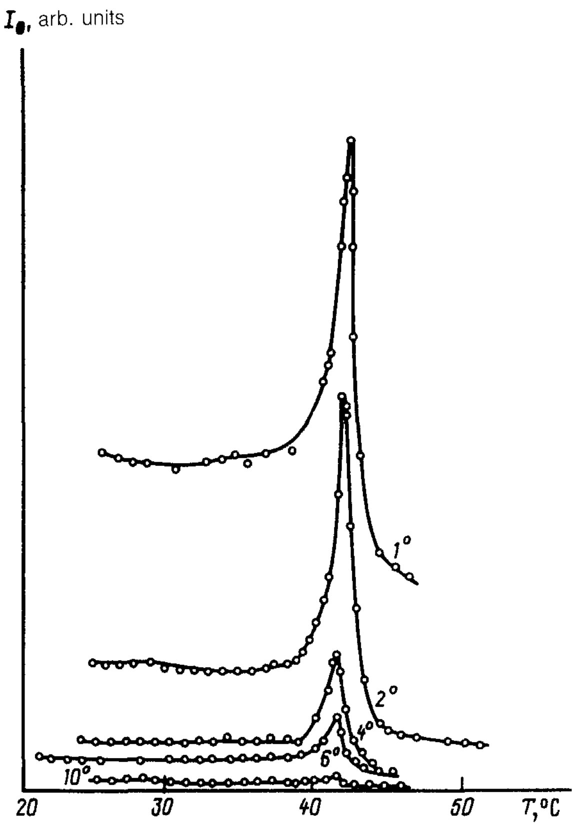

FIG. 1. Relative intensity of the light scattered into a solid angle $\Delta\Omega = 2\times 10^{-5}$ sr versus the temperature in a $PbSc_{1/2}Ta_{1/2}O_3$ crystal with $s = 0.95$, for various observation angles.

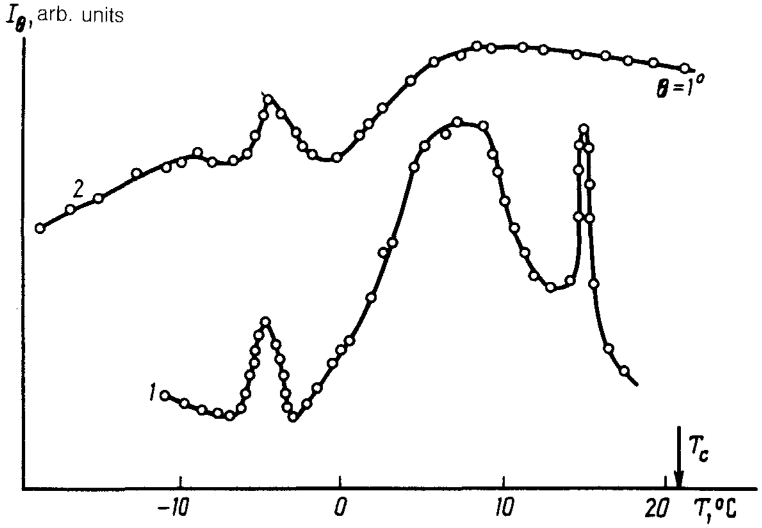

FIG. 2. Relative intensity of the light scattered into a solid angle $\Delta\Omega = 2\times 10^{-5}$ cr versus the temperature in a $PbSc_{1/2}Ta_{1/2}O_3$ crystal with $s = 0.7$, for an observation angle of 1°. 1—Crossed Nicol prisms; 1—parallel Nicol prisms.

Furthermore, pronounced fluctuations in $c(\mathbf{r})$ can cause local phase transitions to something other than the rhombohedral phase.

To test these theoretical arguments, we used small-angle scattering of light in crystals with various degrees of disorder of the Sc and Ta ions: $s = 0.95$, $T_C = 43$ °C, and $s = 0.7$, $T_C = 21$ °C. The light source was an LG-126 He–Ne laser. The test sample and the photodetector were mounted on a GS-5 goniometer. The temperature dependence of the intensity of the scattered light was measured by a U2-8 tuned amplifier for various photodetector observation angles, at a spatially constant angular aperture. Figure 1 shows the relative intensity of the scattered light as a function of the temperature for various observation angles in a PST crystal with $s = 0.95$. We see that at a temperature T^+, which lies ~ 1.5–2 °C below the temperature at which $\varepsilon(T)$ reaches its maximum, there is an anomalous peak in the scattered light, with a width ~ 1 °C. With increasing scattering angle, the peak becomes rounded, and at an angle $\sim 10^\circ$ it degenerates into a step. The temperature T^+ corresponds to the percolation threshold of the polar phase, near which there is an intense merging of polar region, and an "infinite" cluster forms.

In PST crystals with a greater disorder ($s = 0.7$) the temperature dependence of the intensity of the scattered light is considerably more complex. Several peaks are observed in the small-angle scattering (curve 1 in Fig. 2). These peaks are apparently a consequence of the presence of macroscopic regions with different values of the parameter s in a given sample; the percolation phase transition occurs at different temperatures in these different regions. Our results agree with data on the temperature dependence of the pyrocurrent,[6] on which there are several anomalies for high disordered PST crystals. Measurements of the polarization characteristics have shown that in samples with $s = 0.95$ the anomalous scattering peak is essentially identical in the cases of parallel and crossed Nicol prisms. In samples with $s = 0.7$, on the other hand, a high-temperature peak is observed only in the case of crossed Nicol prisms, in contrast with the low-temperature peak (curve 2 in Fig. 2). One possible reason for this difference might be a complex polydomain structure of clusters. Another possibility is that at large values of s, there might be a local phase transition to something other than the rhombohedral phase (to a tetragonal phase, for example[7]).

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[1] N. Setter and I. E. Gross, J. Appl. Phys. **51**, 4356 (1980).
[2] P. Groves, Ferroelectrics **76**, 81 (1987).
[3] L. S. Kamzina *et al.*, Pis'ma Zh. Tekh. Fiz. **14**, 1760 (1988) [Sov. Tech. Phys. Lett. **14**, 764 (1988)].
[4] B. I. Shklovskiĭ and A. L. Efros, Usp. Fiz. Nauk **117**, 401 (1975) [Sov. Phys. Usp. **18**, 845 (1975)].
[5] A. L. Korzhenevskiĭ, Fiz. Tverd. Tela (Leningrad) **29**, 2754 (1987) [Sov. Phys. Solid State **29**, 1583 (1987)].
[6] C. A. Randall and A. S. Bhalla, Ferroelectrics Lett. **9**, 47 (1988).
[7] Yu-Jin Chang and Zhi-Li Chen, Ferroelectrics Lett. **4**, 13 (1985).

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