The effect of dislocations on the phase transition and scattering of light near the phase transition in a NH_4Br crystal

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An anomalous, small-angle scattering of light as a result of the phase transition in a NH_4Br crystal was observed. It is shown that this anomaly is caused by a diffraction of light by the inclusions of the new phase, which are produced near the dislocations.

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An anomalous scattering of light (ASL) in a phase transition (PT) has been observed in many crystals. According to current views, ASL occurs in static microinhomogeneities produced near the PT. A theoretical analysis shows that the microinhomogeneities can occur near the defects which play the role of "condensation" centers of the new phase.[1-3] An indirect confirmation of this hypothesis is a decrease of the ASL after annealing of the crystal.[4] A separation of a new phase near the dislocations was observed in a Ni_4Mo alloy by using an electron microscope.[5] It was shown in Refs. 6 and 7 that the ASL in the $\alpha \rightarrow \beta$ PT in quartz is caused by the appearance of microinhomogeneities in the form of columns $\sim 30\ \mu m$ in diameter, which produce a characteristic picture of the diffraction. The nature of the microinhomogeneities and the reason for their appearance, however, remained unexplained.

In this paper we observed for the first time a small-angle ASL in the $\beta \rightarrow \gamma$ PT in NH_4Br crystals and showed that it is attributable to the inclusions of a new phase that are produced near the dislocations.

At $T_c = 235$ K a first-order $\beta \rightarrow \gamma$ PT, which is close to the second-order PT (temperature hysteresis $\approx 0.05 \pm 0.03$ K[8]) occurs in a NH_4Br crystal. The high-temperature β phase is characterized by an orientational disordering of the NH_4^+ ions, has a O_h^1 symmetry, and is optically isotropic. In the γ phase there is an antiparallel ordering of ions, and the crystal becomes uniaxial, optically negative and acquires a

D_{4h}^{7} symmetry. The optical axis may appear along any one of the three C_4 symmetry axes of the β phase. If, however, the temperature gradient in the sample is produced along the C_4 axis, then the optical axis in the γ phase will be oriented in this direction, which we shall denoted as [0,0,1].

NH_4Br single crystals of good optical quality were grown from a solution in a mixture of water and formamide by using the evaporative method at room temperature. It is crucial that the samples were not mechanically processed. The crystals were thermostatically controlled with an accuracy of ± 0.003 K. The cryostat design made it possible to produce both a small (~ 0.1 K/mm) and a large (~ 1 K/mm) temperature gradient in the sample. The polarized spectra of the Raman scattering of light (RSL) and the microstructure of the sample were investigated simultaneously with the small-angle scattering.

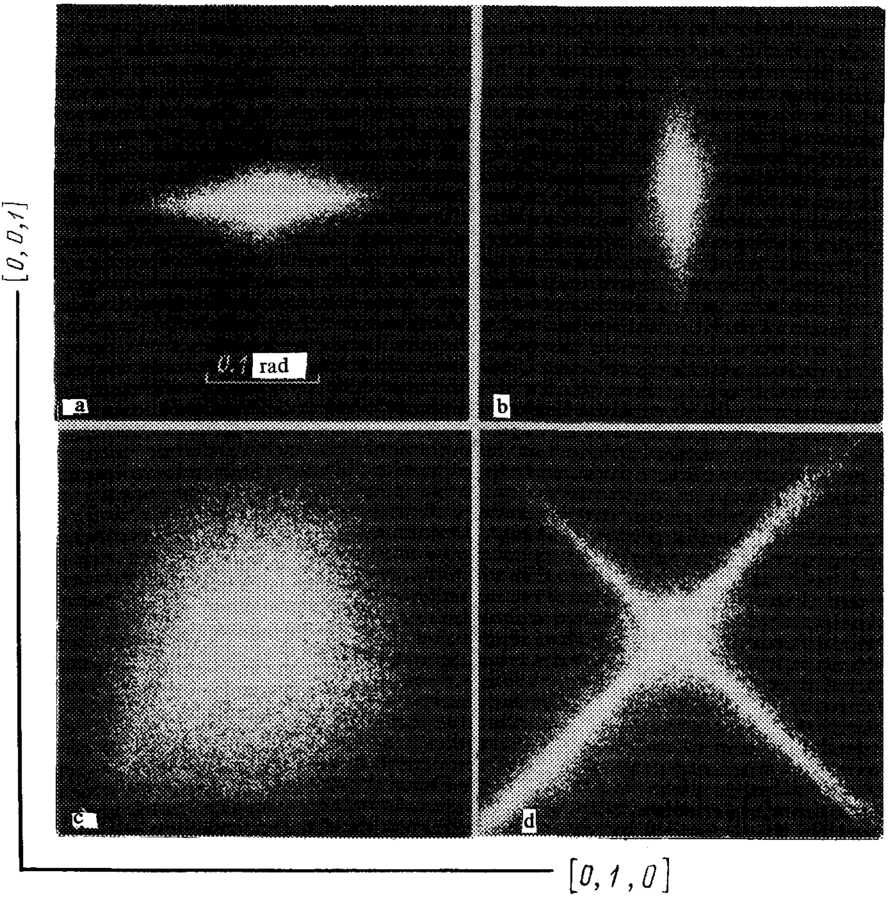

FIG. 1. Diffraction of light ($\lambda = 514.5$ nm) by microinhomogeneities produced in a NH_4Br crystal. The temperature gradient is ~ 0.1 K/mm. The polarization of light: a, E‖[0,1,0]; b, c, and d, E‖[0,0,1]. a and b, β phase, $T - T_c \approx 0.3$ K; c, PT, $T \approx T_c$; d, γ phase, $T - T_c = -50$ K.

It was observed that as a result of approaching the PT to the γ-phase ($T - T_c \approx 0.5$–0.3 K) the cross section of the laser beam that was transmitted through the sample was expanded into a band with angular dimensions of ~ 0.15 rad. At $\mathbf{k}\parallel[1,0,0]$ the band is oriented along [0,1,0] for $\mathbf{E}\parallel[0,1,0]$ and along [0,0,1] for $\mathbf{E}\parallel[0,0,1]$ (Figs 1a and 1b), where **k** and **E** are the wave vector and polarization of the incident light. For the intermediate polarization, we observed a cross, which is an overlapping of the bands. We observed the same pattern for the propagation of light along the temperature gradient ($\mathbf{k}\parallel[0,0,1]$). In the PT the cross section of the laser beam was smeared out (Fig. 1c) and in the γ phase it was transformed into a cross with the rays along $[0, \pm 1, 1]$ (Fig. 1d). This pattern, which can be observed only for $\mathbf{k}\perp[0,0,1]$, is almost independent of the polarization of light and remains to $T \approx 80$ K. The γ phase and the direction of the optical axis produced in it were controlled according to the spectra of the RSL. Investigations using a polarizing microscope showed that the γ phase produces a "domain" structure oriented along $[0, \pm 1, \pm 1]$, which is responsible for the observed pattern of small-angle scattering. We shall not discuss in this paper, however, the optical properties and the microstructure of the γ phase.

A photograph of the microstructure of the β phase produced near the PT to the γ phase, which leads to a ASL, is shown in Fig. 2. The produced microinhomogeneities, which are stretched almost along [1,0,0], [0,1,0], and [0,0,1], form a nonperiodic, three-dimensional lattice. Observation without an analyzer reveals only inhomogeneities oriented perpendicularly to the polarization of the incident beam. They are invisible in a light polarized along the microinhomogeneities. This means that the refractive index of light polarized along the inhomogeneity coincides with the refractive index of the β phase and the refractive index of the light polarized perpendicularly to the inhomogeneity differs from it. The observed microstructure of the β phase accounts for the pre-transition picture of the ASL.

It was shown in Ref. 9 that even small mechanical stresses in NH_4Cl crystals, which are similar in the physical properties to NH_4Br, produce bands in the crossed

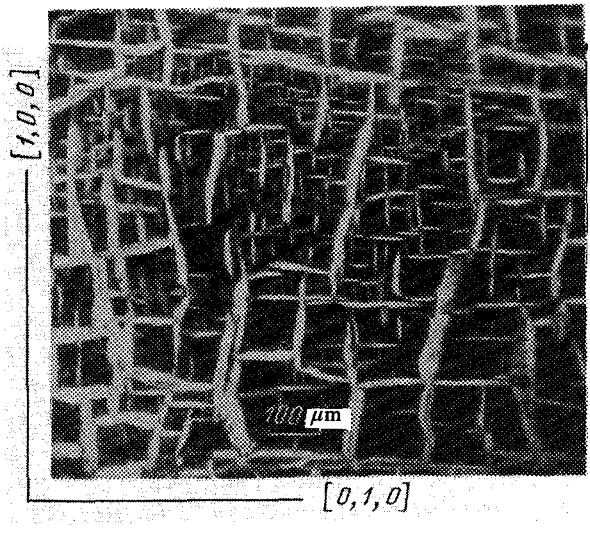

FIG. 2. The microstructure of the β phase of NH_4Br produced near the PT into the γ phase. Observation along the temperature gradient (~ 0.1 K/mm). The polarization of the incident and analyzed light is orthogonal and directed at an angle of 45° to the axes of the crystal.

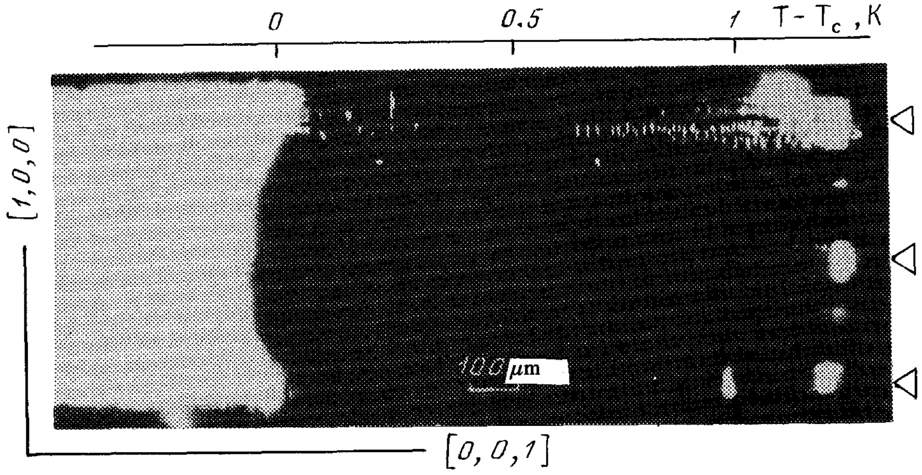

FIG. 3. Phase boundary in a perfect crystal. The polarization of light is analogous to that in Fig. 2. The temperature gradient is ~1 K/mm. The light region represents the γ phase and the dark region denotes the β phase. The light lines are the inclusions of the γ phase which are located along the dislocation slip planes. The locations of the dislocation sources are indicated by triangles.

polarizers that depend on the dislocation slip planes. We observed analogous peculiarities in the NH_4Br crystals at room temperature.[1] We noticed that as we approached the $\beta \rightarrow \gamma$ PT the microinhomogeneities first were formed near the dislocation slip planes.

For the control experiment, we used fresh samples removed very carefully from the solution and inserted into the crystal. At room temperature there were no optical inhomogeneities in them. After the first PT these crystals showed no evidence of the presence of a pre-transition microstructure, and the boundary between the β and γ phases was very sharp (Fig. 3). The interphase boundary could be observed without the analyzer if $E \perp [0,0,1]$; for $E \parallel [0,0,1]$ the interphase boundary is invisible. This indicates that the optical properties of the γ phase are similar to those of the microinhomogeneities produced in the β phase near the PT, and allows us to assume that they are inclusions of the γ phase.

To verify the hypothesis of the origin of the new phase near the dislocations, we performed the following experiment. At $T \approx T_c$ we introduced into a perfect crystal, by touching with the edge of a razor blade, dislocation slip planes along which the inclusions of the new phase were produced immediately (Fig. 3). We note that the average distance between the inclusions decreases as we approach the dislocation source, although the temperature of the sample in this case increases. It is worth noting that we observed no microstructures either in the β phase or in the γ phase in the samples that were mechanically processed (ground and polished). The phase boundary was highly smeared and lightening of the crystal in the crossed polarizers started several degrees before the PT, in agreement with the results of measurement of the birefringence.[8]

We can assume that the effect of dislocations on the PT observed in the NH_4Br has a general nature.

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