Incommensurate phase transition in a $TlInS_2$ crystal

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(Submitted 8 January 1984)
Pis'ma Zh. Eksp. Teor. Fiz. **39**, No. 6, 245–247 (25 March 1983)

A transition to an incommensurate phase occurs at 220 K in $TlInS_2$. The anomalous features in the dielectric constant are shown to result from changes in a modulated structure. A transition to a commensurate phase through a quadrupling of the volume of the unit cell has been observed for the first time.

The $TlInS_2$ crystal is one of the highly anisotropic layered crystals whose properties have recently become the subject of extensive research. A study of this crystal by IR spectroscopy[1] has revealed structural features at 189 K and near 213 K on the temperature dependence of the dielectric function. It has been shown that the feature at 189 K is associated with the softening of a mode active in the IR spectrum, and it has been suggested that there is a transition to a ferroelectric phase at this point. The nature of the phase transition responsible for the feature at 213 K has not been determined.

In this letter we report the use of neutron diffraction and dilatometry to determine the nature of the phase transitions in the $TlInS_2$ crystal. The test samples were plates cleaved from a single crystals grown by a modified Bridgman method in evacuated quartz ampoules.

The neutron-diffraction measurements were carried out in a Neĭtron-3 triaxial spectrometer[2] in the conventional diffraction regime. The wavelength of the incident neutrons was 2.44 Å; higher-order reflections were eliminated by a pyrolytic graphite filter. The dilatrometric measurements were carried out on a galvanomagnetic dilatometer[3] as the sample was heated continuously at 0.5 deg/min.

On the curve of $\alpha = f(T)$ (curve 1 in Fig. 1) we can clearly see anomalous features in the thermal-expansion coefficient at 220 K, in the interval 202–195 K, and at 170 K. These features can evidently be linked to phase transitions in the crystal (PT1, PT2, and PT3, respectively). Figure 2 shows part of a neutron diffraction pattern obtained at 80 K. The hatched peaks are the basic structural peaks corresponding to the high-temperature monoclinic structure of $TlInS_2$. We can clearly see superstructural reflections with $\mathbf{q}_1 = (0; 0; 0.25)$, which are evidence of a quadrupling of the unit cell, and also some additional satellites with $\mathbf{q}_2 = \frac{1}{3}\mathbf{q}_1$, whose nature has not been definitely established.

We studied the two-dimensional distribution of the scattering intensity in the (110) and $(1\bar{1}0)$ planes near the $(\bar{1}; 1; 1.25)$ and $(1; 1; 1.25)$ reflections, respectively. We found that in the temperature interval 216–200 K there exists an incommensurate phase with $\mathbf{q}_{inc} = (\delta; \delta; 0.25)$. Symmetry operations of the monoclinic group transform this vector into a four-point star $(\bar{\delta}; \delta; 0.\bar{2}5)$, $(\bar{\delta}; \bar{\delta}; 0.\bar{2}5)$, and $(\delta; \bar{\delta}; 0.25)$. We measured the reflections corresponding to all four points of the star. We found δ to be

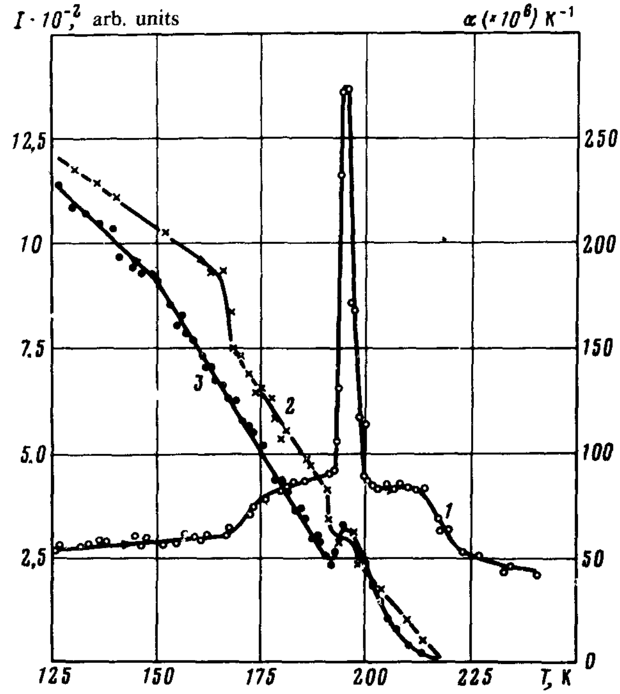

FIG. 1. Temperature dependence of the thermal-expansion coefficient α (curve 1) and of the neutron scattering intensity at the point (1; 1; 1.25) (curves 2 and 3).

0.012 ± 0.003 and to remain constant, within the resolution of these measurements, between PT1 and PT2. Below 200 K there is a change in the modulation of the structure, accompanied by the appearance of a commensurate structure with $\mathbf{q}_1$ and a new type of deviation from commensurability. We were not able to determine the magnitude or direction of this deviation, evidently because it does not lie in the plane

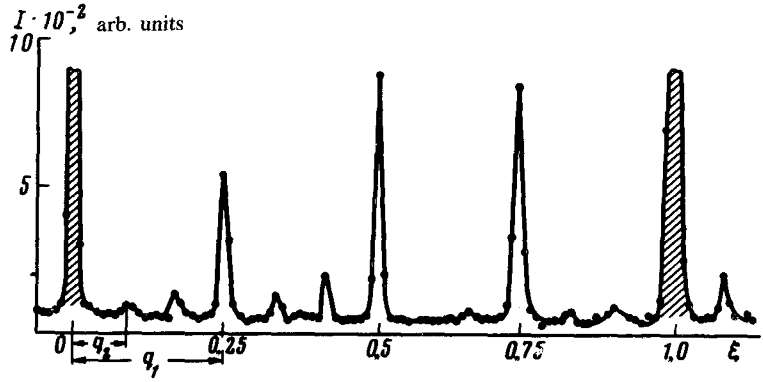

FIG. 2. Part of the neutron diffraction pattern of a $TlInS_2$ single crystal at 80 K {scanning from a (110) point in the [001] direction}.

in which the measurements were taken. A further cooling results in the final phase transition to the commensurate phase (LOCKIN) with a quadrupling along the *c* axis.

Figure 1 shows the temperature dependence of the scattering intensity at the (1; 1; 1.25) point; curves 2 and 3 correspond to heating and cooling, respectively. We see that in each case the superstructure arises at ~216 K (PT1); the positions of the features on curves 2 and 3 which are associated with PT2 and the intensity of the peak on the $\alpha = f(T)$ curve also agree, showing that there is no thermal hysteresis at these transitions. It may thus be suggested that PT1 and PT2 are approximately second-order phase transitions. At PT3 the positions of the slope changes on curves 2 and 3 differ by nearly 30°; this hysteresis implies that PT3 is a first-order phase transition.

Comparing our results with those of Ref. 1, we note the following: The feature at 213 K on the temperature dependence of the dielectric constant is evidently due to a transition to an incommensurate phase. The transition PT2, which is accompanied by a change in the modulation of the structure, is apparently a transition to a ferroelectric phase. The transition to the commensurate phase, seen here for the first time, does not lead to any anomalies in the dielectric properties.

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Translated by Dave Parsons
Edited by S. J. Amoretty