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TEMPERATURE DEPENDENCE OF BIREFRINGENCE OF THIOUREA CRYSTALS

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The birefringence of thiourea crystals at the (010) cleavage plane was studied using the interference method in polarized light in the range from liquid nitrogen temperature to room temperature. Anomalies were found at 163.5 K, 175 K, 178 K and 208 K, which correspond to the consecutive phase transitions. In the range of phase I and phase V stability, the birefringence changes were suggested to result from a small but continuous reorientation of the molecules in the unit cell.

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1. Introduction

Although several papers on the temperature dependence of the birefringence of molecular crystals appeared in the last years [1–5], they were exclusively of experimental character. They showed a large sensitivity of the birefringence to the microscopic changes in the crystal lattice.

Thiourea was chosen because of the phase transitions which occur at low temperatures. This was found by Goldsmith and White [6] from dielectric permittivity studies. The ferroelectric phases of thiourea appear between 176 and 180 K and below 169 K, while the antiferroelectric phases are stable between 169–176 K and 180–202 K. The high temperature phase is paraelectric.

Additionally, the structural investigations done using X-rays diffraction [6] and diffraction neutrons [7] have led to a detailed knowledge of the structure of the molecule and crystal of thiourea, including the positions of the hydrogen atoms. It is now known that the crystals of phases I and V are orthorhombic, with the space groups being $P2_1ma$ and $Pnma$, respectively. There are no indications that intermediate phases would belong to some other crystallographic system. This suggestion is consistent with the fact that all

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transformations are of the type of crystal-to-crystal, in which no large changes in symmetry are expected to occur. Each unit cell of phases I and V is filled with four molecules. While passing from phase V to I the molecules shift by a small distance and additionally the molecule along the *b*-axis causes a slight rotation within the *ac* plane.

Since birefringence is very sensitive to the microscopic changes of the crystal lattice, the temperature dependence of the birefringence of the thiourea crystal was studied. In this paper a test of the microscopic interpretation of the temperature dependence of birefringence for the phase I and V thiourea is presented.

2. *Experimental*

The optical birefringence was measured by means of the interference method in polarized light [1]. Changes in the birefringence of a sample were measured with an accuracy of 0.0002. The sample was placed in the cryostat with temperature regulation using a tyrystoric regulator. The temperature was controlled with a copper-constantan thermocouple. To assure better thermical contact, the sample was placed between glass plates in a silicone oil layer. The cooling velocity during measurements was 0.3 K/min, but near to the phase transition point of 0.2 K/min.

Thiourea was purified by several recrystallizations from water using charcoal. Monocrystals of thiourea were obtained from a methanolic solution by slow evaporation of the solvent at room temperature. The monocrystals obtained were in the form of thin plates of (010) orientation as determined by the optical and X-ray studies. As always in an orthorhombic crystal, the directions of the *a*, *b*, *c* axes coincide with the principal axes of the dielectric tensor. In this case the refractive indices, n_α, n_β, n_γ, coincide with the crystallographic directions, *a*, *b*, *c* respectively.

3. *Results and discussion*

Experimental results on the temperature dependence of the birefringence in the temperature range of 77 K–293 K are shown in Fig. 1.

Temperature range of 158 K–218 K small non-linear changes of birefringence occured which corresponded to the successive phase transition (Table I). We have not attempted to find the dependence between the structure and birefringence for the intermediate phases thiourea because there are no data about the situation of the atoms in their unit cell.

However, the birefringence changed linearly and the temperature range corresponding to the stability of phases I and V increased with a temperature decrease. From the structural data [7] an increase in intermolecular interactions at the cleavage plane (010) during transition from phase V to phase I was reported. This effect clearly results in the changes of the temperature birefringence coefficients for both phases causing a decrease in this coefficient for phase I (Table II).

The orientation of the thiourea molecules in the crystal is unusual because the mirror symmetry plane of the crystal coincides with the molecule symmetry plane (Fig. 2 and

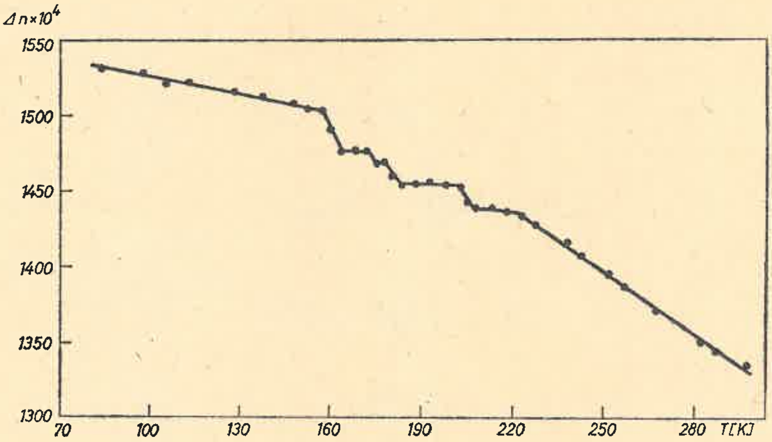

Fig. 1. Temperature dependence of birefringence of thiourea crystal at (010) cleavage plane

TABLE I

Phase transition temperatures of thiourea crystals

According to Ref. [6] T, K	This work T, K
169	163.5
176	175.0
180	178.0
202	208.0

TABLE II

Temperature of the birefringence function for I and V phases of thiourea

Birefringence	Temperature dependence function	Measurement range T, K
$n_\alpha - n_\beta$	$0.1335 - 1.36 \times 10^{-4}\,T$	Phase V (293–228)
	$0.1505 - 4.0 \times 10^{-5}\,T$	Phase I (153–77)

Fig. 3). This gives the molecule a possibility of rotation around axis only once. Using this, a test of the microscopic interpretation of the temperature dependence of birefringence for the I and V thiourea phases is given.

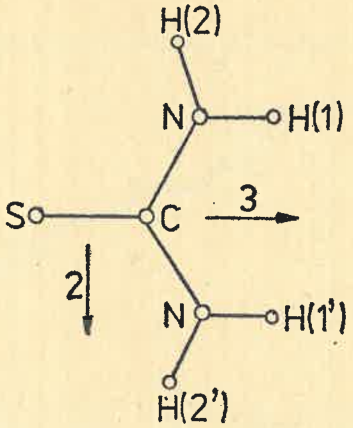

Fig. 2. System of 1, 2, 3 molecular axis

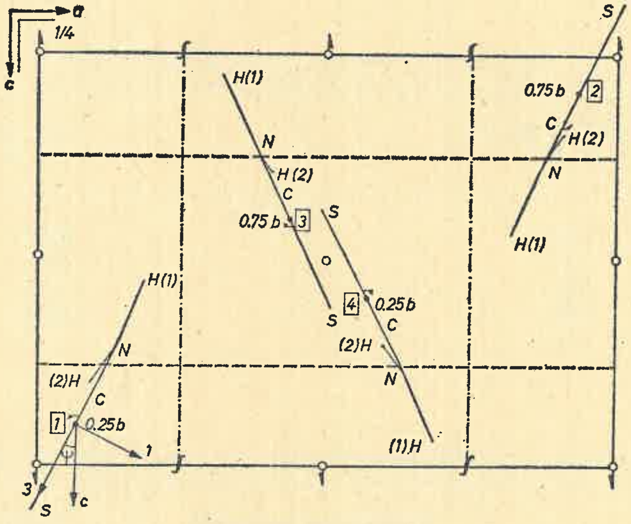

Fig. 3. Projection of the structure of thiourea phase V at the (010) plane

To interpret the birefringence changes for these two phases, it was assumed that the thiourea crystal complies with the oriented gas model[8]. The same model was previously used to explain the experimentally obtained intensities of IR bands in thiourea [9]. A good agreement between the calculated and experimental dichroism was obtained. The usefulness of the oriented gas model let us to conclude that the effect of intermolecular interactions of the N—H ... S type between thiourea molecules on the orientation of these molecules in the crystal lattice can be neglected.

The optical anisotropy of molecular crystals depends on the polarizability of the molecules in the crystal and the symmetry of the crystal structure. The molecular structure of thiourea is not dependent on temperature [10] so that birefringence observed changes must be a result of the re-orientations of the molecules in the unit cell. Libration amplitude of molecules in the unit cell increases with temperature. These librations are of the anharmonic type so continuous changes of the molecules orientation occur with temperature increases.

To calculate the angle of the thiourea molecule rotation with regard to the internal Carthesius axes located in the molecule mass center, a modified Lorenz–Lorentz equation was used, assuming its proper character for each optical direction [11]:

$$\frac{n_i^2-1}{n_i^2+2} = \tfrac{4}{3}\pi N\Gamma_i, \tag{1}$$

where Γ_i ($i = a, b, c$) is polarizability of the unit cell, N denotes the number of the cells in 1 cm^3 and n_i is the value of the refractive indices in the i direction ($i = \alpha, \beta, \gamma$).

Using oriented gas model, Γ_i can be obtained as a sum of the polarizabilities of the nonequivalent molecules in the unit cell crystal:

$$\Gamma_i = \frac{1}{Z}\sum_{i=1}^{Z} A_i\alpha_i A_i^T, \tag{2}$$

where A_i is the orientation matrix of axes of the molecules 1, 2 and 3 with regard to the crystal axes abc, where Z denotes the number of the molecules in the unit cell and α_i is the matrix of polarizability of the thiourea molecule. Orientation matrix, A_i, was calculated from the structural data given by Elcombe and Taylor [7]. Refractive indices, n_i, were measured using the immersion method for $\lambda = 546$ nm and $T = 293$ K and are equal to $n_\alpha = 1.635$, $n_\beta = 1.792$ and $n_\gamma = 1.807$, respectively. Using equations (1), (2) and experimental data temperature reorientation coefficients $d(\Delta\psi)/dT$ of the thiourea molecules in phase I and phase V of the crystals were evaluated. Results of the calculations are given in Table III.

TABLE III

Temperature reorientation coefficients of the thiourea molecules

	$\Delta\psi$, min[a]	$\Delta(n_\alpha - n_\beta)$[b]	$\frac{d(\Delta\psi)^{c}}{dT}$, $\frac{\text{min}}{\text{deg}}$
Phase V (293 K–228 K)	96	0.0105	1.47
Phase I (153 K–77 K)	25.2	0.0025	0.33

[a] The change of angle between 3 axis molecule and crystallographic c axis cause reorientation at the molecules in the unit cell.

[b] Birefringence change.

[c] Temperature reorientation coefficients of the molecules.

The feasibility of a similar rotation in anthracene is shown by the studies of Mason [12] concerning the structure of this crystal at 95 K and 290 K. It follows from Mason's data that between these two temperatures the anthracene molecule becomes rotated through an angle of about 2.5° around the axis perpendicular to the molecular plane.

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