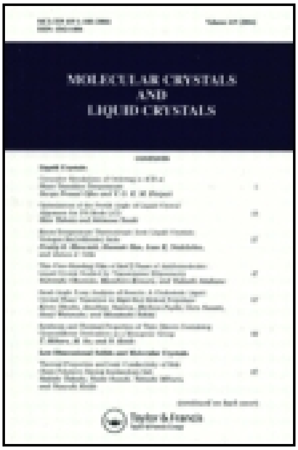

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Thermal Expansion and Elastic Properties of Thiourea Crystal at Room Temperature

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Thermal Expansion and Elastic Properties of Thiourea Crystal at Room Temperature

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The method of obtaining crystals of thiourea from water solution at room temperature has been described. The results of the measurements of the elastic constants by means of Brillouin scattering have been presented. It has been shown that there exists a correlation in orientation between the tensors describing elastic properties and thermal expansion. Debye's temperature and components of the tensor of Grüneisen parameter of the thiourea crystal in the V polimorphic modification have been determined.

Thiourea $SC(NH_2)_2$ is a molecular crystal belonging to the orthorhombic system. It belongs to the Pnma space group at room temperature and the unit cell consists of four molecules. The crystal plane of symmetry is perpendicular to the crystallographic axis b and it coincides with the molecular plane of symmetry.[1,2] The molecular mass of thiourea is $M = 76{,}11$ kg. kmol^{-1}, specific heat $C_p = 105.9\ 10^3$ J.K^{-1}. kmol^{-1} at 293 K,[3] and density d = 1.406 10^3 kg·m^{-3}. Thiourea is one of a few molecular crystals exhibiting ferroelectric properties.[4-6] Investigations of thermal and elastic properties of thiourea are described in[3,5,2] and[8-10] works respectively. The carried structural investigations allowed to determine exactly atom positions in the thiourea crystal[1,2,11] and to estimate the distribution of intermolecular forces decisive in the investigations of properties which are the subject of the present work.

Crystals used in our investigations were obtained from supersaturated solution of thiourea in water at 303 K. The constant supersaturation was reached using a specially designed crystallizer, the scheme of which is presented in Figure 1. Crystallizer K consists of two vessels joined in lower and upper part by means of two pipes which allow convection of the solution. The convection driving force is the temperature difference T_1 and T_2 between the two arms of the crystallizer. Saturated solution at T_2 temperature becomes supersaturated when it flows into the part where $T_1 \sim T_2$.

If we put a crystal seed in this part of the crystallizer the substance in excess willl crystallize on it. The substance precipitated from the solution is

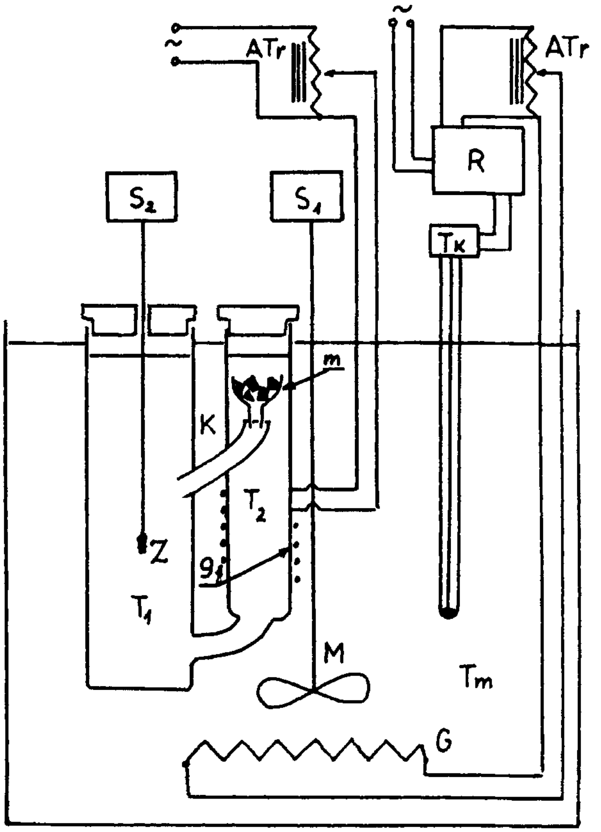

FIGURE 1 Scheme of the device for growing crystals of thiourea K-crystallizer, Z-crystal seed, m-small vessel containing the substance excess, g-addition heater, Tm-thermostat, G-heater, Tk-contact thermometer, M-mixer, S_1 and S_2-electric motors.

replaced when it flows for the second time through the vessel at T_2 temperature in which a small vessel containing spare substance is placed. In order to provide for isothermal conditions the crystallizer has been placed in the thermostat (Tm) in which the temperature stabilization has been obtained by means of a thermoregulator working with a contact thermometer. Samples of dimensions $5 \times 5 \times 5.10^{-9}\,\mathrm{m}^3$ and of various crystallographic orientations have been prepared from the crystals obtained by this method.

Orientation of samples was determined by means of a polarizing microscope using conoscopic figures. Thiourea forms biaxial crystals in which the optic plane (001) is perpendicular to the cleavage plane.[12]

The presented results of thermal expansion investigations[7] indicate that the distribution of intermolecular forces is decisive in the orientation of the thermal expansion tensor in the crystal. The distribution of intermolecular forces will also have a decisive influence upon the elastic properties of the crystal which can be described by means of the tensor of elasticity (c_{ij}), or the tensor elastic flexibility (s_{ij}) and the tensor of compressibility (β_i) (double-suffix notation is being used).

For the purpose of (correlative) comparison between the thermal expansion tensor and the tensor describing mechanical properties the compressibility tensor is the most suitable one, as compressibility coefficient determines the reaction of a crystal-in the form of volume change-to the external hydrostatic pressure. By linear compressibility we mean the relative length decrease of a crystal having a linear shape and on which an elementary hydrostatic pressure is exerted. In the case of anisotropic bodies the quantity of deformation will depend on the direction in the crystal. So the compressibility coefficient describes crystal deformation caused by non-directed factor: hydrostatic pressure. Whereas the thermal expansion coefficient also describes the crystal deformation under the influence of the other non-directed factor: temperature. So in both cases there will appear elements of nondisturbed symmetry of anisotropic properties of a crystal. The compressibility coefficient in direction of unit vector **l** in the crystal belonging to orthorhombic system is described by the equation[13]:

$$\beta = (s_{11} + s_{12} + s_{13})l^2 + (s_{21} + s_{22} + s_{23})m^2 + (s_{31} + s_{32} + s_{33})n^2$$

where l,m,n, the directional cosines of the vector **l**, s_{ij}, the components of the elastic flexibility tensor.

The elasticity tensor components are experimentally determined either by means of ultrasonic wave propagation[14] or by means of Brillouin scattering.[15,10] Benoit and Chapelle determined the elasticity tensor components (c_{ij}) for thiourea crystals in a wide temperature range by means of Brillouin scattering. According to their data the elastic flexibility (s_{ij}) and compressibility (β_i) tensor components were determined. The obtained

TABLE I

Elastic tensor components

$c_{ij}\cdot 10^{-9}$ N.m^{-2}	c_{11}	c_{22}	c_{33}	c_{44}	c_{55}	c_{66}	c_{12}	c_{13}	c_{23}
Benoit and Chapelle	10.25	25.37	14.86	2.0	5.7	0.7	2.4	7.2	5.0
Our data	11.18	27.66	16.4	2.45	7.0	0.74	7.0	6.0	4.8

TABLE II

Elastic flexibility tensor components

$s_{ij}\cdot 10^{10}$ N^{-1}m^{2}	s_{11}	s_{22}	s_{33}	s_{44}	s_{55}	s_{66}	s_{12}	s_{13}	s_{23}
Benoit and Chapelle	1.48	0.42	1.07	5.0	1.75	14.29	0.0014	−0.72	−0.14
Our data	1.26	0.43	0.76	4.08	1.43	13.51	−0.25	−0.39	−0.031

TABLE III

Compressibility and thermal expansion tensor components

$\beta_i\cdot 10^{10}$ N^{-1}m^{3}	β_1	β_2	β_3	$\alpha_i\cdot 10^{4}$ K^{-1}	α_1	α_2	α_3
Benoit and Chapelle	0.76	0.28	0.21	[7]	2.26	0.41	0.95
Our data	0.62	0.15	0.34				

results have been shown in Tables I, II, III, row 1. Since in crystals belonging to the orthorhombic system, principal axes of tensors of physical properties coincide with crystallographic axes it is possible to make a correlative comparison between them directly. The values of the principal thermal expansion coefficients obtained from dilatometric measurements[7] have been shown in Table III. According to the presented values it is possible to note that following relations are fulfilled:

$$c_{22} > c_{33} > c_{11};\ s_{22} < s_{33} < s_{11};$$
$$\alpha_2 < \alpha_3 < \alpha_1;\ \beta_3 < \beta_2 < \beta_1$$

Since the last relation is contradictory to the preceding ones the measurements of the elasticity tensor components at room temperature were repeated. In the present work the velocity of elastic waves was also determined by means of Brillouin scattering.

In order to calculate the tensor components (c_{ij}) it is necessary to know the principal indices of refraction of thiourea for the light wavelength $\lambda = 4.88\ 10^{-7}$ m emitted by the laser used in our measurements. The obtained values of principal indices are as follows:

$$n_1 = 1.637,\ n_2 = 1.823,\ n_3 = 1.79$$

The comparison between these values of the refraction indices and those given in the work[9] where $n_1 = 1.634$, $n_2 = 1.806$, $n_3 = 1.789$ measured for $\lambda = 6.328\ 10^{-7}$ m indicates some difference in the value of n_2.

In Tables I, II, III, row 2, the values of tensor components (c_{ij}), (s_{ij}), (β_i) obtained from our measurements are displayed. On the basis of these data it follows that besides the fulfilled relations

$$c_{22} > c_{33} > c_{11} \text{ and } s_{22} < s_{33} < s_{11}$$

the expected relation $\beta_2 < \beta_3 < \beta_1$ is also satisfied.

Figures 2 and 3 represent polar diagrams of the section of the compressibility and thermal expansion ellipsoids in (010) and (100) planes of thiourea. So it follows that a good criterion in the tensor orientation exists which may serve as a criterion of correctness in determining the components of one of them. Figure 3 shows on the contrary the correlation discrepancy for the section in (100) plane where the compressibility ellipsoid calculated on the basis of data[9] has a completely different orientation from the thermal expansion and compressibility ellipsoids calculated from our data (c_{ij}).

While analyzing the unequalities satisfied by the components of tensors describing mechanical properties and thermal expansion of the thiourea crystal it is possible to say that for the direction in which the expansion is the

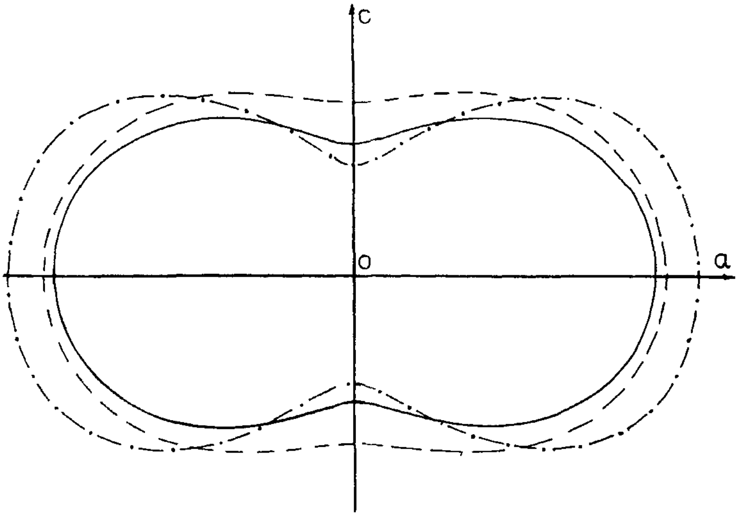

FIGURE 2 Polar diagram of the (010) section of the compressibility and thermal expansion tensors of the thiourea crystal. Full line denotes the section of expansion tensor. Broken and dotted line denotes the section of compressibility obtained from the $(c_{ij})^9$ data. Broken line denotes the section of compressibility tensor obtained from our data (c_{ij}).

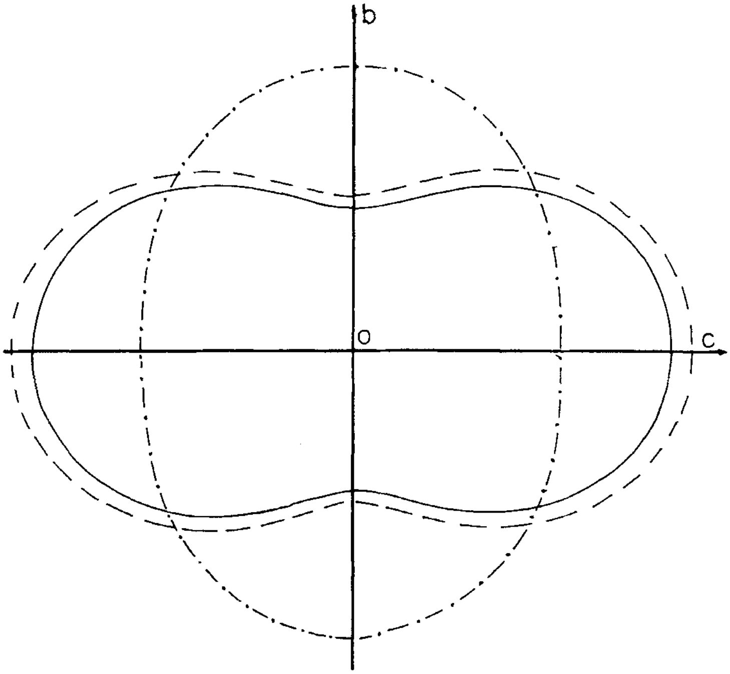

FIGURE 3 Polar diagram of the (100) section of the compressibility and thermal expansion tensors in the thiourea crystal (notation as in Figure 2).

smallest, the biggest elasticity coefficient and the smallest compressibility is observed. Such relation is conditioned by the distribution of intermolecular forces in the crystal. In the case of thiourea the strongest forces come from specific interactions of the S . . . H-N type which stiffen the crystal lattice along the b crystallographic axis. This explains the smallest α_2, β_2 and the biggest c_{22} values. The (100) plane is the perfect cleavage plane in the thiourea crystal and from structural data it follows that the weakest interactions occur in the direction parallel to the a crystallographic axis. This explains the biggest value of α_1 and β_1 and the smallest c_{11} value.

On the basis of the obtained data which describe thermal and mechanical properties of thiourea and proper relations[16,14] the Debye temperature (θ) and the tensor components of Grüneisen's parameter (γ_i) have been computed at room temperature for the V polymorphic modification[5] of thiourea.

$$\theta = 145\text{ K}, \gamma_1 = 1.74, \gamma_2 = 1.63, \gamma_3 = 1.67$$

The obtained temperature is much lower than the phase transition temperature (202 K) which indicates that the considerable dependence of the expansion coefficient on the temperature[7] is caused not by quantum effects but is rather due to anharmonicity. The obtained values for the tensor components of Grüneisen's parameter which describes Debye temperature dependence on volume (and indirectly on temperature) indicate that it is a tensor which has a slight anisotropy.

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