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# Thermal Expansion of Thiourea in the Range of Phase Transition

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By means of a quartz dilatometer three principal expansion coefficients have been determined in the temperature range 100–273°K, and their anisotropy within (100) plane. The appearance of singular points, corresponding to phase transformations, depends on direction of measurements but most drastic changes are observed along the crystallographic *c*-axis, in agreement with the direction of the weakest intermolecular interactions. The calculated pressure necessary to shift the phase equilibrium I/II to room temperature is in good agreement with the value observed in a direct experiment.[11]

The discovery of the ferroelectric behavior of thiourea made by Solomon in 1956 has shown[1] that ferroelectric crystals can also be met among "true" molecular crystals, i.e. in a type of solids where the ionic contribution to molecular forces can be neglected. Basing on measurements of dielectric permeability in the temperature interval 123 to 273°K Goldsmith and White[2] have found five different phases in thiourea with following equilibrium temperatures between neighbouring phases: $T_{V/IV} = 202$, $T_{IV/III} = 179$, $T_{III/II} = 176$, and $T_{II/I} = 169$°K. Phases I and III are ferroelectric, II and IV are antiferroelectric and phase V, stable above 202°K, is paraelectric. However, of these four only two transitions appear on $C_v(T)$ curve, as found by measurements of the heat capacity made by Nakagawa and coworkers,[3] at temperatures 202 and 167°K. The $C_v(T)$ curve of Nakagawa and $\varepsilon(T)$ curve of Goldsmith and White are both shown in Figure 1. While studying the thermal properties of thiourea, Futama observed on $C_v(T)$ curve only one singular point at 169°K and two points on thermal expansion curve, at 202 and 160°K.[4]

The structural investigations made by means of X-rays diffraction[2,5], diffraction of electrons[6,7] and neutrons [8] have led to a detailed knowledge

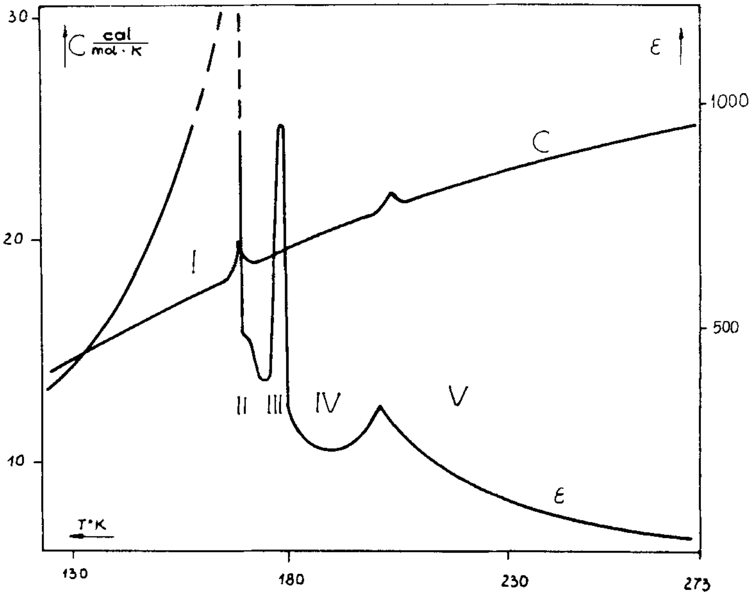

FIGURE 1 $\varepsilon(T)$ curve for thiourea according to the results of Goldsmith and White,[2] and $C(T)$ curve according to Nakagawa and coworkers.[3]

of the structure of molecule and crystal of thiourea, including the positions of hydrogen atoms. It is now known that crystals of phases I and V are orthorhombic, space groups being $P2_1ma$ and Pnma, respectively, and there are no indications that intermediate phases would belong to some other crystallographic system. This suggestion is consistent with the fact that all transformations are of the type crystal-to-crystal, in which no drastic changes of symmetry are expected to occur. The unit cells of phases I and V are filled with four molecules each and have dimensions shown in Table II.

The interactions between atoms forming a molecule are, as a rule, much stronger than intermolecular interactions within the crystal. A change of crystal symmetry need not necessarily involve a change in the structure of the molecule. Therefore, the appearance of ferroelectric properties in thiourea has been explained by some shift of the molecule as a whole rather, than of individual atoms.[7,8] As a further consequence of mutual shifts of molecules and, maybe also a small change of their orientation with respect to the frame of crystallographic axes, some alteration of lattice parameters can occur. This is why we undertook a study of the thermal expansion of thiourea in our Laboratory.

## EXPERIMENTAL

The linear expansion of crystal samples has been measured on a quartz dilatometer[9] developed in our laboratory. Using a microscope equipped with an ocular micrometer the absolute changes of the length of a sample could be measured with a sensitivity of $2 \cdot 10^{-5}$ cm. The sample was placed in a metal cylinder, the lower end of which was immersed in a liquid air bath while the upper one was kept at room temperature. Therefore, the temperature of the sample could be changed simply by moving it along the cylinder axis. The temperature was controlled with a copper-constantan thermocouple.

The crystals were grown from a supersaturated solution of thiourea in water at 30°C. The constant supersaturation was reached using a self-circulating circuit composed of two glass vessels. In the first vessel kept at constant temperature a crystalline seed was immersed hanging on a thin glass thread. In the second vessel, kept at somewhat higher temperature, the stock substance was dissolved to give a saturated solution. Both vessels were immersed in a thermostating bath. Using this method we were able to grow single crystals of phase V up to dimensions $3 \times 8 \times 50$ mm$^3$, optically homogeneous, with a very good cleavage plane (100). From these parallelopipeds $3 \times 2 \times 8$ mm$^3$ samples were cut at various orientations in relation to the *b*-axis. The orientation of other samples was determined by means of a polarizing microscope in relation to the plane of optic axes, (001).

## RESULTS AND DISCUSSION

Relative elongation of four samples cut at various angles in relation to the *b*-axis on (100) plane is shown in Figure 2. The behavior of samples cut along the three crystallographic axes *a*, *b*, and *c* is shown in Figure 3. As always in an orthorhombic crystal, the directions of *a*, *b*, *c* axes coincide with the principal axes of the thermal expansion tensor. It may be seen that along the *a*-axis only one transformation is visible that occurs at 192°K. The curve along *b* shows two anomalies, at 213 and 173°K. The most drastic changes occur along the *c*-axis where the slope along the curve changes as much as three times, and moreover the expansion coefficient reverses its sign at 193°K. Particular segments of curves fulfill the quadratic equation with respect to the temperature, *t*°C

$$\frac{\Delta 1}{1} = C + Bt + At^2 \tag{1}$$

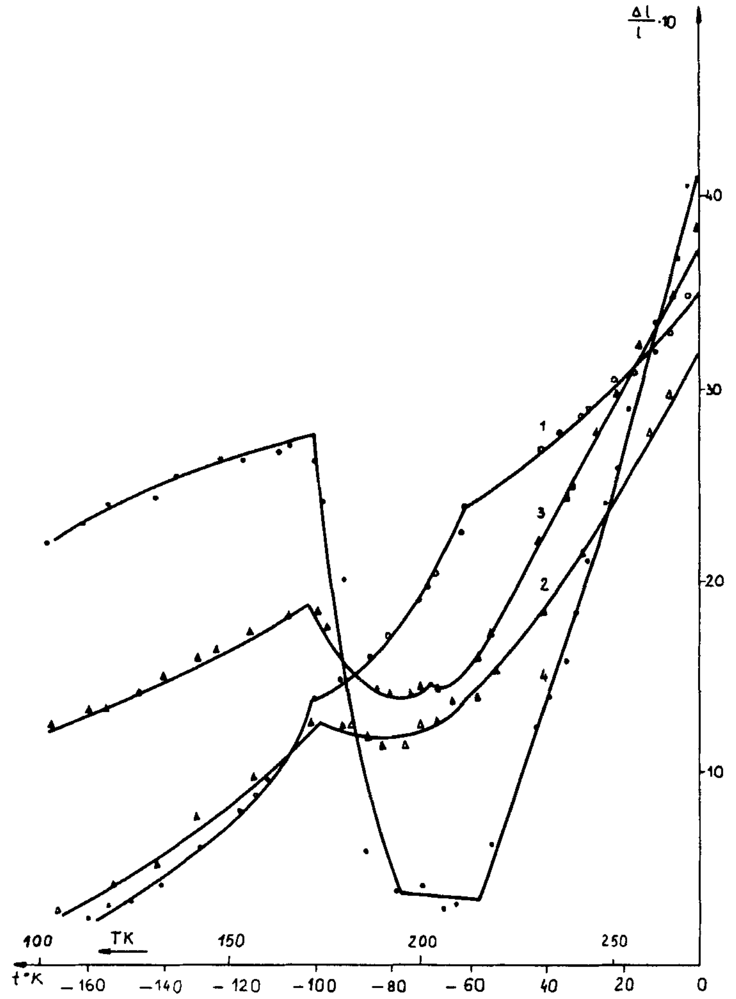

FIGURE 2 Relative elongation of samples cut in (100) at various angles, $\varphi$, respective to the crystallographic $b$-axis. Curves 1–4 refer to values of $\varphi = 0, 32, 50$ and 90°.

where $t = T - 273$, $B$ corresponds to the linear expansion coefficient and $A$ describes its dependence on temperature, $C$ is an experimental constant corresponding to zero point on a scale of length at 0°C. $A$, $B$, and $C$ constants were determined from experimental points by the method of least squares and are given in Table I. The curves on Figures 2 and 3 were drawn according to (1) with corresponding constants taken from Table I. The thermal expansion coefficients,

$$\alpha_i = B_i + 2A_i t \qquad (2)$$

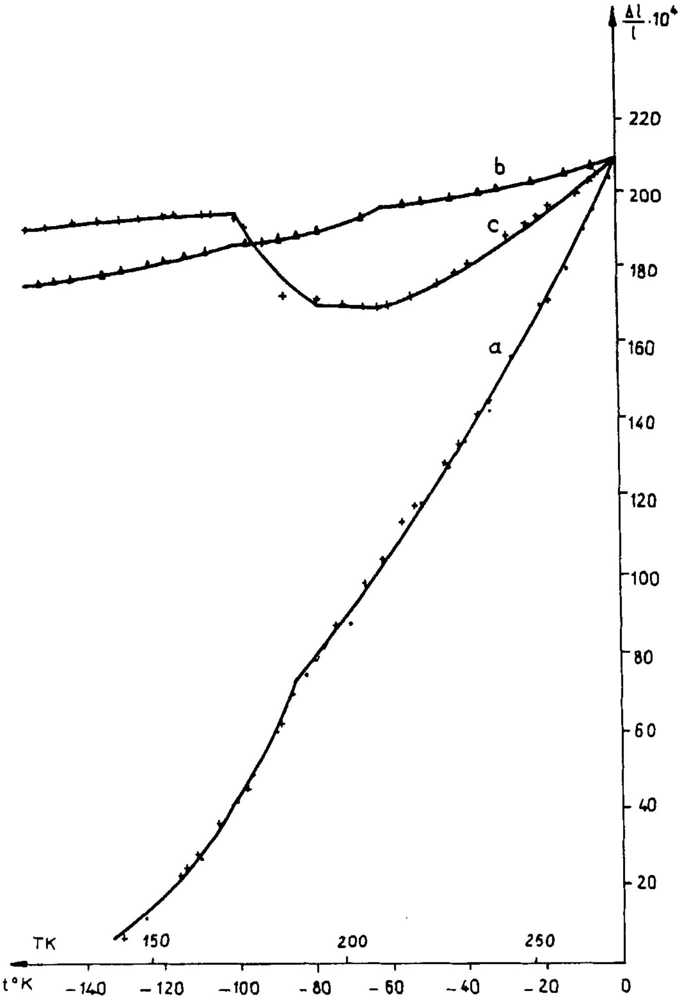

FIGURE 3 Relative elongation of samples cut along three crystallographic axes, *a*, *b* and *c*, respectively.

are shown in Figure 4. Using the values for *a*, *b*, and *c* axes at a given temperature we can calculate the volume expansion coefficient,

$$\beta = \alpha_a + \alpha_b + \alpha_c \tag{3}$$

which is shown in Figure 5. $\beta$ is discontinuous at two points, 202 and 167°K, which agrees very good with the two transition temperatures as determined by other measurements,[2,3] cf. Figure 1.

TABLE I

Experimental values of parameters $A$ and $B$

| Crystallographic direction | Temperature range of stability of a given phase | $A \cdot 10^6$ deg$^{-2}$ | $B \cdot 10^4$ deg$^{-1}$ |
|---|---|---|---|
| $a$ | 293–188°K | 0.54 | 2.256 |
| | 188–123°K | 1.93 | 2.325 |
| $b$ | 293–213°K | 0.21 | 0.406 |
| | 213–173°K | 0.51 | 0.407 |
| | 173–123°K | 0.09 | 0.237 |
| $c$ | 293–213°K | 0.33 | 0.95 |
| | 213–193°K | 0 | 0 |
| | 193–173°K | 2.55 | −0.615 |
| | 173–123°K | −0.03 | 0.072 |

Using the thermal expansion data found in this paper and the unit cell parameters at room temperature given by X-ray experiment,[2,5] Table II, we can calculate the unit cell parameters at 123°K in the following manner. Starting, for example, with $b_{290}$ at room temperature we calculate its value at the first transition point, 213°K. The value $b_{213}$ is next the starting point for the second temperature interval, 213 → 173, etc. We obtain

$$b_{213} = 8.537(1 - 0.406 \cdot 10^{-4} \cdot 80 + 0.0021 \cdot 10^{-4} \cdot 6400) = 8.521,$$

$$b_{173} = 8.521(1 - 0.407 \cdot 10^{-4} \cdot 40 + 0.0051 \cdot 10^{-4} \cdot 1600) = 8.514,$$

$$b_{123} = 8.514(1 - 0.237 \cdot 10^{-4} \cdot 50 - 0.0009 \cdot 10^{-4} \cdot 2500) = 8.506.$$

The data calculated in this manner for the three crystallographic axes are shown in Table II, and we can see that they compare quite well with direct X-ray experiment at 123°K. This illustrates a good consistency between X-ray and dilatometric results for the thiourea crystal. Small discrepancies may be assigned to somewhat greater value of the dilatometric expansion coefficient in comparison to X-ray results.

A glance on experimental values of $\alpha_a$, $\alpha_b$ and $\alpha_c$ indicates that the direction of largest thermal expansion is parallel to the $a$-axis. It can be deduced from the structural data[8] that this direction corresponds to the weakest intermolecular interactions both in phase V and I. The singularity point on the curve 3$a$ has not been noticed by Futama.[4]

The expansion coefficient along the $b$-axis has the smallest value and its temperature dependence indicates two phase transformations. The intermolecular interactions are of the hydrogen bonding type, N—H···S, and are stronger than usual van der Waals forces. The direction of the line joining N and S atoms coincides with the $b$-axis.

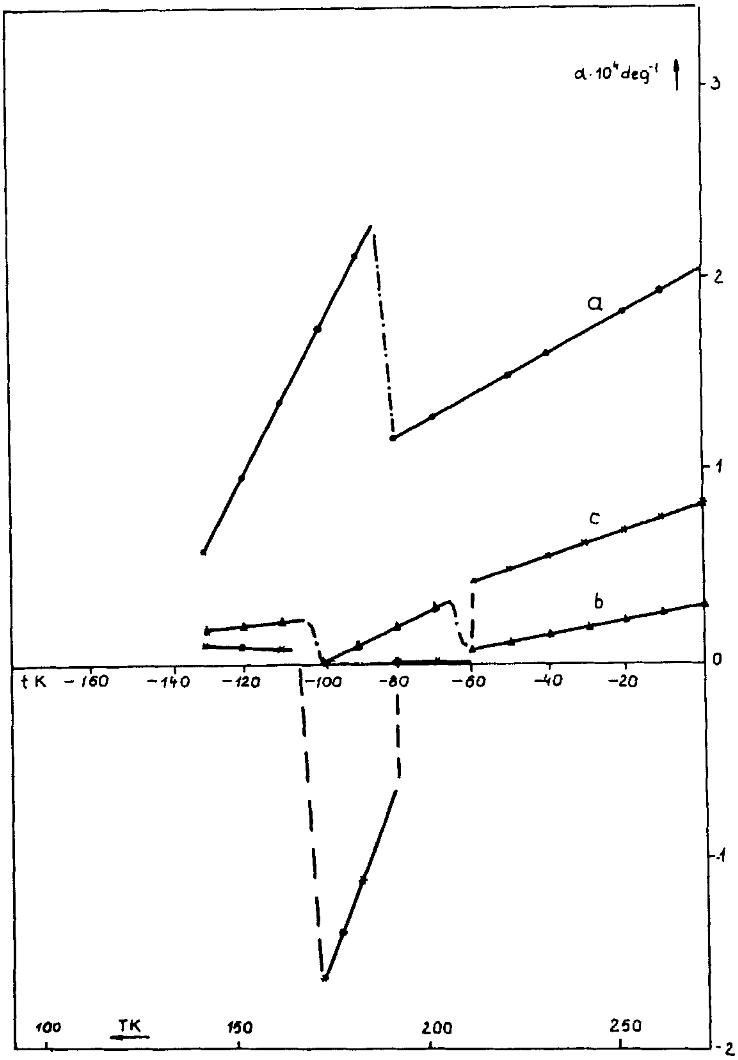

FIGURE 4 The temperature dependence of three principal thermal expansion coefficients.

The largest anomalies on the curve $\alpha(T)$ occur along the $c$-axis. That direction corresponds to the most dramatic changes in intermolecular interactions: while cooling phase V, the contacts (I) split into two contacts IA and IB, and additionally two new contacts appear: IIB and IIIA. This is shown in Table III where the interatomic distances between sulphur and hydrogen are given according to the structural data.[6-8] The atoms belong

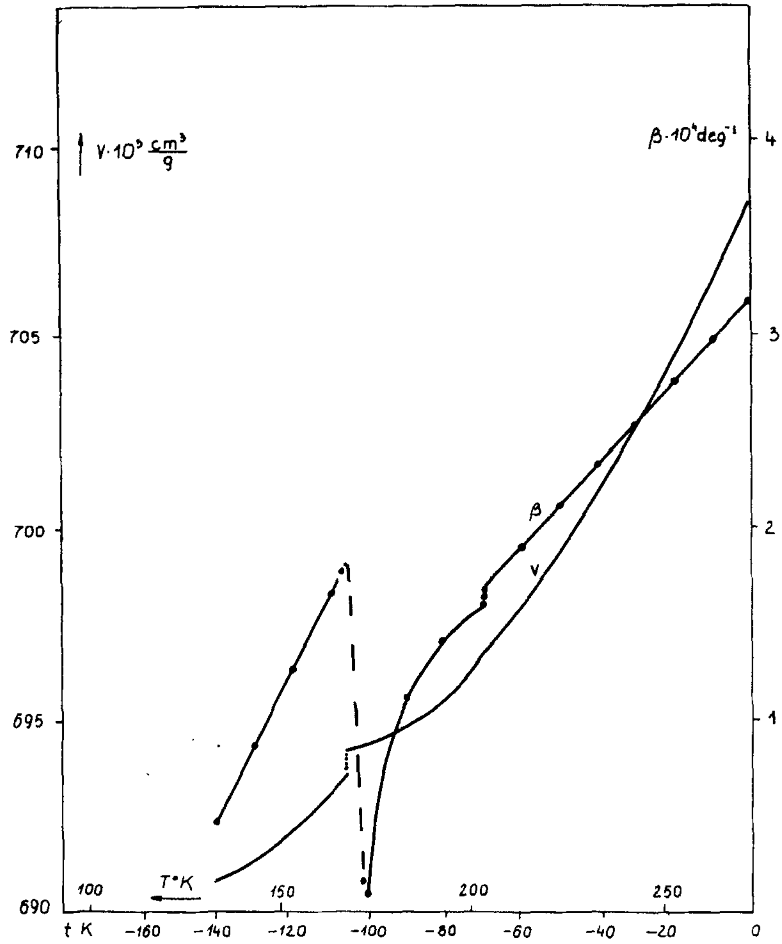

FIGURE 5 Volume expansion coefficient, $\beta$, and specific volume, $V$, as functions of temperature.

TABLE II

Unit cell parameters at various temperatures

| $T$, °K<br>Axis, Å | 293<br>According to Ref. 2 | 123<br>According to Ref. 2 | 123<br>Calc., this work |
|---|---|---|---|
| $a$ | 7.655 ± 0.007 | 7.516 ± 0.007 | 7.467 |
| $b$ | 8.537 ± 0.007 | 8.519 ± 0.01 | 8.506 |
| $c$ | 5.520 ± 0.007 | 5.494 ± 0.005 | 5.500 |

to neighbouring molecules. While passing from phase V to I the molecules shift by a small distance and, additionally, every second molecule along the *b*-axis makes a slight rotation within the *ac*-plane. The result of these small displacements is that one single distance H---S in phase V corresponds to two distances in I, A and B. The lowest value of the sum of van der Waals radii for sulphur and hydrogen amounts to 2.75 Å.[10] Therefore, we can assume that distances shorter than 2.70 Å are due to the interactions of the hydrogen bonding type, N—H---S. In phase V we have only one type of N—H---S interactions with its length parallel to *b*, while in phase I three different types of N—H---S interactions occur. As a result of consecutive phase transformations the interactions along the *a*-axis become only slightly stronger but in the direction of the *c*-axis the changes are much more important. The most significant changes occur in the direction of the *b*-axis.

This picture of interatomic interactions and their changes while passing from phase V to I explains the anisotropy of thermal expansion and the directional character of the phase transformation as observed in dilatometric measurements. The sections of the thermal expansion tensor corresponding to phase V and I are drawn in the projection of the crystal structure on (010) in Figures 6 and 7, respectively. Broken lines denote N—H---S interactions.

Basing on principal linear expansion coefficients we can calculate the volume expansion coefficient. Figure 5 shows how the specific volume of thiourea crystal changes with temperature. The discontinuity at 167°K amounts to $\Delta V = 0.0005$ cm$^3$/g and indicates that this phase transformation is of the first order. As there are no other significant discontinuities on $V(T)$ curve, Figure 5, we can assume that $\Delta V$ corresponds to the overall volume effect between phases V and I. The enthalpy of this transformation has been measured by Nakagawa at 167°K and amounts to $\Delta H = 3$ cal per mole[3] while the result found by Futama is 6.6 cal per mole.[4] From these data and using the Clausius–Clapeyron equation we can calculate the coefficient $dp/dT$, giving information how the temperature of coexistence of phases I and II depends on pressure. Inserting the value given by Nakagawa we obtain $dp/dT = 20.2$ kG/(cm$^2 \cdot$ K), while that given by Futama yields $dp/dT = 44.4$

TABLE III

Types of intermolecular contacts in phase I and V, Å

| Interatomic interactions | | Phase V | Phase I | |
|---|---|---|---|---|
| | | | *A* | *B* |
| —H(2) --- S | I | 2.397 | 2.354 | 2.415 |
| —H(1) --- S | II | 2.767 | 3.038 | 2.549 |
| —H(1) --- S | III | 3.055 | 2.669 | 3.360 |

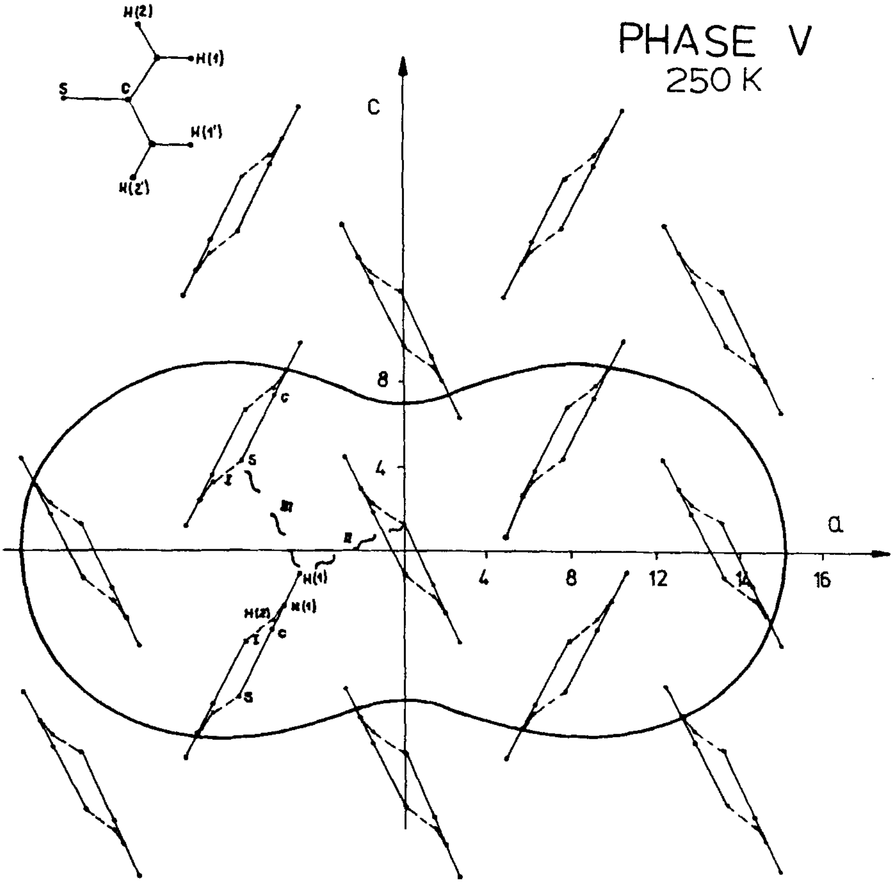

FIGURE 6 Polar diagram of the (010) section of the thermal expansion tensor at 250°K (phase V). Broken lines denote intermolecular interactions of the hydrogen-bonding type (I), and wave lines are interactions of the atom-atom type (II and III in Table III).

kG(cm$^2$ · K). If we assume that the I/II equilibrium temperature depends linearly on pressure, we can calculate the pressure, $p_d$, which is necessary to achieve the equilibrium at room temperature, 293°K

$$p_d = \left(\frac{dp}{dT}\right) \cdot \Delta T = 2545\ \mathrm{kG/cm^2},$$

or

$$= 5590\ \mathrm{kG/cm^2},$$

depending on value which is used for the enthalpy change.

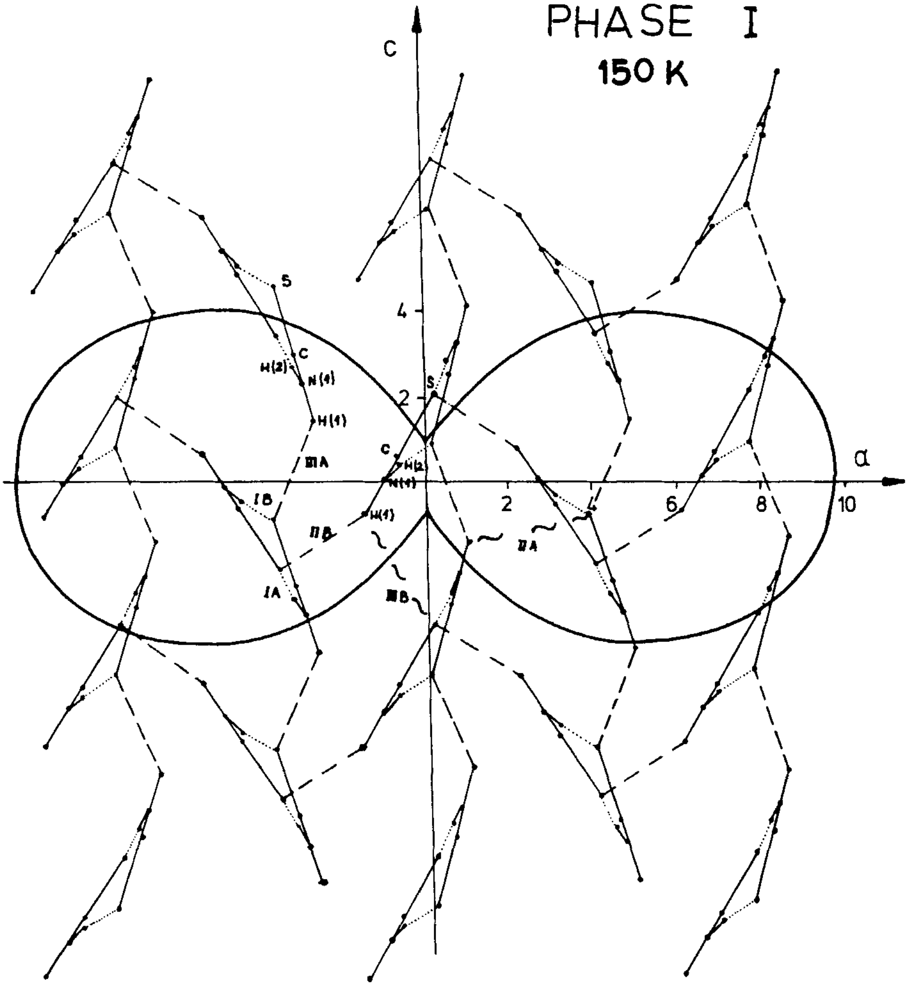

FIGURE 7 Polar diagram of the (010) section of the thermal expansion tensor at 150°K (phase I). Broken lines denote intermolecular interactions of the hydrogen-bonding type, and wave lines are atom–atom interactions (cf. Table III).

This result can be compared with the direct value obtained by Kabalkina[11] who studied the structural changes in thiourea as a function of pressure. She found that the direction of the strongest compressibility of the unit cell is parallel to *a*-axis, which is in good agreement with our previous discussion concerning the relation of interatomic forces and the direction of highest thermal expansion. The compressibility along the *b*-axis is as much as 2.5 times smaller. Because of a not very high accuracy of the measurements it is hard to conclude what happens along the *c*-axis. Additionally, Kabalkina has found that the pressure, $p_k$, that is necessary to transform phase V into I amounts to

$$p_k = 3600 \pm 200\,\mathrm{kG/cm^2}.$$

The comparison of $p_k$ with $p_d$ indicates that the phase transformation I → II is, indeed, of the first order but a more reliable value of enthalpy change in this process seems to be that given by Nakagawa and collaborators.

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