

The Model of Ferroelectricity in Thiourea

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In this paper we propose a mechanism of the phenomenon of ferroelectricity in the molecular crystal of thiourea ($\text{SC}(\text{NH}_2)_2$). The mechanism is based on the model of interaction between two molecular electric dipoles. The dipoles are not idealized to points — they have a finite length. Besides, they can reorient mutually and the reorientation is determined by the crystal structure specified by the experimental structural research. On the basis of this theory, a formula for the potential energy of interaction of a pair of two nonpunctual dipoles as a function of the angle of reorientation is derived and discussed.

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1. Introduction

The phenomenon of ferroelectricity in solid states has been studied with both experimental and theoretical methods. Theoretical research is usually performed for assuming a certain model of the substance studied. A very interesting and intensively studied ferroelectric crystal is thiourea ($\text{SC}(\text{NH}_2)_2$). The ferroelectricity in thiourea was discovered by Solomon [1] and further studied by Goldsmith and White [2]. On the basis of the dielectric studies they found a few phases in different temperature ranges:

- phase I: below 169 K,
- phase II: between 169 K and 176 K,
- phase III: between 176 K and 180 K,
- phase IV: between 180 K and 202 K,
- phase V: above 202 K.

The phases I and III were ferroelectric. These authors reported the structural study of the thiourea crystal and proposed the model of dielectric polarization in it assuming the reorientation of pairs of molecules and their electrical dipoles. Dielectric properties of thiourea were also studied by Futama [3]. In Ref. [3] the temperature dependence of the lattice constants of the thiourea crystal was presented (within the limit of the phase transition the anomalies of linear thermal expansibility are observed) and the form of dependence of the potential energy of the pairs of interacting molecules on the angle between them was proposed. The presented experimental results on the physical properties of thiourea crystal provide a complex picture of physical processes taking place in the crystal. According to most authors it is the mutual reorientation of the pair of molecules, visible in the projection

onto the xy plane, that is responsible for the effect of ferroelectricity in thiourea. Consequently, the resultant dipole moment of a given pair of molecules is perpendicular to the z axis. This conclusion was drawn on the basis of the assumption that the electric dipole moment of the molecule is directed along the $\text{S}=\text{C}$ bond. This situation is shown in Figs. 1 and 2 (made on the basis of the structural research of Elcombe and Taylor [4]), corresponding to the phases V and I, respectively.

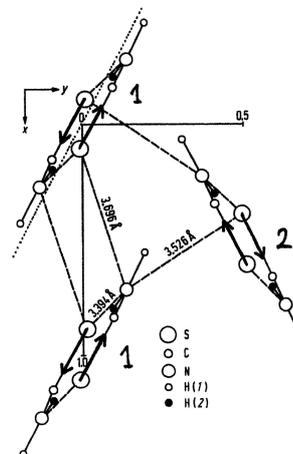


Fig. 1. The projection of the structure of thiourea crystal in phase V onto the xy plane, according to [4], with the electric dipole moments of the molecules and with the sublattices 1 and 2 indicated. The dipole moments are antiparallel — the resultant dipole moment of a given pair of molecules is equal to zero.

Consider phase I. The resultant dipole moment of the pair of molecules can be decomposed along the two coordinates: x and y axes. The coordinates directed along the x axis, originating from the sublattices 1 and 2, cancel each other, and the coordinates along the y axis add

2. The model

In this paper we introduce a model of potential energy of two nonpunctual molecular electric dipoles in the thiourea crystal as a function of the angle of mutual reorientation between the interacting dipoles. The model was deduced on the basis of the following assumptions: 1. The molecular electric dipoles in the crystal are not idealized to points, but they have a finite length of d . 2. The molecular electric dipoles in the crystal can reorient mutually only within given constraints. Their mutual orientation is determined by the chemical bonds and by the effect of molecular packing, dependent on the crystal structure and the constitution of molecules. 3. The value of the electric moment m of the nonpunctual molecular electric dipole is constant. 4. The dipole electric moment of the molecule of thiourea in the crystal is directed along the S=C bond. 5. The nonpunctual molecular electric moment in the crystal is placed in the electric field generated by neighbouring dipoles.

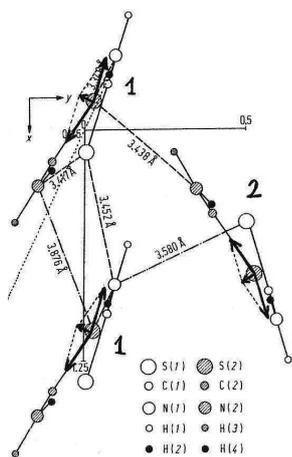


Fig. 2. The projection of the structure of thiourea crystal in phase I onto the xy plane, according to [4], with the electric dipole moments of the molecules and with the sublattices 1 and 2 indicated. The resultant dipole moments of the pairs of molecules in sublattices 1 and 2 are non-zero.

to each other. The coordinates of the dipole moment of a pair of molecules along the y axis, originating from sublattices 1 and 2, are equal because of the identical angle of mutual reorientation of the molecules in both sublattices. The second interesting information in [4] is the fact that the molecules in a given pair reorient mutually in such a way that the bisectrix of the angle of reorientation (marked in Figs. 1 and 2 by a dotted line) makes a constant angle (of 65°) with the y axis, irrespectively of the sublattice and temperature. Besides it was found that it is the mutual reorientation of molecules in the unit cell that determines the pre-polarization of that crystal, but the translation of the molecules is not of great weight (Fig. 3).

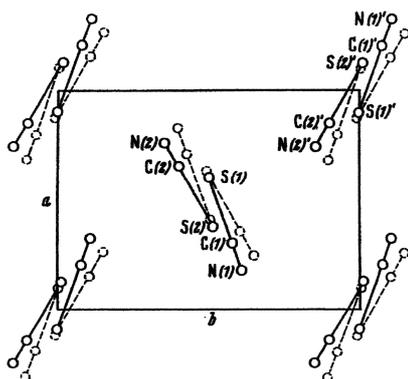


Fig. 3. The mechanism of pre-polarization of the thiourea crystal according to Goldsmith and White [2]. The solid and dashed lines refer to the states with opposite polarization.

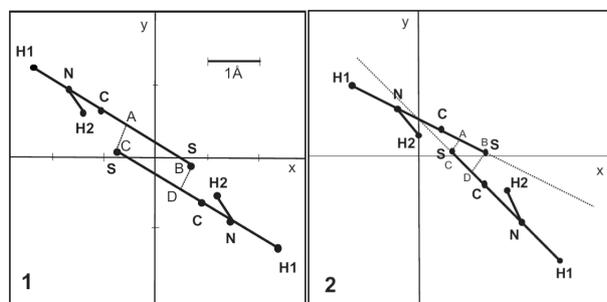


Fig. 4. The projection of the pair of interacting molecules in the thiourea monocrystal onto the xy plane. 1 — phase V, 2 — phase I.

The above assumptions are in agreement with Fig. 4 (made on the basis of [4]) showing the projection of the pair of interacting molecules of thiourea monocrystal in phases V and I onto the xy plane.

Figure 4 shows that the lengths of the segments AB and CD are constant in phases V and I, irrespectively of the orientation of molecules. Therefore the length of the segments AB and CD equal to d can be treated as the length of the substitute electric dipole of the molecule of the crystal of thiourea. On the basis of Fig. 1 we assume that the two molecular electric dipoles can reorient in such a way that the lengths of segments AD and BC are constant ($AD = BC = L$). The considered pair of the substitute nonpunctual electric dipoles in the projection onto the xy plane is illustrated in Fig. 5.

Analysis of Fig. 5 brings the following formulae for the lengths of the segments AC and BD :

$$|AC| = d\sqrt{\delta^2 - \cos^2 \frac{\theta}{2}} - d \sin \frac{\theta}{2}, \tag{1}$$

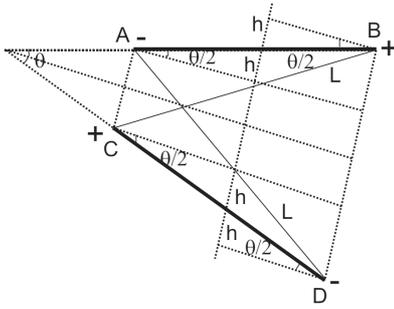


Fig. 5. The projection of the pair of the substitute nonpunctual electric dipoles of the crystal of thiourea onto the xy plane, with restricted possibilities of reorientation ($AB = CD = d$, $AD = BC = L$).

$$|BD| = d\sqrt{\delta^2 - \cos^2 \frac{\theta}{2}} + d \sin \frac{\theta}{2}, \quad (2)$$

where $\delta = L/d$, and θ is the angle of reorientation between the projections of the two substitute electric dipoles onto the xy plane. As follows from the neutron scattering study of the structure of thiourea monocystals [4], reorientation of the projections of the pairs of dipoles onto the xy plane occurs in such a way that the line perpendicular to the bisectrix of the angle of reorientation θ makes a constant angle $\beta = 25^\circ$ with the ferroelectric axis y , irrespectively of the orientation between the dipoles. In this situation, the segments AB and CD maintain the same direction with respect to the crystallographic axes x , y and z , irrespectively of the angle θ . In Fig. 5 we can see that if $\theta = 0$, then the resultant dipole moment of a given pair of dipoles is equal to zero; whereas if $\theta \neq 0$, then the resultant dipole moment is nonzero. The resultant dipole moment of a pair of dipoles in the projection onto the xy plane is presented in Fig. 6.

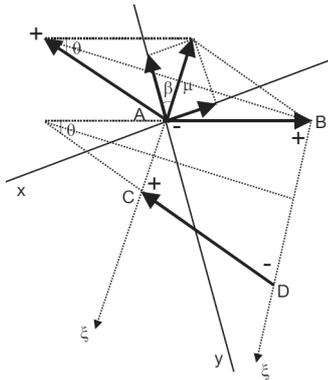


Fig. 6. The construction of the resultant dipole moment for a pair of substitute dipoles of the molecules of thiourea crystal.

On the basis of Fig. 6 we can calculate the value of the resultant dipole moment μ of the pair of dipoles A , B :

$$\mu = 2m \sin \frac{\theta}{2}, \quad (3)$$

where $m = 4.86$ D is the value of the dipole moment of the molecule of thiourea proposed by Calvo [5]. To obtain the formula for the energy of interaction of a given pair of dipoles A and B (Fig. 6), it was assumed that in points C and D there exists an electric field characterized by potentials towards the constant direction ξ :

$$\phi_C = -E_0 \xi_C - E' \xi_C, \quad (4)$$

$$\phi_D = E_0 \xi_D - E' \xi_D, \quad (5)$$

respectively, where $\xi_C = AC$, $\xi_D = BD$ are given by formulae (1) and (2). As follows from formulae (4) and (5) in the points C and D there act the local electric fields with the opposite directions of the intensity E_0 , and the local electric fields with the same directions and the intensity E' . The field E_0 can be treated as a result of the intermolecular bonds; but the field E' is a result of the action of the two dipoles on the molecular field of a given system: of short-range one (for example the Onsager field) and the long-range one related to the polarization P of the crystal. According to the above we can assume

$$E' = a\mu + bP \cos \beta, \quad (6)$$

where a and b are the proportionality coefficients. The energy of interaction of the pair of dipoles takes the form

$$U = q(-E_0 - E')\xi_C - q(E_0 - E')\xi_D, \quad (7)$$

where q is the modulus of the electric charge of the substitute non-punctual molecular dipole. Simple mathematical transformations lead to the following formula:

$$U = -2E_0 m \left(\sqrt{\delta^2 - \cos^2 x} - s \sin^2 x - \sigma \sin x \right), \quad (8)$$

where $x = \theta/2$, $s = 2am/E_0$, $\sigma = bP \cos \beta/E_0$. The formula (8) expresses the potential energy of interacting substitute nonpunctual molecular electric dipoles (the dipoles A and B in Fig. 6) in the crystal of thiourea as a function of the angle of reorientation $\theta = 2x$. Formally, the energy U depends on three parameters: δ , s and σ , where $\delta > 1$.

Analyzing the diagrams of $U_w(x) = U(x)/2E_0 m$ the two cases were considered: I. $\sigma = 0$ and II. $\sigma \neq 0$.

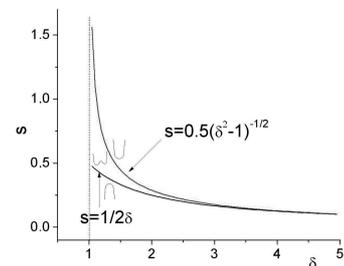


Fig. 7. The areas of existing different types of relationship $U_w(x)$ in coordinates δ and s .

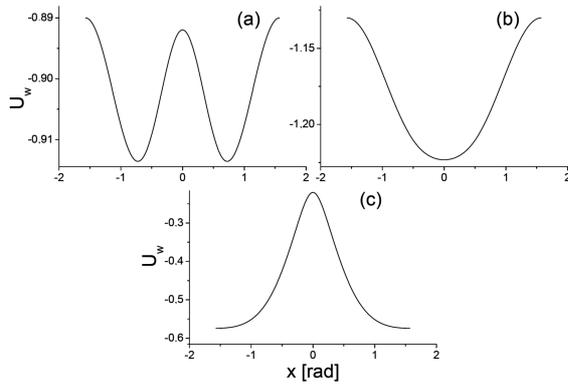


Fig. 8. The plots of the function $U_w(x)$ for selected values of parameters δ and s , for $\sigma = 0$. (a) $s = 0.45$ and $\delta^2 = 1.8$; (b) $s = 0.45$ and $\delta^2 = 2.5$; (c) $s = 0.45$ and $\delta^2 = 1.05$.

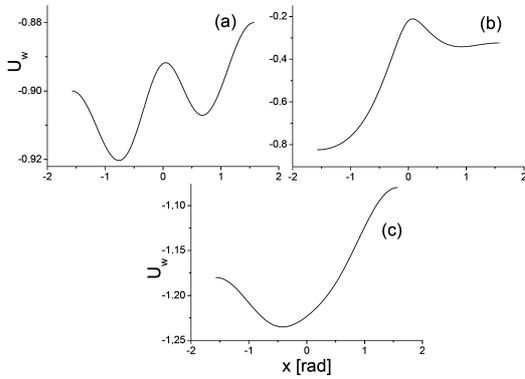


Fig. 9. The plots of $U_w(x)$ for selected values of the parameters δ , s and σ . (a) $\sigma = 0.01$, $s = 0.45$ and $\delta^2 = 1.8$; (b) $\sigma = 0.25$, $s = 0.45$ and $\delta^2 = 1.05$; (c) $\sigma = 0.05$, $s = 0.45$ and $\delta^2 = 2.5$.

- The case I: $\sigma = 0$. In this case we can draw a map in coordinates δ and s marking the areas within which a given type of diagram exists (Fig. 7). Exemplary diagrams are presented in Fig. 8.
- The case II: $\sigma \neq 0$. In this general case we can obtain different diagrams of the function $U_x(x)$. This situation is shown in Fig. 9.

Analysis of changes in $U_w(x)$ leads to a conclusion that diagram (a) in Fig. 9 is obtained under the following conditions:

$$s < (1 - \delta^{2/3})^{3/2} / 2(\delta^2 - 1)^{1/2}, \quad (9)$$

$$s > 0.5(1/\delta - \sigma), \quad (10)$$

$$s > 0.5(1/\delta + \sigma), \quad (11)$$

diagram (b) is obtained for

$$s < (1 - \sigma^{2/3})^{3/2} / 2(\delta^2 - 1)^{1/2}, \quad (12)$$

$$s > 0.5(1/\delta - \sigma), \quad (13)$$

$$s < 0.5(1/\delta + \sigma), \quad (14)$$

and diagram (c) for

$$s > (1 - \delta^{2/3})^{3/2} / 2(\delta^2 - 1)^{1/2}, \quad (15)$$

$$s > 0.5(1/\delta + \sigma). \quad (16)$$

3. Discussion

Thermodynamical theories of the ferroelectrics do not give an insight into the mechanism of this phenomenon, but fortunately are free from hypothetical assumptions. However, as we are interested in what happens inside the ferroelectric material, we wish to find such a mechanism of this phenomenon which would explain all hitherto unexplained evidence [6].

The ferroelectric properties of thiourea monocystal was theoretically described by many authors. Especially important are the articles by Calvo [5], Piekara [6, 7] and Piekara and Więckowski [8] emphasizing the great role of hydrogen bonds in this crystal and their influence on the effect of ferroelectricity. A very interesting theoretical model of the mechanism of the ferroelectric phase transitions in thiourea crystal was proposed by Futama [3], who suggested a special form of the potential energy of interaction between two different molecules in this crystal as a function of the angle of their mutual reorientation; this is the curve with several inequivalent minima. But the specific formulae have not been given. In the model presented in this paper the formula for the potential energy of interaction of two molecular dipoles was derived, under sensible assumptions, being in agreement with the structural research. Analyzing Figs. 7–9 we can deduce several possible mechanisms of creation of different ferroelectric, antiferroelectric and paraelectric phases. This model implies that different phases are related to different values of distances between the dipoles. The distance between the interacting dipoles is described by the parameter $\delta = L/d$.

For example, from Eqs. (9)–(16) it follows that the two nonequivalent minima of the potential energy for $\sigma = 0$ can be created only if the following inequality is fulfilled:

$$\frac{1}{4s^2} < \delta^2 < 1 + \frac{1}{4s^2}, \quad (17)$$

but the condition of existence of a single minimum, for $\theta = 0$, has the form

$$\delta^2 > 1 + \frac{1}{4s^2}. \quad (18)$$

For $\sigma \neq 0$ two inequivalent minima of the potential energy can appear if

$$\frac{1}{(2s - \sigma)^2} < \delta^2 < 1 + \frac{(1 - \sigma^{2/3})^3}{4s^2}, \quad (19)$$

and a single minimum exists under the condition

$$\delta^2 > 1 + \frac{(1 - \sigma^{2/3})^3}{4s^2}. \quad (20)$$

This distance depends on temperature, and its anomalous temperature dependence has been studied by Futama [3]. The general problem of dependence of the number of phase transitions upon the form of the intermolecular interactions was described by Hoyer and Hemmer [9] and it seems to be of universal character. The distances between the molecules of thiourea and thus the ferroelectric phase transitions are also affected by the hydrostatic pressure which was discovered by Gesi [10] and Klimowski et al. [11, 12]. The effect of the high hydrostatic pressure on the phase transitions in thiourea was studied by using the Raman scattering method in the article of Banerji and Deb [13]. Similar effects in thiourea can be expected under the influence of the gamma radiation. The effect of the gamma radiation on the phase transitions in thiourea was studied in the articles by Wanarski and Zagórski [14] and Wanarski [15].

4. Conclusions

In this paper the assumption that the dipoles of the molecules are of finite length and that they can perform reorientations only within given constraints, has led to the unconventional form of the potential energy of interaction between these dipoles in the crystal as a function of the angle between them, with one or two minima. From the simple numerical analysis it follows that the difference in the values of the two inequivalent minima of the potential energy of interaction of two nonpunctual molecular electric dipoles in thiourea crystal depends on

the polarization of the crystal. It gives a possibility to apply such a model for description of different ferroelectric and antiferroelectric states.

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