

# OPTICAL AND DILATOMETRIC PROPERTIES OF $(\text{CH}_3)_2\text{NH}_2\text{Al}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ CRYSTALS IN PARAELECTRIC AND FERROELECTRIC PHASES

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Experimental investigation of the thermal linear expansion  $l(T)$  and temperature dependencies of the interference optical path difference  $D(T)$  were carried out for  $(\text{CH}_3)_2\text{NH}_2\text{Al}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  crystal, in the range of 120–310 K for three crystal physical directions. Decrease in electrostriction coefficients  $g$  of crystal was observed on approaching the phase transition point  $T_c \approx 150$  K in ferroelectric phase. Relative temperature changes of the lengthening  $\delta l/l$  and refractive index  $\delta n/(n-1)$  are of the same order of magnitude. Peculiarities of temperature dependence of dilatometric and optical parameters of  $(\text{CH}_3)_2\text{NH}_2\text{Al}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  testify for qualitative reconstruction of chemical bonds in the crystal when temperature changes in the same phase.

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## 1. Introduction

Crystal of dimethylammonium aluminium sulphate hexahydrate  $(\text{CH}_3)_2\text{NH}_2\text{Al}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  (DMAAS) has been widely studied recently by different experimental methods [1–8]. It undergoes ferroelectric phase transition (PT) of second order  $2/m \rightarrow m$  at  $T_c = 150$  K. The transition is associated with ordering of DMA cations when instead of four bonds averaged in time only two more strong N–H...O bonds appear. This leads to the rearrangement of  $(\text{SO}_4)^{2-}$  tetrahedra, which come closer to DMA cations. In such a case noncompensated dipoles arise, which is followed by the appearance of the microscopic polarization [1].

The nature of ferroelectric and ferroelastic phases has been drawn from the investigations of dielectric [2–4], birefringence [2, 5], dilatometric [6], piezoelectric [7], electro- and piezooptic [8] properties of DMAAS. Temperature dependencies of

refractive indices of DMAAS in the range of ferroelectric phase transition have not been investigated till now. One of the aims of the present paper is the study of temperature dependencies of refractive indices of DMAAS in the range of ferroelectric phase transition using the interference optical method [9]. Such an investigation gives information on the temperature behaviour of electron subsystem of a crystal in the range of phase transition.

## 2. Experimental

Temperature dependencies of the optical path difference  $D = (n - 1)l$  for two interfering light beams, one of which has passed through a sample studied, and the other one through air, were measured with the help of the Jamen type interferometer using a monochromatic light  $\lambda = 632.8$  nm [9]. The error of determination of relative retardation  $\delta D/D$  was of  $\approx 10^{-5}$  order of magnitude. For determination of temperature changes of the principal refractive indices  $n_i$  ( $i = 1, 2, 3$ ) of DMAAS crystals the experimental measurements of its thermal linear expansion were conducted using the known electrical capacitive method with accuracy of  $\delta l/l \approx 10^{-5}$ , where  $l$  is the initial length of a sample [10].

## 3. Results and discussion

Results of dilatometric measurements of DMAAS crystals for three orthogonal principal crystal physical directions  $X \equiv 1 \equiv n_p$ ,  $Y \equiv 2 \equiv n_m$ ,  $Z \equiv 3 \equiv n_g$ , showed anomalies characteristic of second order PT (Fig. 1). Positive coefficient of thermal linear expansion  $\alpha_2$  is characteristic only of  $Y$ -direction coinciding with twofold axes  $L^2$  of the  $2/m$  point group of symmetry of crystal in paraelectric (PE) phase. Negative coefficients of thermal linear expansion  $\alpha_1$ ,  $\alpha_3$  are peculiar for  $X$ - and  $Z$ -direction. Taking into account a known relation between coefficients of volume  $\gamma$  and linear  $\alpha$  thermal expansion

$$\gamma = \alpha_1 + \alpha_2 + \alpha_3, \quad (1)$$

one can summarise a negative coefficient of thermal volume expansion  $\gamma$  for DMAAS in the temperature range of 120–310 K (Fig. 2). This reflects a compacting of the crystal structure of DMAAS at the increase in temperature.

The results described agree with the data of [6] by the character of temperature anomalies at  $T_c \approx 150$  K and by the sign of  $\alpha_2$  coefficient. Our results show only negative coefficients  $\alpha_1 < 0$  and  $\alpha_3 < 0$ . This does not contradict the results of the paper [6], in which the coefficients  $\alpha'_1$  and  $\alpha'_3$  for other two mutually perpendicular directions  $X'$  and  $Z'$  in the same plane of crystal's symmetry  $XZ \equiv X'Z'$  are characterised by different signs,  $\alpha_{X'} < 0$  and  $\alpha_{Z'} > 0$  ( $X'$  is the direction of spontaneous polarization in DMAAS). Negative coefficient  $\gamma$  of thermal volume expansion was detected in [6] for DMAAS, too.

One can see clear shoulder on the temperature dependence of the thermal linear expansion coefficient  $\alpha_2(T)$  at  $T \approx 125$  K besides big extrema of  $\alpha_i(T)$  at  $T_c$  (Fig. 2). Similar anomaly was observed here on the temperature dependencies of dielectric loss tangent  $\tan \delta(T)$  [11] and was explained by the formation of some new domain structure or diminishing space regions of correlated dipoles caused by "freezing" of H-bonds under an influence of spontaneous polarization.

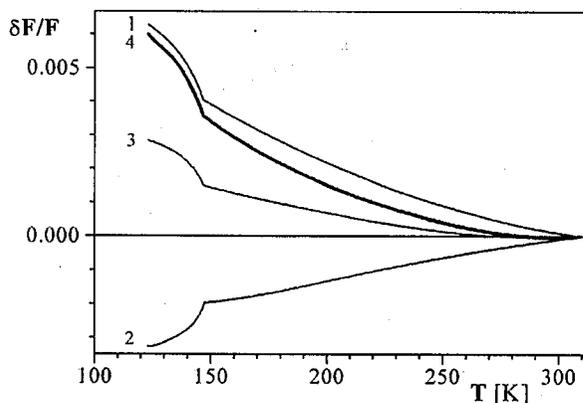


Fig. 1. Temperature dependencies of relative changes of linear dimensions of  $\delta F/F = \delta l/l$  along three crystal physical directions  $X$  (1),  $Y$  (2),  $Z$  (3) and volume  $\delta F/F = \delta V/V$  (4) for DMAAS crystal.

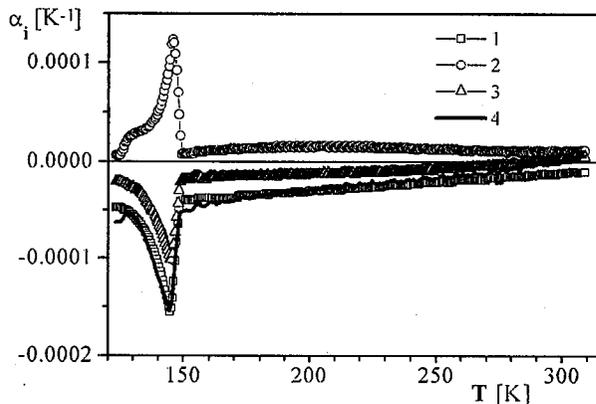


Fig. 2. Temperature dependencies of principal coefficients of linear thermal expansion  $\alpha_1$  (1),  $\alpha_2$  (2), and  $\alpha_3$  (3) and coefficient of volume thermal expansion  $\gamma$  (4) for DMAAS crystal.

On the basis of data presented in Fig. 1 we derived temperature dependencies of spontaneous increases in relative expansions  $\delta l_i^{(s)}/l_i$  ( $i = 1, 2, 3$ ), subtracting the linearly approximated temperature dependencies of  $\delta l_i/l_i$  from paraelectric phase into ferroelectric one from such dependencies measured in ferroelectric phase. The temperature dependence of  $\delta l_2^{(s)}/l_2 = f(T)$  (as an example) obtained by such a way is shown in Fig. 3. Taking into account that the paraelectric phase is characterised by the center of symmetry, one can state that the spontaneous lengthenings  $\delta l_i^{(s)}/l_i$  are caused by electrostriction effect

$$\delta l_i^{(s)}/l_i = g_i P_s^2, \quad (2)$$

where  $P_s$  is spontaneous polarization, and  $g_i$  are corresponding electrostriction coefficients. Presenting a temperature dependence of spontaneous polarization  $P_s(T)$

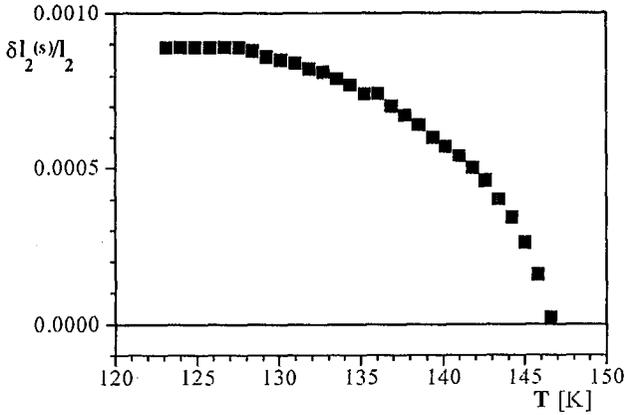


Fig. 3. Temperature dependence of spontaneous relative change of linear dimension of  $\delta l_2^{(s)}/l_2$  for DMAAS crystal.

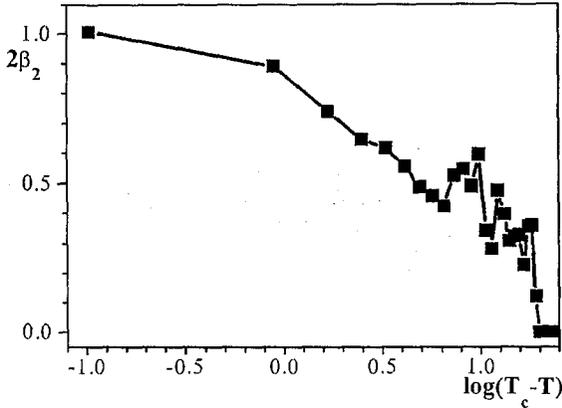


Fig. 4. Temperature dependence of derivative for spontaneous relative change of linear dimension of  $\delta l_2^{(s)}/l_2$  in log-log presentation for DMAAS crystal.

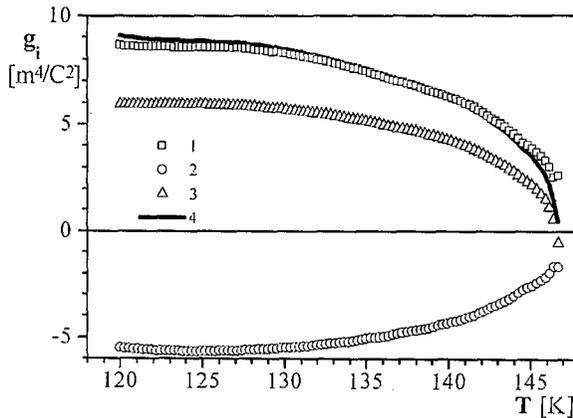


Fig. 5. Temperature dependencies of linear  $g_1$  (1),  $g_2$  (2),  $g_3$  (3) and volume  $g_V$  (4) electrostriction coefficients for DMAAS crystal.

in the form of power dependence [9]:

$$P_s \sim (T_c - T)^\beta, \quad (3)$$

relation (2) can be written in the form

$$\delta l_i^{(s)}/l_i = g_i P_s^2 = a(T_c - T)^{2\beta}. \quad (4)$$

Here  $\beta$  is a characteristic index of corresponding power-like temperature dependencies, and  $a$  is some temperature independent coefficient. Taking a logarithm of relation (4), one obtains the relation

$$\log[\delta l_i^{(s)}/l_i] = 2\beta_i \log(T_c - T) + \log a. \quad (5)$$

By means of differentiating of this equation we can calculate the double index  $2\beta_i$ :

$$2\beta_i = d/d[\log(T_c - T)]\{\log[\delta l_i^{(s)}/l_i]\}. \quad (6)$$

The temperature dependence of derivative (6) for  $i = 2$  is presented in Fig. 4. It is seen from this figure that double index  $2\beta_2$  decreases with the increase in the temperature difference  $(T_c - T)$ . Similar temperature behaviour of the  $2\beta_i$  indices is characteristic of other two principal crystal directions ( $i = 1, 3$ ). This result is in good agreement with the data [3] of temperature investigation of spontaneous polarization. Thus, power-like temperature dependence of the relative spontaneous lengthenings  $\delta l_i^{(s)}/l_i \sim (T_c - T)^{2\beta_i}$  describes unsatisfactorily corresponding experimental results on DMAAS in the relatively narrow temperature range  $(T_c - T) < 10$  K, which implies in the decreasing double index  $2\beta$  at increasing  $(T_c - T)$ .

The results obtained can be presented in another viewpoint. Using our previous data on the temperature dependence  $P_s(T)$  of DMAAS [3], and our present data on  $\delta l_i^{(s)}/l_i(T)$ , we calculated the temperature dependencies of coefficients of linear and volume electrostriction,  $g_i(T)$  and  $g_V(T) = \sum g_i(T)$ , respectively (Fig. 5). The main peculiarity of these dependencies decreases the absolute magnitude of electrostriction coefficients of DMAAS crystal at approaching  $T_c$  in ferroelectric phase.

Phase transition in DMAAS at  $T_c \approx 150$  K is also clearly implied on the temperature dependencies of the relative changes of optical path difference  $\delta D/D$  related to the variable part of refractive index  $(n - 1)$  in the form of anomalies, which are characteristic of second order PTs (Fig. 6). Since the relative changes of optical path difference  $D_{ij} = (n_i - 1)l_j$  of sample measured can be presented in the form

$$\frac{\delta D_{ij}}{D_{ij}} = \frac{\delta n_i}{n_i - 1} + \frac{\delta l_j}{l_j}, \quad (7)$$

we calculated the temperature dependencies of  $\delta n_i/(n_i - 1)$  (Fig. 7) on the basis of temperature dependencies of  $\delta D_{ij}/D_{ij}$  and  $\delta l_j/l_j$  measured. Here  $n_i$  are principal refractive indices of a sample ( $i = 1, 2, 3$ ). Taking into account the relation between refractive index  $n$  and electron susceptibility  $\chi$ ,  $n^2 - 1 = \chi$ , one can see that for  $n = 1.5$  relative temperature changes of  $\delta n/(n - 1)$  and  $\delta \chi/\chi$  are almost equal one to another:  $\delta \chi/\chi = 2n\delta n/(n^2 - 1) = 1.2\delta n/(n - 1) \approx \delta n/(n - 1)$ .

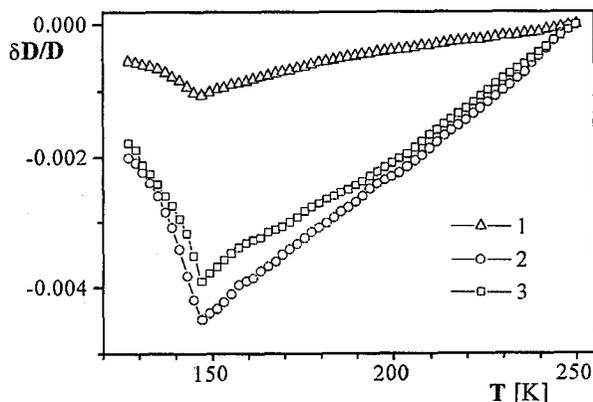


Fig. 6. Temperature dependencies of relative changes of optical path differences  $\delta D_{21}/D_{21}$  (1),  $\delta D_{32}/D_{32}$  (2), and  $\delta D_{12}/D_{12}$  (3) for DMAAS crystal.

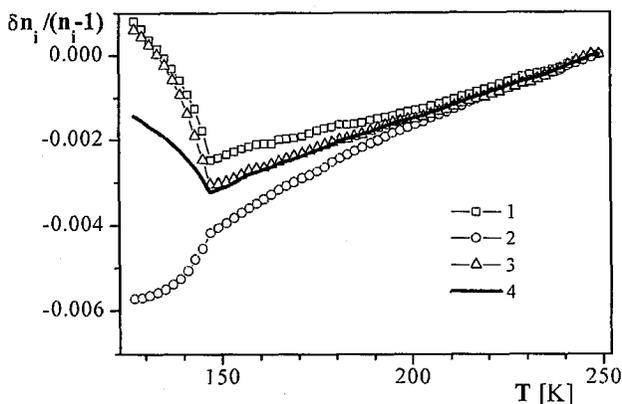


Fig. 7. Temperature dependencies of relative changes of the variable part of refractive indices  $\delta n_1/(n_1 - 1)$  (1),  $\delta n_2/(n_2 - 1)$  (2), and  $\delta n_3/(n_3 - 1)$  (3) and variable part of the averaged refractive index (4) for DMAAS crystal.

It is seen from Fig. 6 that three temperature dependencies of the relative changes of optical path differences  $\delta D_{ij}/D_{ij}$  measured are characterised by the sharp changes of temperature slope at  $T_c$ . Similar temperature dependencies are peculiar for the relative changes of variable part of refractive index  $\delta n_i/(n_i - 1)$  along  $X$ - and  $Z$ -directions of the crystal ( $i = 1, 3$ ) (Fig. 7). Positive temperature derivatives of  $d/dT[\ln(n_i - 1)] = (n_i - 1)^{-1} dn_i/dT$  is peculiar for  $Y$ -direction in the whole temperature range studied. The average coefficients of thermal linear expansion  $\alpha_i = d/dT(\ln l_i)$ , volume expansion  $\gamma = \sum \alpha_i$ , and temperature changes of variable part of refractive indices  $d/dT[\ln(n_i - 1)]$  and  $\sum d/dT[\ln(n_i - 1)]/3$  of DMAAS are presented in Table.

One can see from Figs. 1, 7 and from Table that the relative temperature changes of characteristic parameters of electron subsystem and dimensions of crystal's unit cell of DMAAS in the paraelectric phase are of the same order of magnitude.

TABLE

Coefficients of thermal linear expansion  $\alpha_i = d/dT(\ln l_i)$ , volume expansion  $\gamma = \sum \alpha_i$ , and temperature changes of variable part of refractive indices  $d/dT[\ln(n_i - 1)]$  and  $\sum d/dT[\ln(n_i - 1)]/3$  of DMAAS averaged in the range of paraelectric phase 249–147 K.

Crystal physical direction $i$ of DMAAS	$\frac{dl_i}{l_i dT}$ [K <sup>-1</sup> ]	$\frac{dn_i}{(n_i - 1)dT}$ [K <sup>-1</sup> ]
1 $\equiv$ X	$-2.3 \times 10^{-5}$	$2.4 \times 10^{-5}$
2 $\equiv$ Y	$1.2 \times 10^{-5}$	$4.1 \times 10^{-5}$
3 $\equiv$ Z	$-0.8 \times 10^{-5}$	$3.0 \times 10^{-5}$
V	$-1.9 \times 10^{-5}$	$3.2 \times 10^{-5}$

Taking into account the known relation for dispersion of electron part of the refractive index  $n(\omega)$  [12],

$$n(\omega) - 1 \sim \frac{N}{V} \sum_k \frac{|D_{nk}|^2 \omega_{nk}}{\omega_{nk}^2 - \omega^2}, \quad (8)$$

one can state a proportionality of the refractive index  $n$  to the sum of squares of dipole moments  $|D_{nk}|^2$  of optical transitions being the parameters of chemical bonds strength in crystal.

Relation (8) shows that refractive index  $n$  is inversely proportional to the volume  $V$  of crystal unit cell. This peculiarity is also a consequence of known relation for molecular refraction  $R$ :

$$R = \frac{(n^2 - 1)M}{(n^2 + 2)\rho} \sim nV = \text{const}, \quad (9)$$

where  $M$  is molecular weight, and  $\rho$  is density of a substance [12]. The latter relation realises very accurately for gases in wide ranges of variables  $n$  and  $\rho$ , even in the ranges including different aggregate states of corresponding substances. Therefore, the joint analysis of temperature dependencies of spatial parameters of crystal ( $V, l_i$ ) and corresponding variable parts of refractive index  $\delta n_i/(n - 1)$  (as one of the characteristics of chemical bonds) can be useful for finding the experimental criteria of structure instability of crystals. From the viewpoint presented above, an equality of signs of the thermal volume expansion coefficient  $\gamma = \sum d/dT(\ln l_i)$  and the temperature derivative of variable part of refractive indices  $d/dT[\ln(n_i - 1)]$  for any of the three crystal physical directions  $i$  in paraelectric phase can be as the mark of relative instability of chemical bonds of crystal in the corresponding direction. In the paraelectric phase of DMAAS negative coefficient  $\gamma$  and positive temperature derivatives  $d/dT[\ln(n_i - 1)]$  for  $i = 1, 2, 3$  take place, which does not correspond to the proposed mark of instability of chemical bonds. But the signs of the coefficient  $\alpha_2 = d/dT(\ln l_2)$  and the derivative  $d/dT[\ln(n_2 - 1)]$  are equal (see Table). These coincide one to another even in the whole temperature range studied 120–250 K. It is evident that an equality of the signs of coefficient of thermal linear expansion  $d/dT(\ln l_2)$  and temperature derivative of variable part of refractive index  $d/dT[\ln(n_2 - 1)]$  for the crystal physical Y-direction of DMAAS and opposite signs of these parameters for the X- and Z-directions in PE

phase proves for qualitative reconstruction of chemical bonds in the crystal when temperature changes in the frame of the same phase.

#### 4. Conclusions

1. Power-like temperature dependence of the relative spontaneous lengthenings  $\delta l_i^{(s)}/l_i \sim (T_c - T)^{2\beta_i}$  describes unsatisfactorily corresponding experimental results on DMAAS in the relatively narrow temperature range  $(T_c - T) < 10$  K, which implies in the decreasing double index  $2\beta$  at increasing  $(T_c - T)$ .

2. Electrostriction coefficients  $g$  ( $\delta l_i^{(s)}/l_i = g_i P_s^2$ ) of DMAAS crystal decrease at approaching the phase transition point  $T_c$  in ferroelectric phase.

3. The relative temperature changes of characteristic parameters of electron subsystem of DMAAS are of the same order of magnitude, that are respective changes for the dimensions of crystal's unit cell.

4. An equality of the signs of coefficient of thermal linear expansion  $d/dT(\ln l_2)$  and temperature derivative of variable part of refractive index  $d/dT[\ln(n_2 - 1)]$  for the crystal physical  $Y$ -direction of DMAAS and opposite signs of these parameters for the  $X$ - and  $Z$ -directions in PE phase proves for qualitative reconstruction of chemical bonds in the crystal when temperature changes in the same phase.

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