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The mechanism of the phase transition in $(\text{CH}_3)_2\text{NH}_2\text{Al}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ studied by EPR of Cr^{3+}

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Received 30 October 1998

Abstract. The electron paramagnetic resonance (EPR) spectra of Cr^{3+} impurity in the ferroic $(\text{CH}_3)_2\text{NH}_2\text{Al}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ monocrystals have been studied in the 80–400 K temperature range with an X-band spectrometer. The spin-Hamiltonian parameters determined at RT are: $D = 0.0923 \text{ cm}^{-1}$, $E = -0.0070 \text{ cm}^{-1}$, $g_x = 1.9736$, $g_y = 1.9749$ and $g_z = 1.9715$. Temperature dependence measurements of these parameters give useful information about the water molecule behaviour. The ferroelectric phase transition (PT) at $T_c = 152 \text{ K}$ is most probably evoked indirectly by slowing down of rotation and reorientation of the H_2O units. A model of the PT is proposed.

1. Introduction

In spite of numerous techniques used to study the $(\text{CH}_3)_2\text{NH}_2\text{Al}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ (DMAAS) crystals, the mechanism of the phase transition at $T_c = 152 \text{ K}$ is still not fully clear. We have performed the EPR and dielectric investigations of DMAAS with several paramagnetic probes [1, 2]. The data for one of them are presented in this paper.

The $(\text{CH}_3)_2\text{NH}_2\text{Al}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ crystal belongs in the monoclinic high temperature phase to the space group $P2_1/n$ [3]. On cooling DMAAS transforms from ferroelastic to ferroelectric phase with symmetry change $2/m \rightarrow m$ at 152 K. At room temperature (RT) the crystal exhibits ferroelastic properties [4]. The unit cell, with parameters $a = 6.403 \text{ \AA}$, $b = 10.747 \text{ \AA}$, $c = 11.128 \text{ \AA}$, $\beta = 100.47^\circ$, consists of two formula units, $Z = 2$. The crystal structure is built of Al^{3+} cations coordinating six water molecules hydrogen bonded to oxygen atoms of SO_4 tetrahedra. The dimethylammonium cation (DMA) is located in a vacancy surrounded by SO_4 groups. The $[(\text{CH}_3)_2\text{NH}_2]^+$ ions are disordered in such a way that a rotation of dimethylammonium takes place around the axis defined by two carbon atoms. This rotation is hampered by the hydrogen bond $\text{O} \cdots \text{H}-\text{N}$. Finally there exist four positions of NH_2 groups related in pairs to each other by a symmetry centre, with occupancy parameters of about 0.4 and 0.1. Despite numerous studies of the DMAAS crystal [4–7] there is no agreement about the role of the water molecules and SO_4^{2-} ions in the ferroelectric phase transition.

Recently we have reported the EPR data of the $\text{H}-\text{N}(\text{CH}_3)_2$ radical [1], formed by x-irradiation, used by us to study the ferroelectric phase transition. We have shown that the EPR spectrum of $\text{H}-\text{N}(\text{CH}_3)_2$ does not change at T_c , but at about 110 K each EPR line is gradually split. This means that the DMA radical with one broken hydrogen bond freezes its motion in two magnetically equivalent but structurally nonequivalent positions.

The aims of the present work are investigations of the water molecule behaviour in the ferroic phases. In order to handle this we have doped the DMAAS crystal with the Cr^{3+} ($S = 3/2$) ions. Because, the spin-Hamiltonian parameters such as the zero-field splitting are sensitive to changes in local crystal fields, the electron spin resonance of Cr^{3+} is used to probe changes which should occur near the structural phase transition.

2. Experimental procedure

Colourless, transparent monocrystals of $(\text{CH}_3)_2\text{NH}_2\text{Al}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}:\text{Cr}^{3+}$ were grown by a method described in [8]. The DMAAS: Cr^{3+} crystals were next investigated with an X-band EPR spectrometer operating with a liquid-nitrogen system of temperature control and stabilization of order 0.5 K in the temperature range 80–420 K. The XYZ orthogonal laboratory frame chosen for the EPR anisotropy pattern was related to the a , b , c crystallographic axes [3] as follows: $Z \parallel c$, $Y \parallel b$, $X \parallel (b \times c)$.

3. Experimental results

3.1. The EPR spectrum analysis at room temperature

Figure 1 shows the EPR spectrum of Cr^{3+} -doped DMAAS consisting of two (A and B) structurally nonequivalent complexes, with the static magnetic field \mathbf{B} parallel to the crystallographic c -axis. The EPR spectrum of Cr^{3+} is described in terms of a spin-Hamiltonian of the form:

$$\hat{H} = \mu_{\beta} \hat{\mathbf{S}} \mathbf{g} \mathbf{B} + D(\hat{S}_z^2 - \frac{1}{2}S(S+1)) + E(\hat{S}_x^2 + \hat{S}_y^2) \quad (1)$$

where μ_{β} is the Bohr magneton, \mathbf{g} is the spectroscopic tensor, D and E are the axial and rhombic zero-field splitting parameters respectively. For our nonaxial case the general solution of the eigenvalue problem is simple for the static magnetic field to be parallel to one of the main axes of the crystal field gradient tensor. Finally we can obtain the following energy levels for the

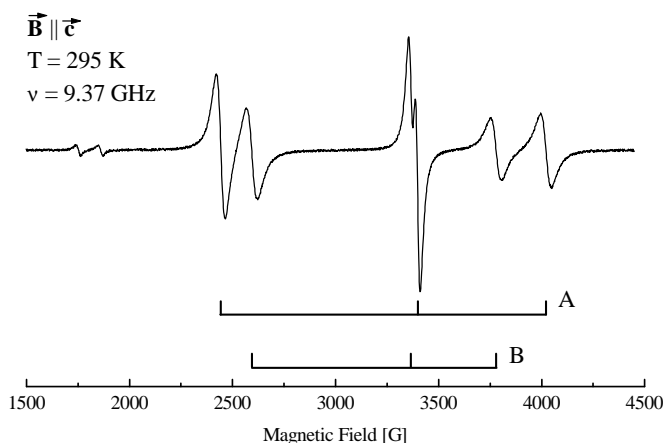


Figure 1. EPR spectrum of Cr^{3+} ions in DMAAS at 295 K for the magnetic field directed along the c -axis.

principal axes of the crystal field:

$$B \parallel z$$

$$W(\pm \frac{3}{2}) = \pm g_z \mu_\beta B + \sqrt{(D \pm g_z \mu_\beta B)^2 + 3E^2} \quad (2a)$$

$$W(\pm \frac{1}{2}) = \mp g_z \mu_\beta B - \sqrt{(D \mp g_z \mu_\beta B)^2 + 3E^2}$$

$$B \parallel y$$

$$W(\pm \frac{3}{2}) = \pm g_y \mu_\beta B \pm \sqrt{g_y^2 \mu_\beta^2 B^2 + D^2 + 3E^2 \mp g_y \mu_\beta B(D + 3E)} \quad (2b)$$

$$W(\pm \frac{1}{2}) = \mp g_y \mu_\beta B \pm \sqrt{g_y^2 \mu_\beta^2 B^2 + D^2 + 3E^2 \pm g_y \mu_\beta B(D + 3E)}$$

$$B \parallel x$$

$$W(\pm \frac{3}{2}) = \pm g_x \mu_\beta B \pm \sqrt{g_x^2 \mu_\beta^2 B^2 + D^2 + 3E^2 \mp g_x \mu_\beta B(D - 3E)} \quad (2c)$$

$$W(\pm \frac{1}{2}) = \mp g_x \mu_\beta B \pm \sqrt{g_x^2 \mu_\beta^2 B^2 + D^2 + 3E^2 \pm g_x \mu_\beta B(D - 3E)}.$$

The angular dependence of the EPR line positions versus magnetic field allows us to obtain the spin-Hamiltonian parameters and direction cosines of the tensors. In tables 1 and 2 we have presented the parameters evaluated from equations (2a)–(2c) and the direction cosines, respectively. Figure 2 shows the angular dependences of the A and B lines in DMAAS:Cr³⁺ as a function of rotation in the $z_A x_A$ main gradient field plane. As can be seen there is an excellent agreement of the experimental and theoretical results obtained from the numerical procedure used for fitting of the general equation:

$$W^4 - W^2(\frac{5}{2}G^2 + 2D^2 + 6E^2) + WG^2(2D - 6D \cos^2 \theta - 6E \sin^2 \theta \cos 2\phi) + \frac{9}{16}G^4$$

$$+ \frac{1}{2}G^2(D^2 - 6D \cos^2 \theta + 9E^2 \cos 2\theta + 12ED \sin^2 \theta \cos 2\phi)$$

$$+ (D^2 + 3E^2)^2 = 0 \quad (2d)$$

Table 1. Spin-Hamiltonian parameters evaluated at RT (295 K).

| Centre | D [cm ⁻¹] | E [cm ⁻¹] | g_z | g_y | g_x |
|---------|-------------------------|-------------------------|--------------------|--------------------|--------------------|
| A | 0.0923 (0.0004) | -0.0068 (0.0003) | 1.9718 (0.0005) | 1.9743 (0.0008) | 1.9736 (0.0003) |
| B | 0.0923 (0.0006) | -0.0071 (0.0005) | 1.9712 (0.0004) | 1.9755 (0.0007) | 1.9735 (0.0002) |
| average | 0.0923 | -0.0070 | 1.9715 | 1.9749 | 1.9736 |

Table 2. Direction cosines of two types of Cr³⁺ ions in DMAAS:Cr³⁺ at RT.

| Centre | Main axes of the complex | Direction cosines | | |
|--------|-----------------------------|-------------------|--------|--------|
| | | X | Y | Z |
| A | x_A | -0.389 | 0.622 | -0.679 |
| | y_A | 0.119 | 0.765 | 0.633 |
| | z_A | 0.914 | 0.165 | -0.372 |
| B | x_B | 0.387 | 0.771 | 0.507 |
| | y_B | -0.054 | 0.568 | -0.822 |
| | z_B | 0.921 | -0.290 | -0.262 |

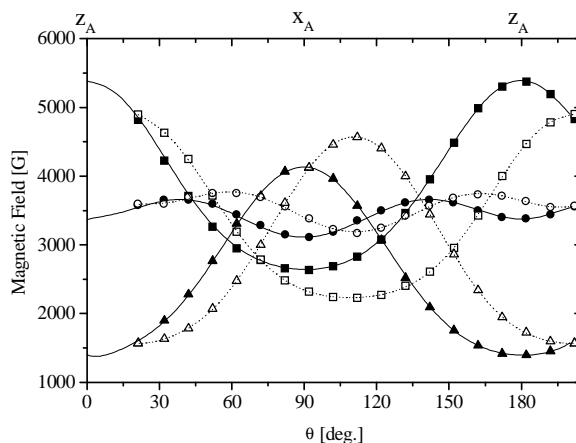


Figure 2. The angular dependence of the Cr^{3+} resonance fields in DMAAS in the $x_A z_A$ main gradient field plane at RT. The filled symbols denote experimental data for the A-type complex, while smooth lines present results calculated according to the theory, open symbols connected by dashed lines denote experimental data for the B-type complex.

where θ, ϕ are polar and azimuth angles of \mathbf{B} with respect to the main crystal field axes and $G_i = g_i \mu_\beta B_i$ ($i = x, y, z$).

3.2. Temperature dependence of the crystal field parameters

Figures 3(a) and 3(b) show the axial and rhombic zero-field splitting parameter behaviour versus temperature. The experimental points were obtained from the EPR spectra records for the static magnetic field parallel to the z_A and x_A principal axes determined at RT (see table 1) and by using equations (2a) and (2c). Solid lines present fits of the D and E parameters changes.

3.3. EPR line broadening

The broadening of resonances as T_c is approached is attributed by us to fluctuations in the fine-structure tensor associated with fluctuations of the orientations of the water dipoles. These fluctuations should be driven by order parameter β . In accord with Landau theory of the second order phase transition near the tricritical point [9] the order parameter versus temperature dependence should change as $\beta^4 \sim (T_c - T)$ and susceptibility as $\chi(0) \sim (T_c - T)^{-4\beta}$ with $\beta = 0.25$. The linewidth anomaly $\Delta B_{pp} \sim \chi(0)$ is presented in figure 4 and below T_c is well described by the equation:

$$\Delta B_{pp}(T) = \Delta B_{pp}(0) \left[1 + \left(\frac{T_c - T}{T_c} \right)^{-4\beta} \right] \quad (3)$$

with $\beta = 0.25$.

4. Discussion and conclusions

In order to describe the temperature dependences of the crystal field parameters we have used the theory successfully applied to description of Cr^{3+} in a class of materials called alums [10].

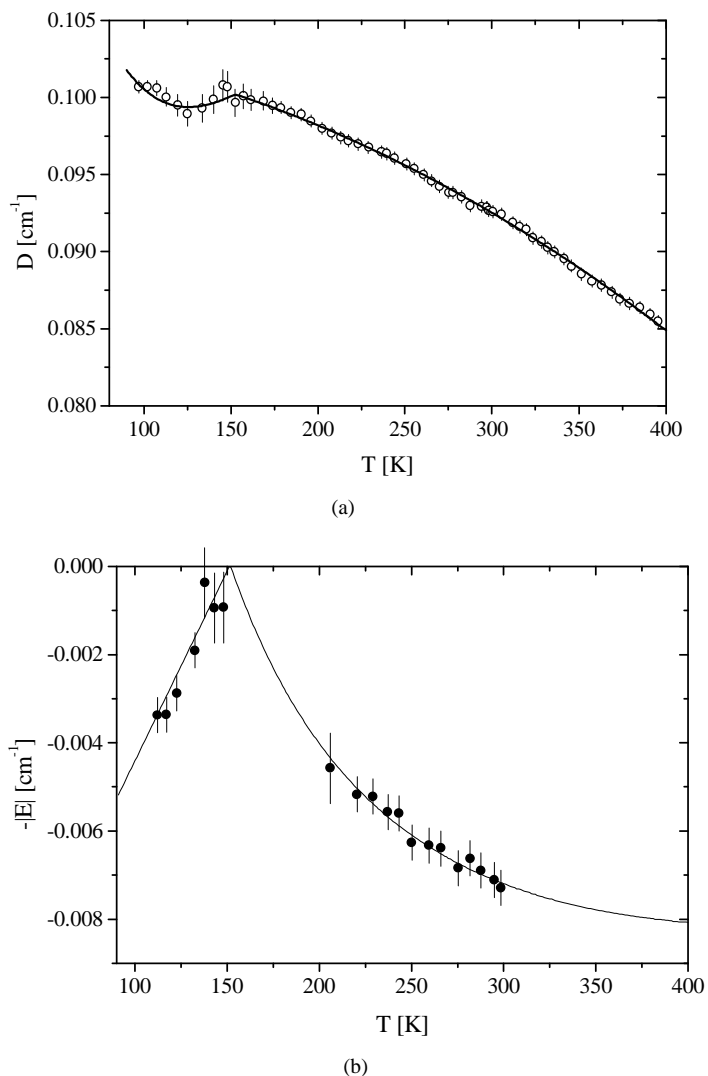


Figure 3. The temperature dependences of the spin-Hamiltonian parameters; (a) axial zero-field splitting parameter; (b) nonaxial zero-field splitting parameter.

The structural data [3] and the anisotropy studies indicate that each Cr^{3+} ion is surrounded by six water molecules (Cr^{3+} replaces Al^{3+}) in a slightly disordered octahedral array. The dipole moments, P , of the H_2O attached the Cr^{3+} ion are tilted at an angle α with respect to the principal axes of the octahedron. The magnitude of the D -parameter can be related to the V_{zz} -component of the electric field gradient by the relation [11]:

$$D = \frac{3}{7} \left(\frac{\lambda}{\Delta} \right)^2 \langle r^2 \rangle V_{zz} \quad (4)$$

where λ is the spin-orbit coupling constant, Δ is the energy difference between the ground 4A_2 and first excited 4T_2 state and $\langle r^2 \rangle$ is the average value for the $3d(Cr^{3+})$ wavefunction.

If one assumes that the dominant contribution to the electric field gradient arise from the

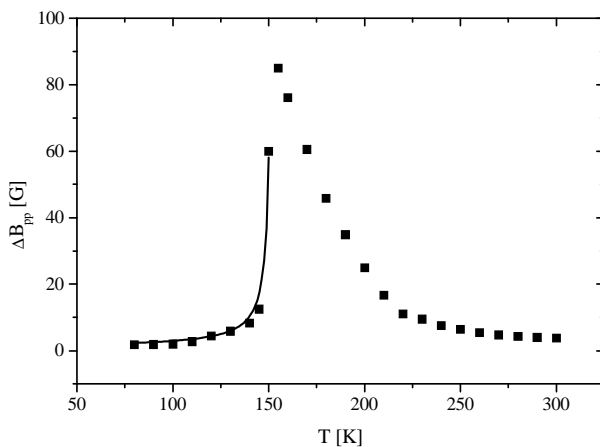


Figure 4. Linewidth of the Cr^{3+} ($1/2 \leftrightarrow -1/2$) in DMAAS versus temperature (symbols: experimental points; solid line: fit according to Landau theory).

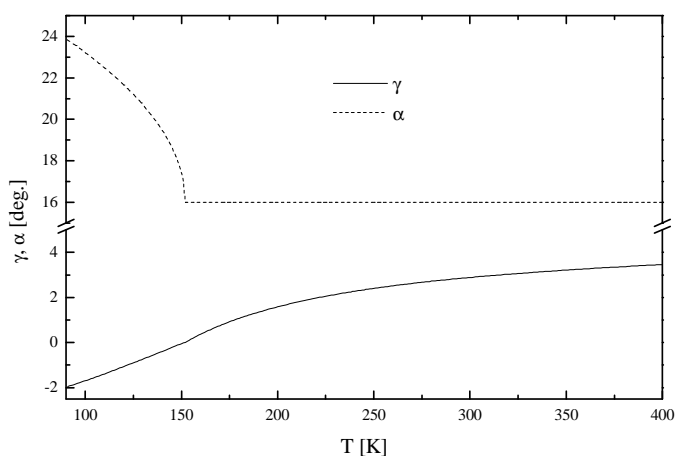


Figure 5. Temperature dependence of the γ - and α -angles.

coordinating water molecules, then V_{zz} is given by:

$$V_{zz} = -\frac{18P}{a^4}(3 \cos^2 \gamma - 1) + \frac{12P}{a^4} \sin \alpha \quad (5)$$

where γ is an angle between the octahedron direction (111) and the main gradient field (z -axis) and the a -parameter is the Cr^{3+} - H_2O distance.

The γ -value can be evaluated from the ratio of nonaxiality E/D of the crystal field according to:

$$\frac{E}{D} = \frac{1 - 3 \cos^2(\gamma_0 - \gamma)}{3 \sin^2(\gamma_0 - \gamma) \cos(2\phi)} \quad (6)$$

where the $\gamma_0 \cong 54.7^\circ$ (pure axial case) and the ϕ is an angle between the x crystal field axis and the external magnetic field B_0 . In figure 5 we present the γ -angle change versus temperature in accord with equation (6), where the E/D -ratios were obtained from fits of $D(T)$ and $E(T)$ presented in figures 3(a) and 3(b) respectively.

If we transform the equation (4) to the simple form:

$$|D| = |D_\gamma - D_\alpha| \tag{7}$$

then,

$$D_\gamma = -\frac{54}{7} \left(\frac{\lambda}{\Delta}\right)^2 \frac{P}{a^4} \langle r^2 \rangle (3 \cos^2 \gamma - 1) \tag{8a}$$

$$D_\alpha = -\frac{36}{7} \left(\frac{\lambda}{\Delta}\right)^2 \frac{P}{a^4} \langle r^2 \rangle \sin \alpha. \tag{8b}$$

We have to take into consideration that the experimental value of the D -parameter (figure 3(a)) consists of three components: D_γ due to changing of the V_{zz} -direction, D_α due to dipole moment projection and D_{vibr} due to lattice vibrations. We are able to evaluate D_γ directly from the anisotropy pattern at several temperatures and equation (8a). The D_α -values were obtained from equation (8b). The α -angle above T_c was taken from structural data [3] as $\alpha_0 = 16^\circ$.

As shown above the linewidth anomaly below T_c is well described by equation (3) with a $\beta = 0.25$ exponent expected for the critical behaviour of the order parameter for the second order phase transition near the tricritical point [9]. This crystal field fluctuation is due to the H_2O molecule in the first coordination sphere of the Cr^{3+} ion. Than we expect that the α -angle should change according to the relation:

$$\Delta\alpha = \alpha_0 \left(\frac{T_c - T}{T_c}\right)^{2\beta} \tag{9}$$

with $\beta = 0.25$. The temperature changes of α - and γ -angles are shown in figure 5.

Keeping in mind that the total D -parameter measured in experiment (figure 3(a)) is

$$D_{total} = D_\alpha + D_\gamma + D_{vibr} \tag{10}$$

we can obtain the expected value of D_{vibr} of the D -parameter. In figure 6 D_α , D_γ and D_{vibr} are presented. The theory [10] of the vibrational part of crystal field estimates the following expression for D_{vibr} :

$$D_{vibr} = \frac{\partial^2 D}{\partial Q^2} \frac{\hbar}{2m\omega} \coth \frac{\hbar\omega}{2kT} \tag{11}$$

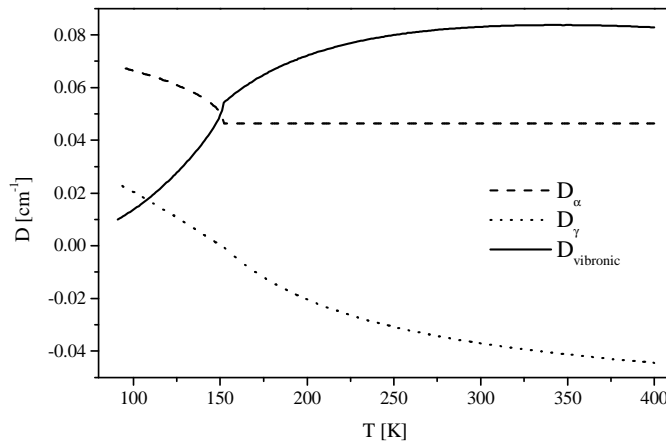


Figure 6. Temperature dependences of the D_γ -, D_α - and D_{vibr} -parameters.

where Q is the normal coordinate and ω is the vibrational frequency of the particular mode of vibration. Because of the complex dependence of $D(Q)$, it is impossible to fit exactly equation (11). However we believe that our D_{vibr} temperature dependence is correct because it tends to zero below 100 K, where the linewidth (figure 4) stops changing with temperature. On the other hand D_α reflects the order parameter temperature dependence similarly as the quadrupole splitting q of ^{27}Al NMR spectra [12] because $D_\alpha \sim q$.

The water molecule reorientation below T_c should modify significantly the hydrogen bond lengths between H_2O , SO_4 and DMA molecules. As a result the breaking of the hydrogen bonds between DMA cations leads to changing of rotational motion of DMA groups to libration motion [13] below T_c . This scenario is confirmed by us with two additional experiments. First, as we mentioned above, the breaking of one hydrogen bond in the DMA radical leads to freezing of the free DMA radical rotation at about 110 K. Second, replacing of Al^{3+} ions by a small amount of Cu^{2+} with large ionic radius $r = 0.72 \text{ \AA}$ in comparison with Al^{3+} radius $r = 0.53 \text{ \AA}$ changes the T_c -value markedly due to shortening of $\text{H}_2\text{O} \dots \text{SO}_4$ and $\text{SO}_4 \dots \text{DMA}$ hydrogen bonds.

All of our results allow us to present a model of the phase transition in the DMAAS crystal in which all units i.e. H_2O , SO_4 and DMA ions are involved. It is our statement that H_2O molecules play the role of a trigger mechanism of DMA cation ordering below T_c .

Acknowledgment

This work was supported by the Polish Scientific Research Committee, grant KBN-2-P03B-028-15.

References

- [1] Bednarski W, Waplak S, Kirpichnikova L F and Shuvalov L A 1997 *Phys. Status Solidi a* **160** R1
- [2] Bednarski W, Waplak S and Kirpichnikova L F 1998 *J. Phys. Chem. Solids* submitted
- [3] Pietraszko A, Łukaszewicz K and Kirpichnikova L F 1993 *Pol. J. Chem.* **67** 1877
- [4] Kirpichnikova L F, Shuvalov L A, Urusovskaya A A and Ivanov N R 1993 *Ferroelectrics* **140** 1
- [5] Kirpichnikova L F, Pietraszko A, Łukaszewicz K, Shuvalov L A, Dolbinina V V and Yakovleva L M 1994 *Kristallografija* **39** 1078
- [6] Kazmirov V Yu, Rider E E, Sarin V A, Shuvalov L A and Fykin L E 1998 *Kristallografija* **43** 1
- [7] Torgashev V T, Yuzyuk Yu I, Kirpichnikova L F, Shuvalov L A and Andreev E F 1991 *Kristallografija* **36** 667
- [8] Kiosse G A, Rozdobreev I M and Kirpichnikova L F 1990 *Izv. AN SSSR, Ser. Fiz.* **54** 749
- [9] Bruce A D and Cowley R A 1981 *Structural Phase Transition* (London: Taylor and Francis)
- [10] Owens F J 1977 *Phys. Status Solidi b* **79** 623
- [11] O'Reilly and Tung Tsang 1967 *Phys. Rev.* **157** 417
- [12] Alsabbagh N, Michel D, Furtak J and Czaplak Z 1998 *Phys. Status Solidi b* **167** 77
- [13] Kazmirov V Yu, Beluskhin A V and Shuvalov L A 1997 *Kristallografija* **42** 471