Pretransitional effect below the ferroelectric–paraelectric phase transition in β-LiNH$_4$SO$_4$

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Abstract. Detailed birefringence measurements of hydrogenated and deuterated β-LiNH$_4$SO$_4$ in the close vicinity of the high-temperature phase transition ($T_1 = 462$ K for hydrogenated, $T_1 = 465$ K for deuterated) are reported. The measurements of the sample were accompanied by simultaneous observation in the polarizing microscope. The temperature dependence of the birefringence data displays an additional anomaly at $T_1' \approx 459$ K for hydrogenated and $T_1' \approx 462$ K for deuterated crystals. In the temperature interval between T_1' and T_1 a regular striped structure was observed in the polarizing microscope. Among several possible interpretations of this phenomenon, the most appealing is the assumption of lamellar coexistence of the paraelectric and ferroelectric phase over a finite temperature interval.

1. Introduction

The β-form of lithium ammonium sulphate (LAS) is an extremely interesting material, which undergoes a number of transitions shown in the diagram presented below:

$$\frac{\text{ferroelastic} + ?}{m} \; T_3 = 28 \text{ K} \; \frac{\text{ferroelastic}}{2/m} \; T_2 = 283 \text{ K} \; \frac{\text{ferroelectric}}{mm2} \; T_1 = 462 \text{ K} \; \frac{\text{paraelectric}}{mmm}.$$

In the temperature range 462–283 K β-LAS is a pure ferroelectric [1], and at 283 K it undergoes a ferroelectric–ferroelastic phase transition [2]. At room temperature β-LAS is characterized by orthorhombic symmetry with lattice parameters $a = 9.204$ Å, $b = 5.280$ Å (ferroelectric axis) and $c = 8.786$ Å. A characteristic feature of the ferroelectric phase is the existence of the domain structure. One of the methods of revealing the domain structure in β-LAS is etching the surface of the crystal perpendicular to the ferroelectric, orthorhombic b-axis with water. At room temperature, the domain structure of the 'as-grown' crystal consists of stripes of different widths oriented along the orthorhombic a-axis. However, the pattern of the domain structure changes drastically, depending on whether the crystal passes to the ferroelectric state from the low-temperature ferroelastic (paraelectric) phase or the high-temperature paraelectric phase. The ferroelectric domains in the crystal which underwent the ferroelastic to ferroelectric phase transition are composed of thin parallel stripes. Their boundaries are oriented along the crystallographic a-axis. This picture of the domain structure is a sort of replica of ferroelastic domains, which constitute very regular thin stripes parallel to the a-axis. Studying the domain structure in β-LAS in the vicinity of the phase transition, by means of the SEM method (which is the only method enabling one to observe both pure ferroelastic and

pure ferroelectric domain structures), we can observe that ferroelastic domains vanish at the ferroelectric–ferroelastic phase transition. Instead of previously existing ferroelastic domains similar stripes of ferroelectric domains appear behind the phase front above T_2. Moreover, the ferroelectric domain walls (DWs) are oriented in the same direction (parallel to the a-axis) as the ferroelastic DWs below T_2. The picture of the domain structure changes drastically when the β-LAS crystal undergoes a paraelectric–ferroelectric phase transition. From chemical etching experiments we found that apart from the domain walls oriented parallel to the a-axis, two other orientations of domain walls appear, forming the angle of $\sim \pm 55°$ with the a-axis. At present it is not clear why the ferroelectric DWs take discrete orientations. In general, for the symmetry change $mmm \rightarrow mm2$ the ferroelectric DWs could be oriented in any direction [3].

Moreover, detailed investigations with optical microscope showed the existence of a regular lamellar structure $\sim$1–3 K below the paraelectric–ferroelectric (pe–fe) phase transition. These regular stripes are oriented at $\pm 55°$ with respect to the a-axis, with an average periodicity of $\sim$15 μm. It seems that in the ferroelectric state the β-LAS crystal 'remembers' its state prior to achieving the ferroelectric state [4]. Unfortunately, the ferroelectric domains are not visible in the polarizing microscope.

The problem we would like to concentrate on in the present work is how to describe the regular striped structure which appears close to the ferroelectric–paraelectric phase transition. For this purpose temperature dependent measurements of the optical birefringence, both for hydrogenated and deuterated β-LiNH$_4$SO$_4$, were performed in the vicinity of the phase transition. In addition, possible orientation of the phase boundary between the pe and fe phase was calculated.

2. Experiment

2.1. Birefringence measurements

A 'hybrid' apparatus for automatic measurements of birefringence was used [5]. The arrangement combines a polarizing microscope with computer–controller automatic birefringence measurements at $\lambda = 546$ nm. A Senarmont compensator is used for Δn measurements. The combination of the Δn measurements with the polarizing microscope allows the observation of the sample's surface during the experiment. For temperature investigations of Δn, the sample is situated in a Linkam THM 600 cooling–heating stage. With the apparatus changes of more than 4×10^{-6} of birefringence can be detected in a sample with 1 mm thickness, the temperature resolution being 0.1 K.

For Δn measurements samples of β-LAS were cut perpendicular to ferroelectric b- and orthorhombic c-axes. Samples' surfaces were polished with 1 μm diamond powder. The samples were transparent and their surfaces did not change chemically over the whole investigated temperature range.

2.2. Dielectric permittivity measurements

Very precise temperature measurements of dielectric permittivity were performed using an hp4284A capacitance bridge. For simultaneous ε measurement and optical observation of the sample we used a Linkam THMS 600 cooling–heating stage and a Jenapol polarizing microscope. Samples of deuterated β-LAS with thickness $\sim$0.30 mm were cut perpendicular to the ferroelectric b-axis.

3. Results and discussion

3.1. Birefringence

Structural phase transitions in crystals are primarily characterized by shifts of ionic nuclei from their positions. As a secondary effect they are accompanied by spontaneous changes of susceptibilities in the optical region. These display themselves as optical index ellipsoid deformation, i.e. as spontaneous changes of refractive indices n. Measurements of n or birefringence Δn often provide the first evidence for the existence of a structural phase transition [6]. The phase transition in the crystal is accompanied by different phenomena, e.g. phase boundaries and presence of domain structure. These phenomena very strongly influence the results of birefringence measurements. Temperature changes of optical birefringence in pure and doped β-LAS were studied by some authors [5, 7, 8]. As shown in the work of Anisimova and Ivanov [7], Δn changes for the orthorhombic c-axis are bigger than for the a- and b-axes. Zimmermann and Schranz [5] observed an additional anomaly below T_1 for β-LAS doped with Cs. The origin of the additional anomaly was not clear until now.
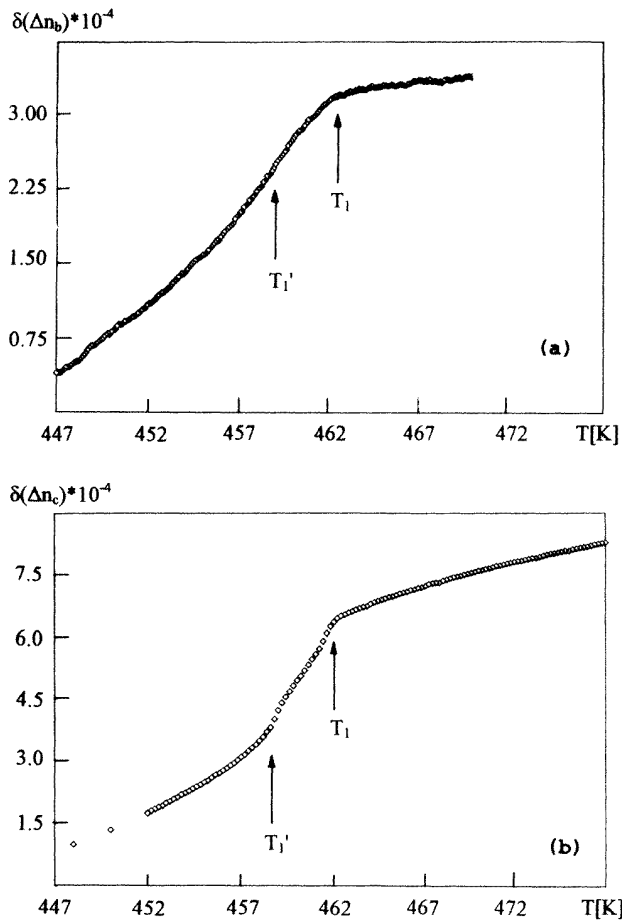
Figure 1. Temperature dependence of birefringence changes of β-LAS for ferroelectric b-axis (a) and for orthorhombic c-axis (b).
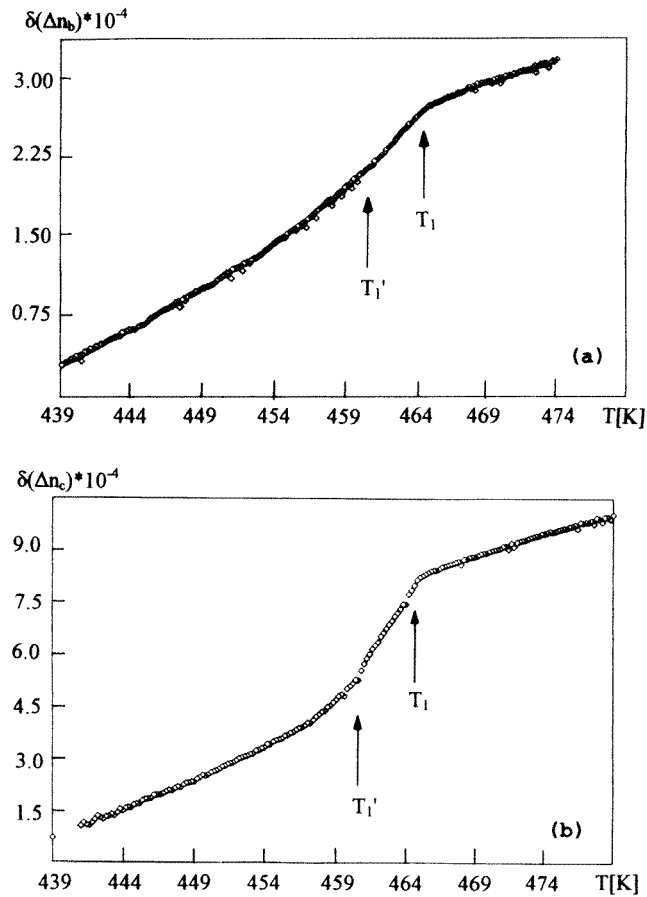
Figure 2. Temperature dependence of birefringence changes of deuterated β-LAS for ferroelectric
b-axis (a) and for orthorhombic c-axis (b).

As the linear birefringence is very a sensitive indicator of changes in the physical
properties of crystals, we performed very detailed temperature birefringence measurements
simultaneously with optical observation of the sample's surface both for hydrogenated
and deuterated β-LAS. Figures 1(a) and 1(b) present temperature dependences of optical
birefringence measured for the ferroelectric b-axis and orthorhombic c-axis. Figures 2(a)
and 2(b) present the same dependences for the deuterated crystal. Besides a slight isotopic
effect ($\Delta T_1 \approx 3$ K) the character of changes Δn is almost identical for hydrogenated and
deuterated β-LAS. Δn changes for the c-axis in both crystals are almost twice as big as for the
b-axis. Moreover, $\Delta n(T)$ for the c-axis displays an additional anomaly below the pe–fe phase
transition. The anomaly appears at the temperature T_1', at which a regular striped structure
appears on the samples cut perpendicular to the ferroelectric b-axis. The phenomena were
observed both for heating and cooling runs.

3.2. Dielectric permittivity

Figure 3 shows the temperature dependence of the dielectric permittivity measured very
precisely in the vicinity of the pe–fe phase transition in deuterated β-LAS. The anomalous
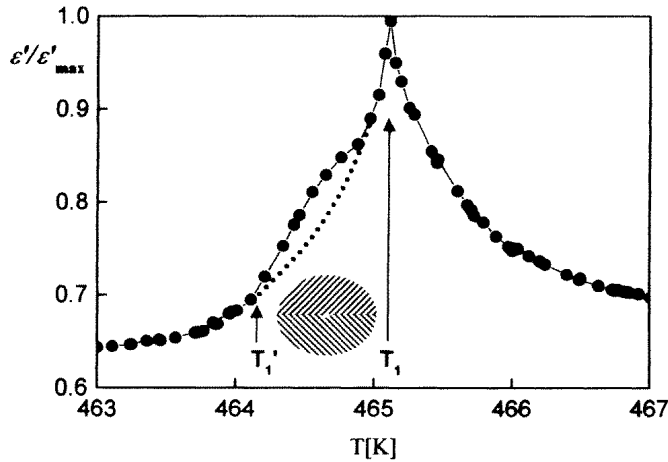
Figure 3. Temperature changes of dielectric permittivity of deuterated β-LAS for ferroelectric *b*-axis.

behaviour of dielectric permittivity which appears below T_1 is characterized by deviation of ε changes from the classical (a dotted line in figure 3) run of $\varepsilon(T)$ below the fe–pe phase transition. Simultaneous observation of sample surface revealed that at T_1' a regular striped structure appears and it disappears at T_1. Similar behaviour of $\varepsilon(T)$ in the close vicinity of the pe–fe phase transition was observed for hydrogenated β-LAS [13].

3.3. Interphase boundary orientation

At phase transitions in solids, regions of a new phase may appear in the initial phase. They grow, interact and form a complex heterophase system. The shape, volume and crystallographic orientation of these regions as well as their structure and their arrangement with respect to each other, i.e. the real structure of the hetero-phase system, significantly affect physical properties of the crystals. Numerous problems linked to the hetero-structure phase studies result in the necessity to investigate stress and elastic energy of the regions in the new phase arising in the ordered phase. The presence of regular macroscopic structures is determined by elastic distortions, which is the result of a link between the order parameter and crystal elasticity. A typical shape of the newly born phase is flat-parallel thin layers [9, 10].

   The regular structures of specific orientation observed by us may correspond to the coexistence of ferroelectric and paraelectric phases. The boundaries between particular 'stripes' would thus be inter-phase boundaries. The orientation of the boundary layer would then preserve the compatibility of strains between two neighbouring phases. This condition is satisfied when

$$\varepsilon_{ij}^s x_i x_j = 0 \tag{1}$$

where ε_{ij}^s are components of spontaneous strain tensor [11]. The strains in the heterophase system result from the contact between two phases with different lattice parameters.

   In the case of the β-LAS single crystal we are dealing with a structural orthorhombic $mmm(D_{2h})$–orthorhombic $mm2(C_{2v})$ phase transition. Using the experimental data concerning the temperature dependence of crystallographic lattice parameters [12] we find spontaneous
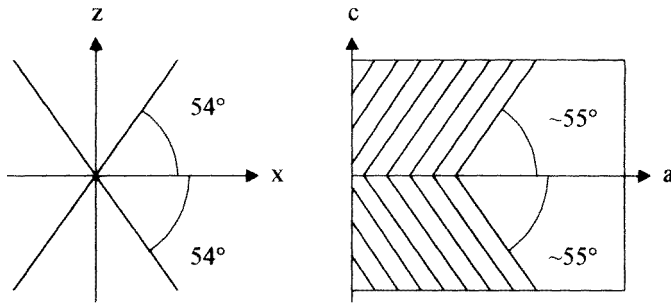
Figure 4. Schematic presentation of regular stripe structure in β-LAS crystal.
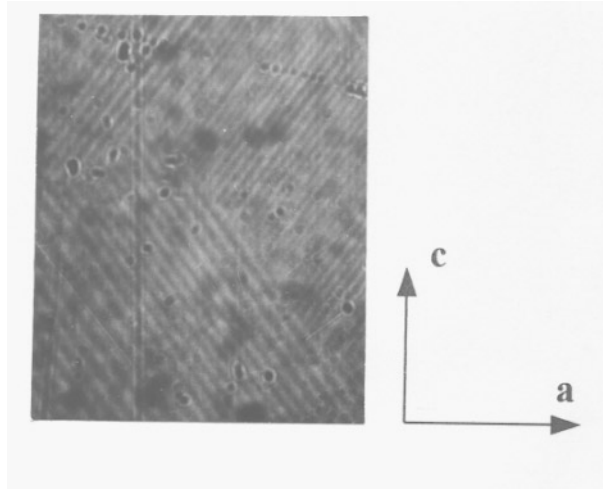
Figure 5. Regular stripe structure observed for β-LAS, at 461 K.

strain components at the phase transition temperature $\sim$462 K. The strain tensor components:

$$\varepsilon_{11} = \frac{a - a_0}{a_0} = \frac{9.17 - 9.19}{9.19} = -0.002\,18$$

$$\varepsilon_{22} \approx 0$$

$$\varepsilon_{33} = \frac{c - c_0}{c_0} = \frac{8.75 - 8.74}{8.74} = +0.001\,14 \tag{2}$$

therefore spontaneous distortion tensor for β-LAS

$$\overset{\leftrightarrow s}{\varepsilon} = \begin{bmatrix} -0.002\,18 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & +0.001\,14 \end{bmatrix} \tag{3}$$

hence from condition (1) on the compatibility of mechanical stresses we obtain the equation for the plane separating two phase regions of the pe and fe phases

$$-0.002\,18x^2 + 0.001\,14z^2 = 0 \tag{4}$$

$$z = \pm\sqrt{\frac{0.002\,18}{0.001\,14}}x \Rightarrow \beta \approx \pm54^\circ. \tag{5}$$

Here β is the angle which determines the orientation of the interphase boundary between ferroelectric and paraelectric phases in the vicinity of the high-temperature phase transition (figure 4). Indeed, this angle corresponds to the orientation of stripes in the striped structure we observed close to T_1 (figure 5). Since the direction of the observed stripe pattern below T_1 is close to the calculated values, we argue that the observed structure reveals the coexistence of the paraelectric and ferroelectric phases.

4. Conclusions

Studies of temperature dependences of birefringence in hydrogenated and deuterated β-LAS show anomalous behaviour in the close vicinity of the pe–fe phase transition for samples cut perpendicular to the c-axis. The anomalous $\Delta n(T)$ behaviour appeared in the temperature range T_1–T_1', in which regular striped structure on the measured samples was observed. Almost identical behaviour of hydrogenated and deuterated β-LAS indicates that hydrogen bonds do not play an important role in the mechanism of phase transition, they only change the absolute value of the temperature of fe–pe phase transition.

The regular large scale structure which appears in the vicinity of the pe–fe phase transition reveals a heterophase system. As determined from mechanical compatibility conditions in the $mmm \rightarrow mm2$ phase transition in β-LAS, the two phases may co-exist along the crystallographic directions $\pm 54°$ with respect to the a-axis which correspond to the orientation of the observed stripes. In our opinion the existence of a hetero-phase below the pe–fe phase transition in β-LAS is displayed in the anomalous behaviour of numerous physical quantities and determines the ferroelectric domain wall orientation. In different experiments, temperature measurements of birefringence and dielectric permittivity, which were carried out simultaneously with optical observations of samples' surfaces, we observe regular striped structure in the temperature range in which the deviation from expected 'classical' runs appeared. Earlier works concerned with DSC studies [13, 14] reported a double peak around T_1. In ultrasonic experiments a double peak was also measured in the attenuation for longitudinal waves propagating in the direction of the ferroelectric axis [15]. Unusual behaviour of β-LAS in the vicinity of the phase transition was observed in isothermal DSC studies [16]. Splitting of phase transition anomalies is sometimes also observed in other systems, and quite often the origin of this behaviour is not clear. For example in fullerene crystals C_{60} a double peak behaviour was very recently observed in specific heat [17] and elastic constant [18] measurements. The explanations range from the assumption of an intermediate phase, via the coexistence of two phases over an extended temperature range [17] to the assumption of a slow relaxational process related to heat-diffusion [18].

It is quite possible that the clarification of the double anomalies in β-LAS would shed some light on these problems.

Acknowledgment

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