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An x-ray scattering study of the low-temperature phase transitions of LiKSO_4

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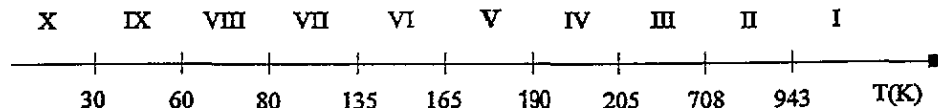
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Abstract. X-ray diffraction studies on solution-grown LiKSO_4 have been performed between 70 K and 300 K. The lattice parameters have been obtained as a function of the temperature. The hexagonal to trigonal phase transition at 205 K is seen by a slight increase of the c lattice parameter, while the ferroelastic transition at 182 K is accompanied by the appearance of an important spontaneous elastic deformation. The deformation and the domain pattern are analysed via a ‘squeezing’ model of the hexagonal lattice which leads to a monoclinic lattice below $T_c = 182$ K.

1. Introduction

Lithium potassium sulphate (LiKSO_4) is a very interesting crystal since it presents a great variety of structural phases, among which are pyroelectric, ferroelastic and, maybe, incommensurate ones. In the past, this system has attracted much attention from the scientific community, and a very large bibliography exists about its properties and phase transitions. In spite of the great number of experimental works devoted to this material, the results and conclusions drawn by the different authors are very often in conflict. Historical reviews and investigations concerning the main controversial points can be found in [1–8].

In order to introduce the present study, let us refer to the recent work of Perpétuo *et al* [8] describing the following sequence of phases:



where the temperatures, given in kelvin, are averaged over the published values in the cooling runs. The structure of phases PI and $PIII$ have been well determined as belonging to the hexagonal $P6_3/mmc$ and $P6_3$ groups respectively [9–11]. Between these two hexagonal phases, PII exhibits a modulated structure [7]. Below room temperature, the crystal undergoes various phase transitions, but the structures (and even the existence of some transitions) of these low-temperature phases remain a matter of controversy. In addition, important kinetic effects and phase relaxations have been reported [3, 12–16]. In the case of PIV and PV , it is now believed that the crystal presents a trigonal $P31c$ structure and a monoclinic Cc one, respectively, as firstly proposed by Bansal *et al* [17] (PIV) and Bhakay-Tamhane and Sequeira [16] (PIV and PV). As stressed by the latter

authors, the presence of twins of small size could have led many authors since Tomaszewski and Lukaszewicz [18] to propose higher symmetry structures (hexagonal and orthorhombic, respectively) for these phases. For the remaining phases, the situation is rather complicated, since the physical anomalies observed at the phase transitions are faint or even absent for some techniques. In any case, all phases below *P*III (including it) are pyroelectric [19–20] and also ferroelastic below *P*V (idem) [21–22].

In a previous work by some of the authors (UAL and AR) [23], birefringence measurements have been carried out on domain controlled LiKSO_4 samples, with special attention to phases *P*IV and *P*V and their phase transitions. In particular, the results show a very interesting temperature dependence of the structural birefringence below *P*V, which is two orders of magnitude higher than that presented by a polydomain sample [24]. Since the structural birefringence in the *ab* plane originates from the elastic deformation in the ferroelastic phases, we have decided to perform a systematic study of the domain formation and of the spontaneous elastic deformation in this crystal between 70 K and 300 K, using x-ray diffractometry. The results, as well as the temperature dependence of the lattice parameters, are presented and discussed in the present work.

2. Experimental arrangement

The x-ray measurements were performed using a double crystal x-ray diffractometer. The direct beam was finely collimated by a set of two very narrow slits (about $100 \mu\text{m} \times 1 \text{mm}$) and the x-ray beam scattered by the crystal was analysed by a bent pyrolytic graphite in front of which were set two narrow slits. All the experiments were performed in reflection geometry from an extended face of the sample crystal. This sample was glued with varnish onto a copper mount and placed in a close cryogenerator with a temperature stability of 0.1 K. The rates of cooling and heating were 25 K per hour. The measurements, taken after sufficient time had been allowed for the temperature to stabilize, lasted five minutes for the lattice parameters and three hours for the grid scans. Owing to the small dimensions of the samples, we can consider that there were no significant temperature gradients in the crystals.

The instrumental resolution in the scattering plane was typically $4 \times 10^{-3} \text{ \AA}^{-1}$ in the direction transverse to the wavevector transfer and $2.5 \times 10^{-3} \text{ \AA}^{-1}$ in the direction parallel to the wavevector transfer.

LiKSO_4 samples were grown by slow evaporation of a saturated solution containing equimolar proportions of $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ and K_2SO_4 at 413 K. The crystals form hexagonal platelets with direct identification of the *c* axis. The *a* axis is perpendicular to *c* and parallel to a natural face of the crystal.

Two samples were used in the experiments. One was a hexagonal platelet ($5 \times 5 \times 4 \text{ mm}^3$) that presented the [0001] direction normal to the natural crystal face (crystal A) and the other has been shaped as parallelepiped ($4 \times 6 \times 5 \text{ mm}^3$) to present its face perpendicular to the [11 $\bar{2}$ 0] direction (crystal B). Let us point out that the hexagonal structure can also be described by a face-centred orthorhombic unit cell, which was used during the experiments. In that case the orthorhombic lattice parameters are derived from the hexagonal ones by the relations: $a_0 = a_1\sqrt{3}$, $b_0 = a_2$, $c_0 = c$ and with $a_1 = a_2 = a_3 = a$.

Both samples were found to be perfect at the best resolution of the instrument. The sample mosaicity was found to be better than 0.04° (FWHM) which is the limit of the resolution the instrument can achieve.

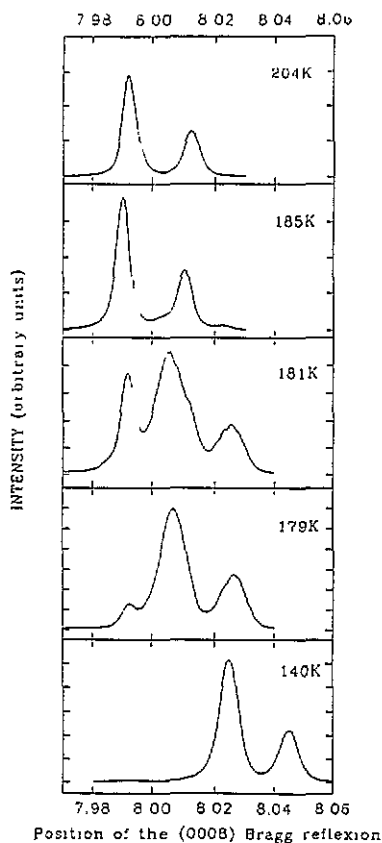


Figure 1. Temperature dependence of the (0008) Bragg reflection. Note that in this kind of scan (longitudinal) each Bragg reflection shows two peaks, corresponding to the $K\alpha_I$ and $K\alpha_{II}$ lines. From 179 K to 185 K two Bragg reflections coexist.

3. Results and discussion

3.1. The lattice parameters

The c lattice parameter was measured as a function of the temperature, using crystal A, by monitoring the evolution of the position of the (0008) Bragg reflection (see figure 1). As shown in figure 2, it is observed that this parameter does not evolve much on cooling to 205 K (the crystal expands slightly on cooling in this direction). At this temperature a slight increase is observed and the parameter then remains constant before displaying an abrupt decrease at $T = 184$ K. At this temperature and over a range of 6 K, two Bragg reflections are observed evidencing the presence of a phase coexistence (shown in figures 1 and 2). On further cooling, the decrease of this parameter occurs at a rate which seems to peak at around $T = 165$ K. On heating, the c lattice parameter displays the same behaviour as on cooling at least until 184 K and jumps again at $T = 188$ K evidencing the presence of a small hysteresis of 4 K. This is the signature of the first-order character of the transition. On further heating, the c lattice parameter remains nearly constant until 240 K, and then, above this temperature displays the same behaviour as shown on cooling.

The a parameter was measured on crystal B by monitoring the evolution of the position of the (040) Bragg reflection ($b_0 = a$). On cooling (figure 3), it was found that the LiKSO_4 lattice contracts in this direction until 186 K and a faint change is observed around $T = 210$ K which is reminiscent of that observed along the c -axis. At $T_c = 178$ K, the (040) Bragg reflection intensity begins to decrease and coexists over a range of 4 K with two other

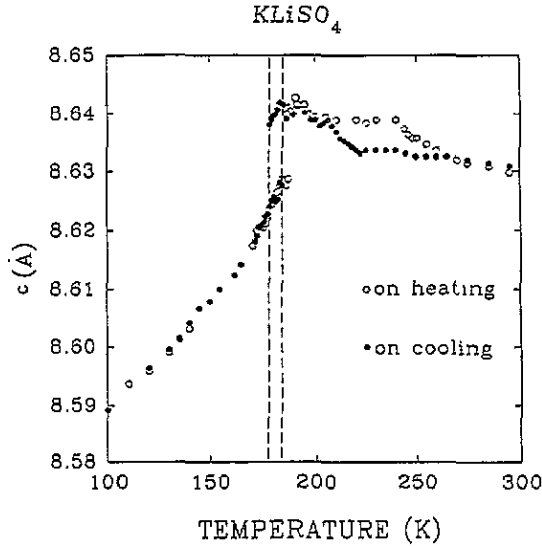


Figure 2. Temperature dependence of the c lattice parameter showing an important jump at the PIV-PV transition. The phase coexistence region on cooling is delimited by two dashed lines.

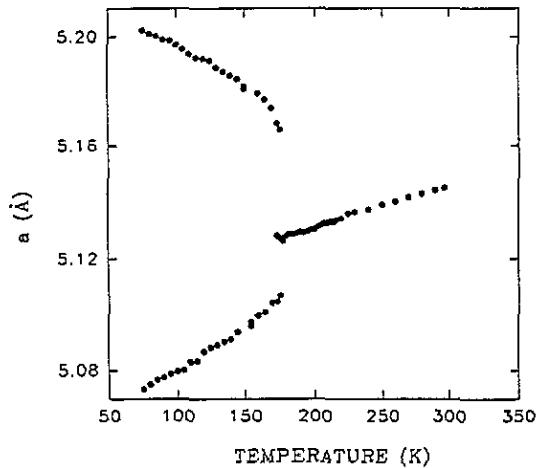


Figure 3. Temperature dependence of the a lattice parameter.

Bragg reflections of the ferroelastic phase. In the longitudinal scan the separation of the two reflections, which increases on further cooling, is characteristic of the elastic deformation which develops at T_c (see figure 4). It is interesting to note that these two reflections, which are located on each side of the high-temperature Bragg reflection, clearly indicate that part of the lattice contracts and part of it expands. This observation can be explained if we consider that the hexagonal lattice is squeezed in the $[10\bar{1}0]$ direction. According to the hexagonal symmetry of the high-temperature phase, the squeezing of the lattice can occur simultaneously in three directions (see the inset in figure 5). A squeeze in the $[10\bar{1}0]$ direction provides an increase of the lattice of parameter along $[1\bar{2}10]$, whereas a squeeze in a direction 60° away from $[10\bar{1}0]$ provides a decrease of the same lattice parameter. The squeeze has two consequences on the lattice: (i) a deviation from $\gamma = 120^\circ$ and (ii) the

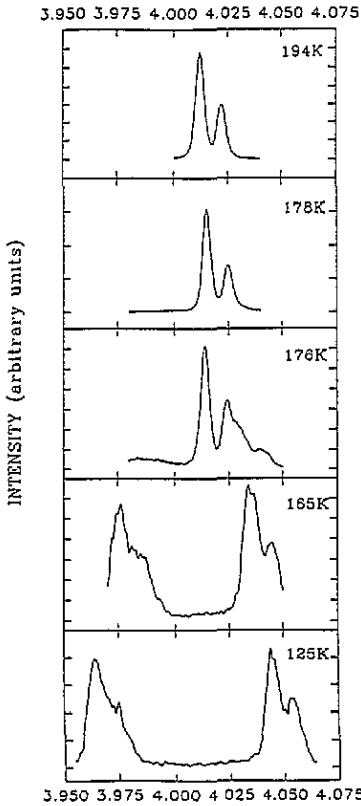


Figure 4. Temperature dependence of the Bragg reflection in the orthorhombic $b_0 = a$.

appearance of two K-K distances. It can be shown that if ϵ is the deviation from 60° and l' is the smallest K-K distance in the distorted lattice, then in the coexistence region close to T_c the three lattice parameters corresponding to the three Bragg reflections observed are related by: $d_1 = l'$, $d_2 = l'(1 + 0.57\epsilon)$ and $d_3 = l'(1 + \sqrt{3}\epsilon)$.

The separation of the Bragg reflections in this regime, with respect to the position of the hexagonal Bragg position (located at Q_2), is given by:

$$\frac{Q_2 - Q_3}{Q_1 - Q_2} = \frac{\sqrt{3} - 0.57}{0.57} = 2$$

and is in perfect agreement with our experimental results since at $T_c - 2$ K, we have: $Q_3 = 3.984$, $Q_2 = 4.014$ and $Q_1 = 4.029$.

This picture is only true if the distortion occurs only in the ab plane. That is to say, if there is no distortion along the c direction. We have checked that in the ac plane there is no domain formation as observed in the ab plane (figure 5). Thus, this result discards the possibility of a triclinic structure for the ferroelastic phase.

From the above equations, it is possible to extract the angular deformation ϵ . We have $0.57\epsilon = (Q_2/Q_1) - 1$ leading to $\epsilon = 0.37^\circ$. This leads to a monoclinic cell $a_m = 5.096 \text{ \AA}$, $b_m = 5.181 \text{ \AA}$, $c_m = 8.611 \text{ \AA}$, and $\beta = 119.63^\circ$ at 150 K.

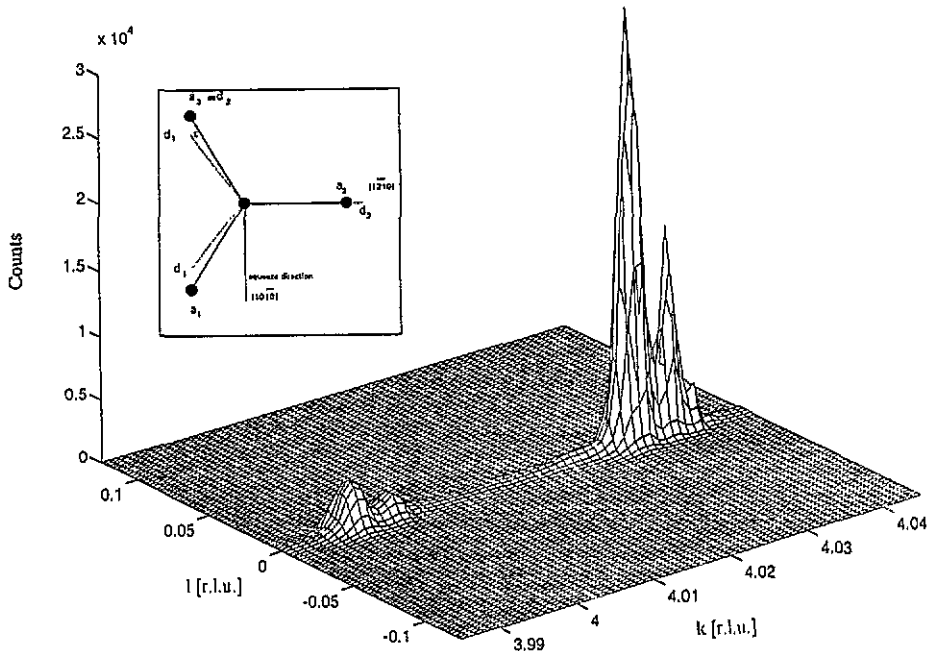


Figure 5. Grid scan of the Bragg reflection (040) in the b_0c_0 plane (equivalent to the ac plane of the hexagonal symmetry) at 150 K, showing that there is no domain formation along the c axis (k and l are given in terms of reciprocal lattice units: rlu). Inset: effects of the squeezing of the lattice in the $[10\bar{1}0]$ direction.

3.2. The domains and the spontaneous elastic deformation

Another consequence of the squeezing effect is the coexistence of mackling domains in the low-temperature phase which are clearly evidenced in the grid scan of the (040) Bragg reflection (figure 6). We observed a complex structure which is related to the accommodation of the three distorted ferroelastic domains. It is interesting to notice that of the three domains two come from d_1 and another from d_3 . Close to T_c and down to 150 K, the domain proportion can be obtained from the integrated intensity of the transverse scan. As expected from the threefold symmetry the ratio of 1:2 in favour of domains with an expanded lattice parameter is observed immediately below T_c . However, 40 K below T_c the domain proportion evolves and tends to be 2:3.

The location of the reflection in the transverse scans has been analysed with respect to the proposed model and it has been found that all the reflections are consistent with ϵ and 2ϵ angles.

The mechanism which governs the accommodation of the distorted ferroelastic domains is not completely explained for the moment. Nevertheless, the temperature evolution of the corresponding peak positions in the longitudinal and transverse scans is completely correlated in the temperature range investigated, indicating that both positions have their origin in the spontaneous deformation ($e = (a - b)/(a + b)$) of the ferroelastic phase(s), presented in figure 7. The temperature dependence of the elastic deformation follows a typical first-order Landau-type curve, between 70 K and 180 K, and displays the same behaviour as the linear birefringence presented by a domain-controlled sample in [23].

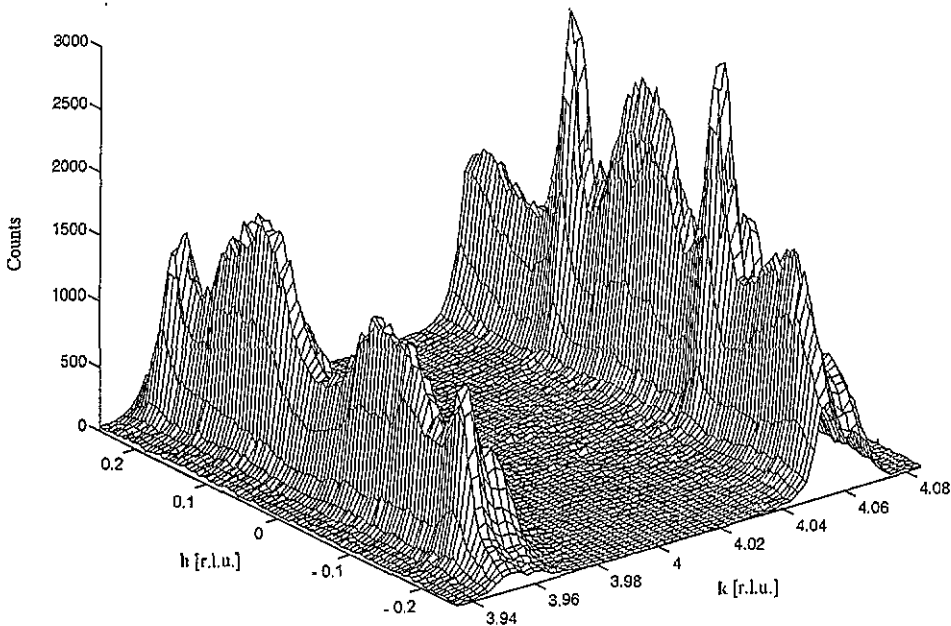


Figure 6. Grid scan of the (040) reflection in the a_0b_0 plane at 120 K, showing the complex structure which appears below T_c .

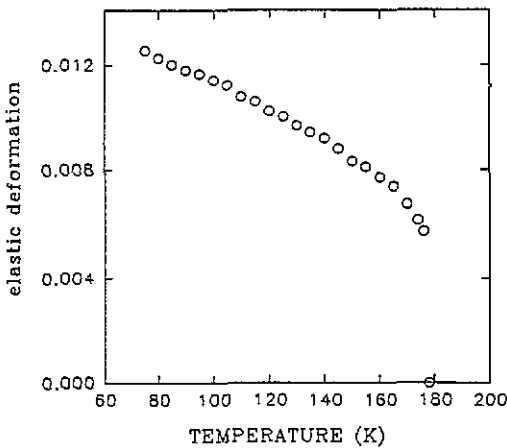


Figure 7. Spontaneous elastic deformation: $e = (a - b)/(a + b)$ as a function of temperature.

4. Conclusions

In the present work, x-ray diffraction studies on solution-grown LiKSO_4 have been carried out between 70 and 300 K, with special attention to the *PIV* and *PV* phases. The phase transition *PIII* to *PIV* occurs in a temperature interval of 1 ~ 10 K around 205 K and is seen by a slight increase of the *c* parameters. The subsequent heating run revealed an important thermal hysteresis (~40 K) which is related to the reconstructive nature of this transition (*P6₃* to *P31c*).

The phase transition *PIV* to *PV* also shows a phase coexistence in a small temperature

interval of ~ 4 K around 182 K. In contrast, this transition is characterized by large changes in both the c and a parameters. The first one shows an abrupt decrease at T_c while the second one splits into two different lengths. This splitting is a consequence of the appearance of a spontaneous elastic deformation in the ferroelastic phase. This transition is also accompanied by a 4 K thermal hysteresis, owing to its first-order character.

The only anomaly observed between 180 K and 70 K was a small change in the slope of the c parameter thermal expansion curve at 165 K, and could be an indication of the proposed phase transition at this temperature.

In the free samples, the elastic deformation gives rise to a complex domain structure observed in grid scans in the plane normal to the c axis. On cooling the sample to below 180 K the elastic deformation has a well defined behaviour, increasing smoothly like a Landau-type order parameter curve. The splitting of the reflections along the c axis and the absence of off-axis domains in the ac plane agree very well with the formation of a monoclinic lattice in PV .

Acknowledgments

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