X-ray study of the ferroelastic incommensurate phase of $LiKSO_4$ under uniaxial pressure

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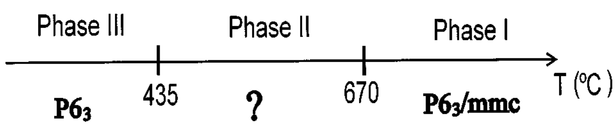
An x-ray study of the intermediate phase (435 °C$<T<$670 °C) of $LiKSO_4$ crystals is presented. Results show the existence of three kinds of incommensurate and ferroelastic domains, each one described by a single wave vector (1$-$**q** model). The temperature dependence of the modulation wave vector is presented. The application of uniaxial pressure inhibits domains with a component of the wave vector in the direction of the applied pressure. [S0163-1829(96)07141-X]

I. INTRODUCTION

Lithium potassium sulfate crystals display a very interesting sequence of structural phase transitions at high temperature as schematized in the diagram below.



The symmetries of phases I and III are well established in the literature.[1–4] The room-temperature phase III ($T<435$ °C) has a hexagonal symmetry $P6_3$ with $a_{III}=5.147(3)$ Å and $c_{III}=8.633(4)$ Å with $Z=2$ units of $LiKSO_4$.[3] Figure 1 shows a sketch of the three-dimensional structure of phase III. The highest temperature phase I ($T>670$ °C) has also a hexagonal symmetry, space group $P6_3/mmc$,[4] and is characterized by a orientational disorder of the sulfate tetrahedra. This structure is isomorphic to that of α-K_2SO_4 and can be described by two models, the ''apex'' model and the ''edge'' model; a schematic drawing of these models can be found in Ref. 5. The description of the structure of the intermediate phase II is still controversial. In 1972, Chung and Hahn[6] proposed an orthorhombic symmetry for this phase. A few years later, Li[4] proposed for this phase a modulated structure described by three wave vectors laying in the basal plane. According to that description, the modulation wave vector would assume incommensurate values between 470 °C$<T$ $<$670 °C and a commensurate value $\chi=0.5$ below 470 °C yielding a hexagonal superstructure of the room-temperature structure with $a_{II}=2a_{III}$, and $c_{II}=c_{III}$.[4] Some authors showed the existence of three kinds of ferroelastic domains in this intermediate phase, oriented at 120° one to another,[7,8] which were incompatible with the hexagonal symmetry suggested by Li.[4] In an x-ray-diffraction study, Sankaran, Sharma, and Sikka[9] described phase II as a normal phase with orthorhombic symmetry, space group $Pmcn$, containing $Z=4$ formulas. Brillouin-scattering measurements have shown an anisotropy in the velocity of the longitudinal acoustic waves propagating in the basal plane,[10] which indicates that the symmetry of phase II should be lower than hexagonal. Recently, Borisov, Charnaya, and Radzhabov,[11] observed anomalies in the velocity of a transverse-acoustic phonon at about 470 °C, which corresponds to the temperature of the lock-in phase transition proposed by Li.[4]

A tentative description to conciliate the contradictory previous results was proposed by Pimenta *et al.*[12] The intermediate phase would correspond to a superposition of three kinds of modulated structures, whose wave vectors could assume incommensurate and commensurate values. The commensurate modulated structure would have an orthorhombic symmetry. Recent results in x-ray diffraction experiments using the precession method reinforced the twinned orthorhombic model.[13]

In order to clarify these points we performed a systematic x-ray diffraction study of $LiKSO_4$ crystals in the temperature range 25 °C$<T<$550 °C with samples submitted to uniaxial pressure applied in directions perpendicular to the c axis. The obtained results will be presented and discussed in the sections below.

II. EXPERIMENTAL DETAILS

$LiKSO_4$ crystals were obtained from aqueous solution by slow evaporation at 40 °C. The samples obtained have hexagonal morphology, plain faces, and high optical quality. The dimensions of the studied samples were 0.3×0.3×0.8 mm^3 for four-circle diffractometer and 1.5×1.5×1.0 mm^3 for precession measurements. Samples were heated up to 600 °C using an air-flow furnace with temperature stability of ±1 °C.

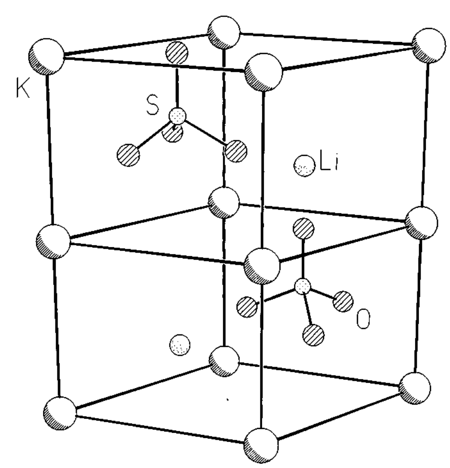


FIG. 1. Unit-cell sketch of $LiKSO_4$ in phase III ($T<435$ °C).

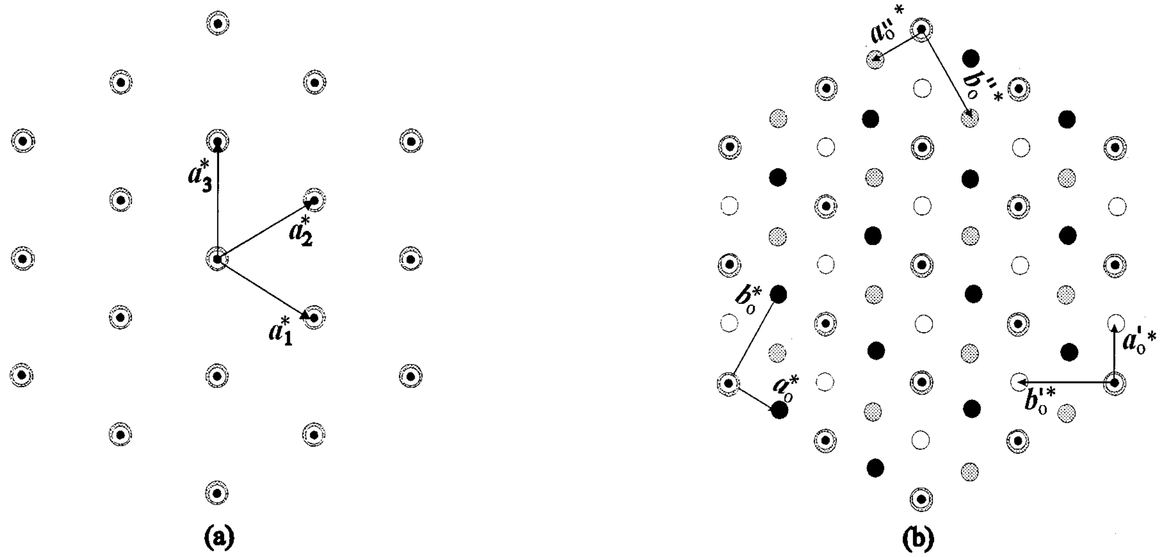


FIG. 2. Diagram of the precession photographs of the xy plane of $LiKSO_4$ crystals at $T=550$ °C, (a) $l=0$ plane and (b) $l=1$ plane. The principal spots are represented by the circles with dots. The $l=1$ diffraction pattern corresponds to a superposition of three domains giving rise to three sets of satellites which are represented by black, hollow, and gray circles.

For high-temperature measurements without applied pressure, the crystal was cemented on top of quartz rods. In the experiments performed under uniaxial pressure a stress apparatus composed of two opposite fine quartz sticks was adapted in the furnace; the pressure value could not be precisely measured.

The z axis of the orthogonal system of coordinates used to describe the experiment coincides with the hexagonal axis; the x axis is parallel to a natural face of the crystal (there are three equivalent x axes in the hexagonal phases whose vectors are denoted by $\mathbf{a}_1$, $\mathbf{a}_2$, and $\mathbf{a}_3$). The y axis is perpendicular to a natural face. Considering an orthorhombic unit cell, **a** and **b** are vectors parallel to the x and y directions, respectively. The pressure is applied along the x and y directions with the x-ray propagating along the z direction.

III. RESULTS AND DISCUSSIONS

The diffraction pattern of the xy plane of $LiKSO_4$ crystals at the room-temperature phase III ($T<435$ °C) is characterized by a set of sharp spots presenting a hexagonal symmetry. Above the phase transition the $l=0$ layer is similar to that displayed in phase III [Fig. 2(a)]. Nevertheless in the $l=1$ layer a set of extra satellite peaks can be observed. Each satellite is placed between a pair of main spots as illustrated in Fig. 2(b).

At first glance one could describe phase II as a hexagonal superstructure with a four-fold unit cell compared to that of phase III; this description corresponds to Li's commensurate structure.[4] However, there is strong experimental evidence against this hexagonal superstructure model,[6–10] including the absence of extra spots in the $l=0$ layer. This led Sankaran, Sharma, and Sikka[9] to propose a Pmcn orthorhombic symmetry for phase II. The diffraction patterns would correspond to a superposition of three orthorhombic domains forming 120° with each other. These domains are represented by black, hollow, and gray circles in Fig. 2(b).

A careful study of the $l=1$ layer new spots has been performed in a four-circle diffractometer between 435 and 530 °C. We observed that these new spots are not exactly equidistant from two main ones, but they are slightly displaced from this middle point along a principal direction in the reciprocal space, as illustrated in Fig. 3. In other words these new spots can be interpreted considering a set of modulation wave vectors $\mathbf{q}_1=\chi\mathbf{a}_1^*$, $\mathbf{q}_2=\chi\mathbf{a}_2^*$, and $\mathbf{q}_3=\chi\mathbf{a}_3^*$, where $\mathbf{a}_1^*$, $\mathbf{a}_2^*$ and $\mathbf{a}_3^*$ are the three equivalent reciprocal axes in the basal plane of the hexagonal structure and χ is an irrational number which reveals the existence of an incommensurate structure. Figure 4 shows the temperature dependence of χ averaged from the four centered first-order satel-

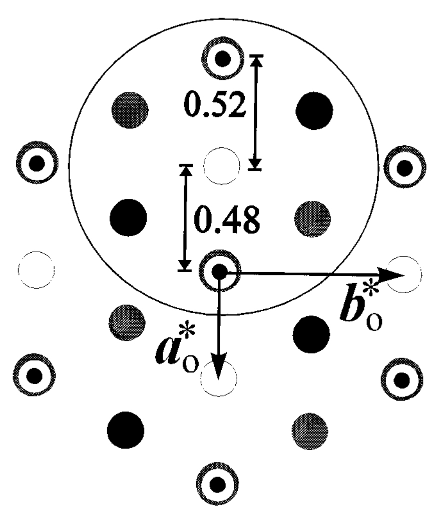


FIG. 3. Diagram of the precession photographs showing the displacement of a satellite spot from the middle point between two principal spots.

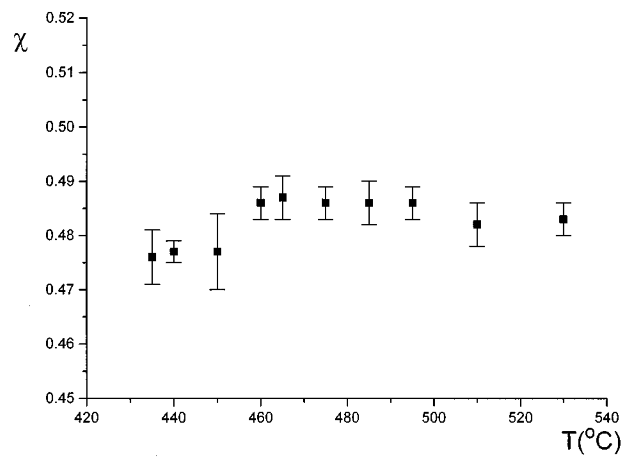


FIG. 4. Temperature dependence of χ.

lite reflections $(1+\chi\ 0\ 1)$, $(1+\chi\ 0\ -1)$, $(0\ -1-\chi\ 1)$, and $(1+\chi\ -1-\chi\ 1)$.

Another important point concerns the lock-in phase transition observed by Li at about 470 °C, below which the modulation wave vector becomes commensurate.[4] Figure 4 shows that χ always assumes incommensurate values over the whole temperature range investigated. We can observe in this figure a discontinuous jump of χ at about 460 °C which could be related to the anomaly in the transverse-acoustic phonon frequency observed by Borisov, Charnaya, and Radzhabor.[11] These results show that the intermediate phase II corresponds to a superposition of three kinds of domains and that the modulation is described by the three wave vectors $\mathbf{q}_1$, $\mathbf{q}_2$, and $\mathbf{q}_3$. The question now is to know if each incommensurate domain is described by a single wave vector ($1-\mathbf{q}$ model) or by a two-dimensional modulation ($2-\mathbf{q}$ model) as previously suggested.[12]

Trying to answer this question we performed a series of measurements where an uniaxial pressure, perpendicular to the c axis, was applied. Sorge and Hempel[8] showed that a monodomain ferroelastic state is induced by applying uniaxial pressure along the x axis; uniaxial pressure applied in a natural face of the crystal (y direction) does not lead to a monodomain state. A series of precession photographs has been obtained at $T=550$ °C (phase II) by applying an uniaxial pressure along the x and y direction. Figure 5 illustrates the results obtained. When pressure is applied along the y direction, one of the set of satellites spots disappears [Fig. 5(a)]. Such a set corresponds to the domain described by the modulation wave vector parallel to the direction of the applied pressure. On the other hand, if the pressure is applied along the x direction, two sets of the satellite reflections have their intensity drastically decreased. Figure 5(b) displays the principal spots and the set of satellites that are not affected. This result reflects the partial inhibition of the two kinds of domains which are described by wave vectors that have a component along the direction of the applied pressure. Probably a monodomain state could be obtained by applying high enough pressures.

IV. CONCLUSION

In this work we present an x-ray study of the intermediate phase II (435 °C$<T<$670 °C) of $LiKSO_4$ crystals. Experiments with applied uniaxial pressure showed that this phase corresponds to a superposition of three kinds of ferroelastic incommensurate domains oriented at 120° to one another. A

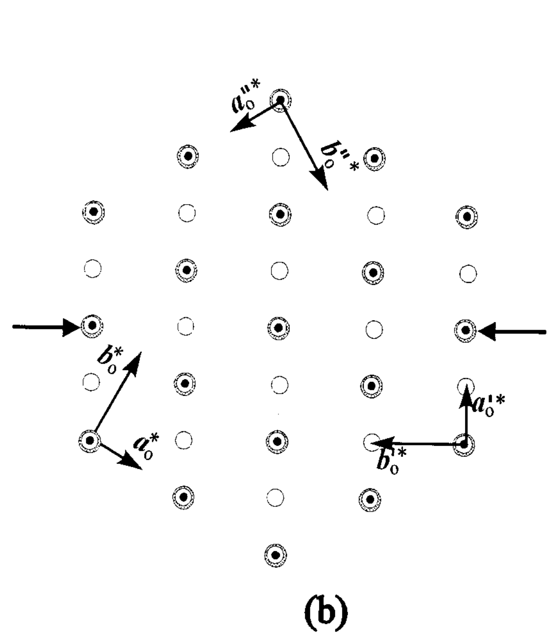


FIG. 5. Diagram of the precession photographs of the xy plane of $LiKSO_4$ crystals under uniaxial pressure, at $T=550$ °C for $l=1$. (a) When the pressure is applied along the y direction one set of satellites disappears. The two others are represented by the gray and black circles. (b) When the pressure is applied along the x direction, two sets of satellites have their intensities drastically reduced. The white circles represent the set of satellites that are not affected.

careful analysis of the diffraction pattern shows that the wave vector of the modulation is very close but not exactly equal to 0.5, in accordance to the previous result pointed out by Li.[4] However, our results disagree with the incommensurate model proposed in Ref. 4 since we observe that the modulation is described by a single wave vector $(1-\mathbf{q}$ model) in each ferroelastic domain, which is along the orthorhombic **a** direction. Moreover, the lock-in phase transition at about 470 °C was not observed in our experiment. The temperature dependence of the incommensurate wave vector shows only a small discontinuity at about 460 °C. The application of uniaxial pressure along the x and y directions led to the inhibition of one and two kinds of domains, respectively. The inhibition occurs for the domains that have a component of the wave vector **q** in the direction of the applied pressure. Studies in the four-circle diffractometer are in progress in order to investigate the structure of the intermediate phase II.

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