

An X-ray diffraction study of structural phase transitions of lithium potassium sulphate

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1989 J. Phys.: Condens. Matter 1 6913

(<http://iopscience.iop.org/0953-8984/1/39/001>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.96

The article was downloaded on 10/05/2010 at 20:10

Please note that [terms and conditions apply](#).

An x-ray diffraction study of structural phase transitions of lithium potassium sulphate

R H Chen and Rong Tzong Wu

Department of Physics, National Taiwan Normal University, Taipei 11718, Taiwan, Republic of China

Received 25 October 1988, in final form 21 March 1989

Abstract. X-ray diffraction methods have been used to study the low-temperature structural phase transitions of KLiSO_4 crystals. X-ray Laue and precession pictures of KLiSO_4 were taken in the temperature range from 295 K to 184 K to cover the controversial phases. The results indicate that there is a structural phase transition sequence: $\text{P6}_3\text{—P6}_3\text{mc—P6}_3$. The mosaic spread of the reflection becomes very broad for temperatures between 230 K and 205 K. It is suggested that the crystal is composed of three twin domains whose structures were nearly but not quite parallel to each other in this temperature range.

1. Introduction

The crystal structure of lithium potassium sulphate, KLiSO_4 , at room temperature was first analysed by Bradley (1925). It has two chemical units in a hexagonal unit cell with the space group P6_3 . This compound showed the merohedral twin and the static positional disorder of SO_4 group from the neutron and the x-ray diffraction studies done by Bhakay-Tamhane *et al* (1984), by Karppinen *et al* (1983), and by Sandormirskii *et al* (1983). Recently, Schulz *et al* (1985) collated x-ray diffraction data on the intensities at several high temperatures and included the anharmonic thermal effect of oxygen and lithium atoms in the structure determination refinements. They revealed a dynamical disorder in the KLiSO_4 crystal.

In the past few years, several phases of the KLiSO_4 crystals above room temperature have been found by many groups using different techniques. Delfino *et al* (1980) measured the thermal and dielectric properties of KLiSO_4 between 300 K and 520 K. The space group of KLiSO_4 remained in the P6_3 in this temperature range. The crystal is pyroelectric in this phase. A phase transition which occurs at 700 K has been found by Ando (1962), Sharma (1979) and Bansal *et al* (1980). The crystal phase could be in an orthorhombic system at 700 K and it would transform to a hexagonal system at 940 K, as proposed by Chung and Hahn (1972).

Most attention has been focused on the low-temperature structural phase transitions. Using Raman scattering, Bansal *et al* (1980) reported a first-order phase transition from the room temperature hexagonal P6_3 phase to the trigonal P31c phase at 201 K, with a reorientation of SO_4 group in the KLiSO_4 crystal. Other measurements (without analysing the structures indicated) showed anomalies at 250 K and 196 K using the data on pyroelectric coefficients and dielectric permittivity obtained by Breczewski *et al* (1981).

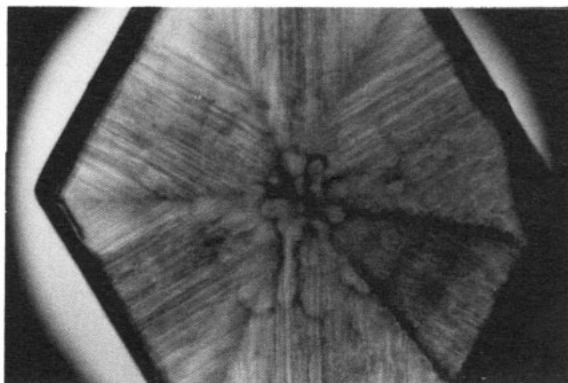


Figure 1. The KLiSO_4 crystal under the polarising microscope at room temperature.

More information about the crystal structure of KLiSO_4 at low temperature was obtained by means of EPR studies. However, the results and conclusions are not all consistent with one another. Holuj and Drozdowski (1981) proposed an incommensurate structure in the temperature range 253–183 K. Fonseca *et al* (1983) reported a different result, that KLiSO_4 crystals undergo a sequence incommensurate–commensurate–incommensurate phase transitions at the temperatures from 226 K and 83 K and re-enter the P6_3 phase on further cooling. But Yu and Chou (1986) interpreted their data taking into account the suggestions that the KLiSO_4 crystals have the structural phase transition from P6_3 to $\text{P6}_3\text{mc}$ at 190 K and have twin domains at 215 K.

X-ray diffraction studies of KLiSO_4 crystals at low temperature have been made by Tomaszewski and Lukaszewicz (1983). By analysis of Weissenberg photographs and the lattice constants of KLiSO_4 crystals at consecutive temperatures, the phase of the crystal transformed from the P6_3 to the $\text{P6}_3\text{mc}$ and to the $\text{Cmc}2_1$ on cooling at 190 K and at 180 K respectively. Since the most convenient way of investigating the symmetry of crystal is by means of the x-ray Laue and the x-ray precession methods, we set up a cooling system employing the ‘gas-stream’ method for those two cameras with the aim of studying the space group and the structural phase transitions of KLiSO_4 crystal below room temperatures.

2. Experiment

The crystals of KLiSO_4 were grown at room temperature by slow-evaporation from aqueous solution made up of equi-molar proportions of K_2SO_4 and $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$. Most of the crystals grown are transparent hexagonal plates with the c axis perpendicular to the plates. Other crystals of rectangular shape along the c axis are also found. The density was measured by the direct measurement of weight loss of the sample crystal in liquid C_7H_{16} . The density of the KLiSO_4 crystal measured by this method is 2.42. The crystals were examined under the polarising microscope. When viewed along the c axis of the crystal, very fine coloured strips perpendicular to the six boundaries of the sample that formed six segments were observed (see figure 1).

The cold gas stream was controlled by Bruker B-VT 1000 variable temperature unit. It allowed us to control the temperature to a stability of better than 0.1 K. The measuring

thermocouples were made of a pure copper wire and a copper-nickel (constantan) alloy. The specimen was immersed in the middle of the cold gas stream. Since thermal gradients are ordinarily expected, two thermocouples are placed as close as possible to the specimen crystal. The temperature of the specimen is thus between the readings of these two measuring thermocouples. The difference in these two readings is about 5 K.

The crystals grown with the hexagonal shape were used by us to do the x-ray diffraction analysis. Both the Laue and the precession pictures, with Mo radiation, were taken for the sample crystals. The sample crystals were cooled down from 295 K to 184 K and then heated back to the room temperature.

3. Results and discussion

Figure 1 shows the twinning of the KLiSO_4 sample crystal under the polarising microscope at the room temperature. Six main domains are observed. In each domain, there are fine coloured strips that are parallel to the c axis when viewed perpendicular to the c axis of the crystal. However, the x-ray diffraction records did not reveal any different orientations as the x-ray beams were incident on the six different parts of a crystal sample in turn. An observation of twinning has been reported by Karppinen *et al* (1983). A twinning model with $\langle 110 \rangle$ as the twin axis or $\{110\}$ as the twin plane was proposed to derive the crystal structure of KLiSO_4 in the x-ray studies by Karppinen *et al* (1983) and in the neutron studies by Bhakay-Tamhane *et al* (1984). The observed intensity of a reflection for a twinned crystal is superposed by two individuals of the twin compositions in such a way that $I_{\text{twin}}(hkl) = I_1(hkl) + pI_2(khl)$, where p is the twin ratio. The ratio of twin compositions is about 0.2 as reported by these authors. This type of twinning with the ratio of twin less than unity does not affect the symmetry of the diffraction pattern.

The Laue diffraction pictures with the direction of x-ray beam normal to $\{0001\}$ plane of KLiSO_4 crystal were taken at 295, 267, 250, 230, 205, 190 and 184 K. Some pictures are given in figure 2. The symmetry of the Laue pattern of the sample is sixfold along the c axis at 295 K and down to 267 K. With the extinction of $(00l)$ with $l = \text{odd}$, the space group of KLiSO_4 crystal in this temperature range is identified as $P6_3$. It is difficult to recognise the twinning and its twin operations from the diffraction pictures. The space group determined in this stage is consistent with that of the most previous works. The reflections indexed as $\{232\}$ and $\{322\}$ in the Laue photographs have different intensities. They become almost equal in the temperature region between 250 and 205 K. The symmetry of the Laue pattern in this temperature range is 6 mm. As the temperature went below 190 K, the symmetry of the Laue diffraction pattern reappeared as sixfold again.

The x-ray precession method can reproduce the crystal symmetry and the undistorted photographs of the reciprocal lattice on flat films. For the zero-level ($l = 0$) precession photographs of the KLiSO_4 sample crystal, the intensities of the $\{210\}$ and $\{120\}$ reflections (also the $\{230\}$ and $\{320\}$ reflections) having normally substantially different intensities, became almost equal, relatively speaking, at temperatures between 250 and 205 K. It was also found for the first-level ($l = 1$) precession photographs that the $\{111\}$ reflections with relatively strong intensities at temperatures above 250 K disappeared in 250 K to 205 K temperature range. Figures 3 and 4 show the zero- and the first-level precession photographs taken at 295 K, 250 K and 190 K respectively.

Both the symmetries of the Laue diffraction pattern and the high-level precession photographs showed that the symmetry of the KLiSO_4 crystal is 6 mm in the temperature

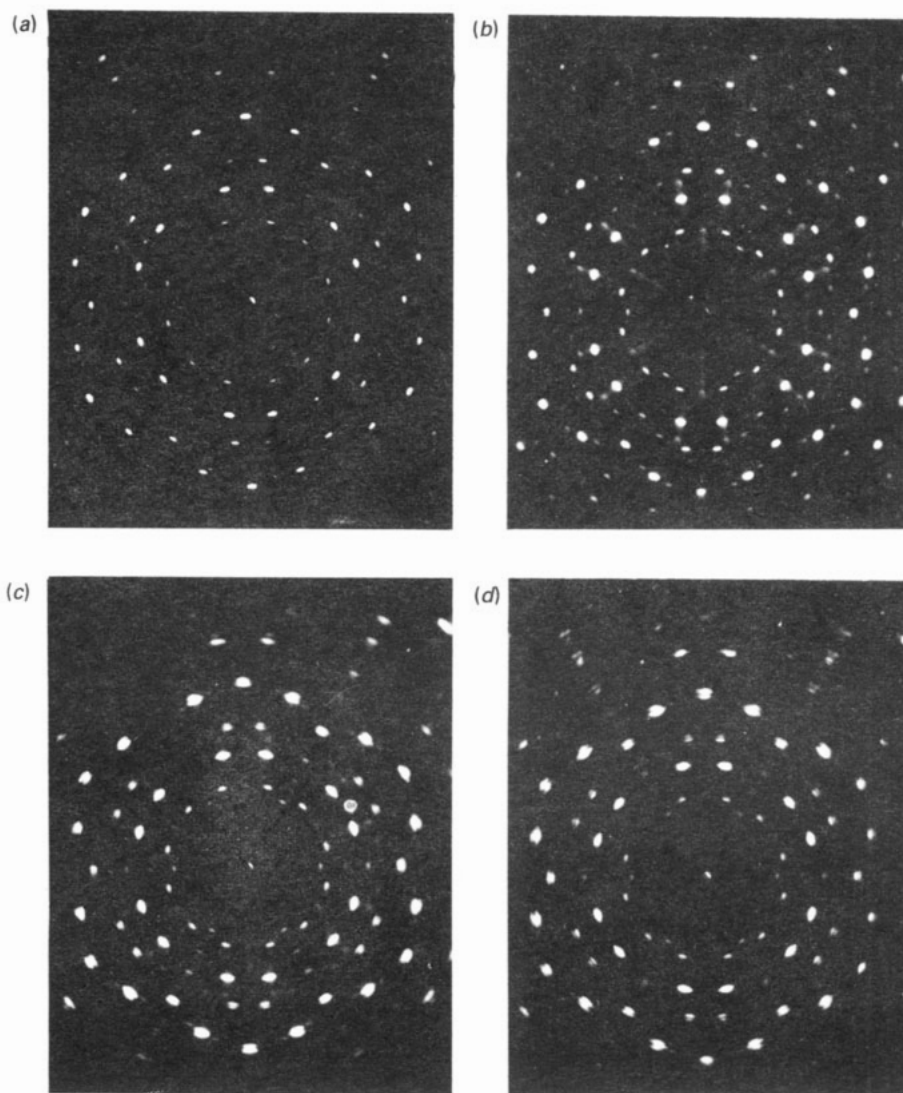
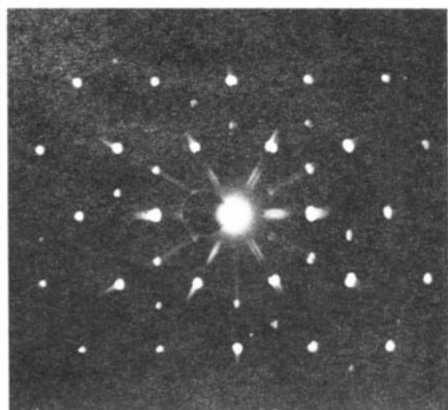
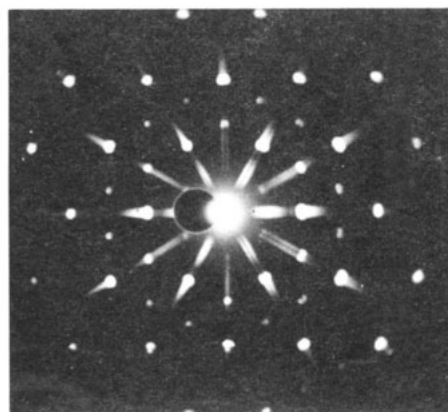


Figure 2. Laue x-ray diffraction patterns, with the *c* axis pointing to x-ray beams at different temperatures. (a) 295 K; (b) 250 K; (c) 230 K; (d) 190 K. The photographs were taken with Mo radiation at 35 kV and 20 mA.

range 250–205 K. The possible reflections and the intensity relations found in the diffraction patterns in this temperature region satisfied the conditions of the space group of $P6_3mc$. The hexagonal $P6_3mc$ phase of $KLiSO_4$ crystal was also proposed by Tomaszewski and Lukaszewicz (1983). The transition temperatures in their studies are at 210 K and 190 K on different samples on cooling and the mixture of the $P6_3$ phase and the $P6_3mc$ phase existed until about 180 K. Since our x-ray diffraction pictures were taken with moderate exposure times, the absence of the $\{111\}$ reflections in figure 4 would be evidence of no co-existence of two phases. However, Tomaszewski and Lukaszewicz (1983) do obtain the pure $P6_3mc$ phase of the $KLiSO_4$ crystal on the reverse heating process in the 187–255 K temperature region. As we can see from the precession



(c)

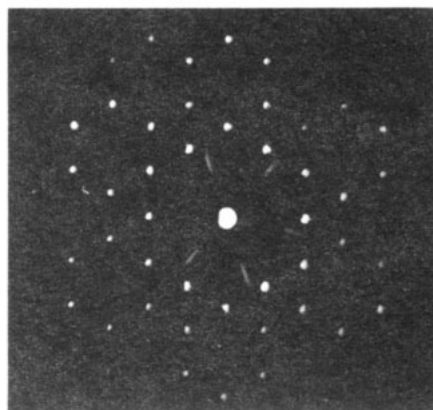


(b)

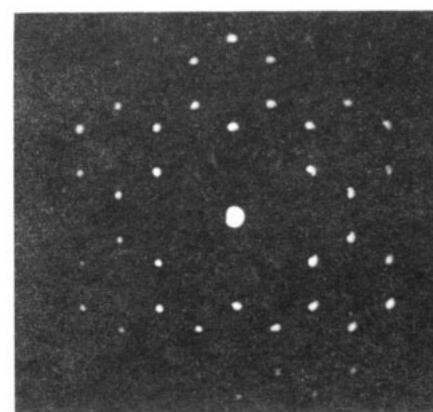


(a)

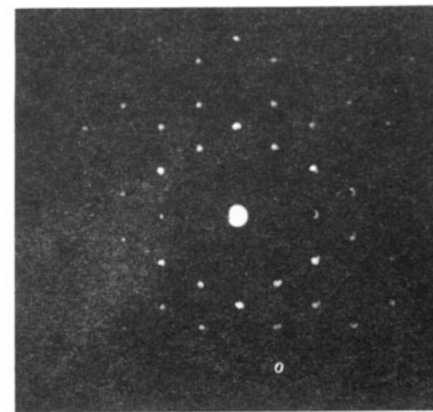
Figure 3. Zero-level precession photographs, with the c axis as the precession axis, taken for (a) 295 K; (b) 250 K; (c) 190 K.



(c)



(b)



(a)

Figure 4. First-level ($l = 1$) precession pictures taken at 295 K, 250 K and 190 K are shown in (a), (b) and (c).

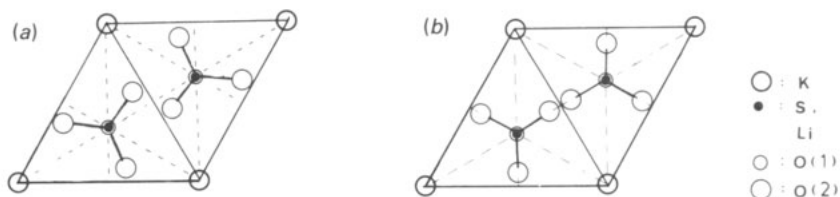


Figure 5. Projection of the atomic position onto the (0001) plane of a hexagonal unit cell of KLiSO_4 in (a) the $P6_3$ phase; (b) the $P6_3mc$ phase.

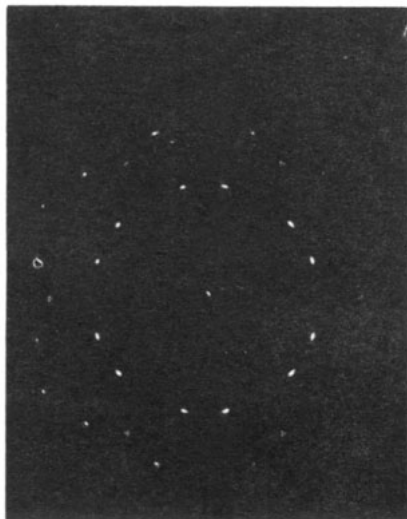


Figure 6. The Laue diffraction pattern for a smaller KLiSO_4 sample crystal taken at 215 K.

photographs of these two phases, most of reflections with stronger intensity are unchanged. Some reflections with the condition $h - k = 3n$ are very strong with $l = \text{even}$, but are rather weak with $l = \text{odd}$. The crystal structure of KLiSO_4 in the $P6_3mc$ phase would be only slightly different from that in the $P6_3$ phase. The projection of the atomic positions on the ab plane for the KLiSO_4 crystal in the $P6_3$ phase and the $P6_3mc$ phases are shown in figure 5. Both of the crystal structures have the K atoms located at the atomic positions $(0, 0, 0)$ and $(0, 0, \frac{1}{2})$; Li atoms, S atoms, and O(1) atoms occupied positions $(\frac{1}{3}, \frac{2}{3}, Z)$ and $(\frac{2}{3}, \frac{1}{3}, Z + \frac{1}{2})$. The atomic positions of O(2), which form the three vertices of the SO_4 tetrahedra, play an important role in the symmetry and the space-group determination. In an untwinned and ordered model of the KLiSO_4 structure in the $P6_3$ phase, the O(2) atoms were at the general positions of $6(c)$, as determined by several experimental groups. As the crystal is in the $P6_3mc$ phase, the positions of the O(2) will transform to the special positions of $6(c)$ of the $P6_3mc$ space group. Tomaszewski and Lukaszewicz (1983) also proposed a phase transition from the hexagonal $P6_3mc$ to the orthorhombic $\text{Cmc}2_1$ on further cooling at 180 K. But it was not experimentally observed in our diffraction data. From the orientation-precession and Laue diffraction pictures, it was also found that the mosaic spread of the reflection spots became very broad at the temperature range 230–205 K.

If a smaller sample crystal of KLiSO_4 were used, some reflection spots were found to have split into three tiny spots at 215 K. The Laue diffraction picture of this is shown in figure 6. It indicates that the KLiSO_4 crystal was composed of three twin domains

whose structures were nearly but not quite parallel to each other in this temperature range. A different type of twin domain of the $\langle 110 \rangle$ and its effect have been reported by Yu and Chou (1986) in an EPR spectrum analysis at 215 K. A complex of twin domains was also observed optically at low temperature by Cash *et al* (1985). Sometimes, the point group or the space group of a crystal could be misjudged by the existence of the twinning in the crystal. One example has been found recently in another sulphate compound, KNaSO_4 , by Yu *et al* (1988). The x-ray diffraction symmetry of KNaSO_4 crystals is augmented by the existence of twinning as the twin ratio approaches unity. It is not found in the case of KLiSO_4 crystals. The present result of the transition of the space group in KLiSO_4 crystals from the $P6_3$ to the $P6_3mc$ is attributed to the atomic displacement of O(2) atoms and not to the twinning in the KLiSO_4 crystal, since the absence of the $\{111\}$ reflections cannot be caused by the twinning in the crystal. Surprisingly, the phase of the KLiSO_4 crystal re-entered the hexagonal $P6_3$ phase below 190 K. The diffraction symmetries of the Laue and the precession pictures taken below 190 K are the same as those taken at room temperature and those taken at the temperature above 250 K, except with stronger intensities. The 're-entrant' transition was also reported by Fonseca *et al* (1983) at 83 K after sequential phase transitions in EPR studies of the KLiSO_4 crystal. But the re-entry-transition temperature obtained by these authors was much lower than ours. However, this result is different from those of Bansal *et al* (1980), Tomaszewski and Lukaszewicz (1983), and Yu and Chou (1986). The diffraction pictures shown in figures 2, 3 and 4 are all reproducible for many sample crystals and for one-sixth of the samples. As the crystal was heated back to the room temperature, the phase of KLiSO_4 crystal transformed through the reverse cycle to the room-temperature phase.

In conclusion, we have found that the phase sequence of KLiSO_4 crystal is $P6_3$ — $P6_3mc$ — $P6_3$. It seems that the twinning existing in the sample crystals has no effect on the determination of symmetry. But the suspicion and the twin law in the KLiSO_4 crystals at low temperature cannot be resolved until analysis of the intensities of reflections is made by further x-ray structure refinement.

Acknowledgment

This work was supported by a grant from the National Science Council of the Republic of China (project number NSC 76-0208-M003-13).

References

- Ando R 1962 *J. Phys. Soc. Japan* **17** 141
- Bansal A L, Deb S K, Roy A P and Sahni V C 1980 *Solid State Commun.* **36** 1047
- Bhakay-Tamhane S, Sequeira A and Chidambaram R 1984 *Acta Crystallogr. C* **40** 1648
- Bradley A J 1925 *Phil. Mag.* **49** 1225
- Breczewski T, Krajewski T and Mroz B 1981 *Ferroelectrics* **33** 9
- Cash R, Tomaszewski P E and Bornarel J 1985 *J. Phys. C: Solid State Phys.* **18** 915
- Chung S J and Hahn T 1972 *Acta Crystallogr. A* **28** 557
- Delfino M, Loiacono G M and Smith W A 1980 *J. Solid State Chem.* **31** 131
- Fonseca C H A, Ribeiro G M, Gazzinelli R and Chaves A S 1983 *Solid State Commun.* **46** 221
- Holuj F and Drozdowski M 1981 *Ferroelectrics* **36** 379
- Karppinen M, Lundgren J O and Liminga R 1983 *Acta Crystallogr. C* **39** 34
- Sandomirskii P A, Meshalkin S S and Rozhdestvenskaya I V 1983 *Sov. Phys.—Crystallogr.* **28** 33

Schulz H, Zukcker Udo and Frech Rotger 1985 *Acta Crystallogr. B* **41** 21

Sharma D P 1979 *Pramana* **13** 223

Tomaszewski P E and Lukaszewicz K 1983 *Phase Transitions* **4** 37

Yu Jiang-Tsu and Chou Shen Yuan 1986 *J. Phys. Chem. Solids* **47** 1171

Yu Jiang-Tsu, Tsai Shu-Fei and Chen R H 1988 *Phys. Rev. B* **38** 11147