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## Phase transitions in $\text{LiKSO}_4$ between 1.5 K and 850 K: an infrared spectroscopic study

Ming Zhang<sup>†</sup>, Ekhard K H Salje<sup>†‡</sup> and Andrew Putnis<sup>§</sup>

<sup>†</sup> Department of Earth Sciences, University of Cambridge, Downing Street, Cambridge CB2 3EQ, UK

<sup>‡</sup> Interdisciplinary Research Centre in Superconductivity, Madingley Road, Cambridge CB3 0HE, UK

<sup>§</sup> Institut für Mineralogie, Westfälische Wilhelms-Universität, Corrensstrasse 24, D-48149 Münster, Germany

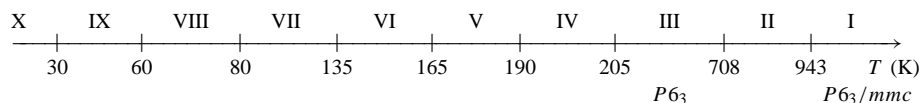
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**Abstract.** A systematic infrared spectroscopic investigation of the sequence of phase transitions in  $\text{LiKSiO}_4$  at temperatures between 1.5 K and 850 K in the region of  $50\text{--}1500\text{ cm}^{-1}$  is reported. IR powder spectra show phase transitions near 35 K, 60 K, 140 K, 190 K, 240 K and 708 K on heating. The transitions are characterized either by the appearance of new IR bands, IR band splitting or a change in the temperature dependence of spectral profiles. The numbers of internal bands show that the phases in the temperature regions of 140–190 K and 190–240 K consist of a monoclinic (space group  $Cc$ ) and a trigonal (space group  $P31c$ ) structure, respectively. The observation of two  $\nu_2$  IR modes between 140 and 190 K rules out the orthorhombic structure of  $C_{2v}^{12}$  ( $Cmc2_1$ ). Symmetry changes occur at the phase transitions at 135 K and 60 K.

### 1. Introduction

Lithium potassium sulphate ( $\text{LiKSO}_4$ ) has been investigated in great detail because of its large variety of physical properties found in its different structural phases (e.g. pyroelectricity, ferroelasticity, ferroelectricity, fast-ionic conductivity and structure incommensurations).  $\text{LiKSO}_4$  belongs to the family of compounds  $\text{LiMAB}_4$  ( $M = \text{Na, K, Rb, Cs, NH}_4$ ;  $\text{AB}_4 = \text{SO}_4, \text{BeF}_4$ ) with structures formed by six member rings of tetrahedra, three  $\text{AB}_4$  alternating with three  $\text{LiB}_4$ . Each sulphate group is linked to four others via a lithium ion. The orientation and deformation of the  $\text{SO}_4$  tetrahedra result in the different structures, so  $\text{LiKSO}_4$  undergoes several phase transitions at high and low temperatures. Extensive studies on the phase transitions in  $\text{LiKSO}_4$  have been carried out in past by a variety of measurements of physical parameters: specific heat (Abello *et al* 1985, Kassem *et al* 1994), electric properties (Breczewski *et al* 1981, Mróz *et al* 1982, Mendes *et al* 1986, Pimenta *et al* 1989, Desousa *et al* 1993), acoustic wave propagation (Borisov *et al* 1994, 1997, Gridnev and Khodorov 1996), thermal expansion (Prasad *et al* 1978), EPR (Dantas *et al* 1991, Hefni *et al* 1994), acoustic phonon frequencies (Mróz *et al* 1989, Czajkowski *et al* 1991), Raman active phonon dispersion (Hiraishi *et al* 1976, Bansal *et al* 1980, Teeters and Frech 1982, Ganot *et al* 1985, Mendes *et al* 1986, Oliveria *et al* 1988, Kim and Frech 1988, Moreira *et al* 1995, Dharmasena and Frech 1995), IR phonon frequencies (Hiraishi *et al* 1976, Pimenta *et al* 1986, 1989, Varma *et al* 1990), optical birefringence (Sorge and Hempel 1986, Leitão *et al* 1994, Moreira *et al* 1995), resonant ultrasound absorption

(Willis *et al* 1996), NMR (Topic *et al* 1988, Lim *et al* 1997), ESR (Holuj and Drozdowski 1981, Fonseca *et al* 1983, Perpétuo *et al* 1992), x-ray diffraction spectra (Tomaszewski and Lukaszewicz 1983, Sankaran *et al* 1988, Chen and Wu 1989, Welberry and Glazer 1994, Désert *et al* 1995, Ventura *et al* 1996, Scherf *et al* 1997) and neutron scattering (Bhakay-Tamhane *et al* 1985, Bhakay-Tamhane and Sequeira 1986, Eckold *et al* 1987, Balagurov *et al* 1986, Mukhopadhyay *et al* 1986, Bhakay-Tamhane *et al* 1991, Rajagopal *et al* 1991, Savenko *et al* 1992). In summary, the following sequence of phases (Perpétuo *et al* 1992) is used here to describe the phases and the transition temperatures between them:



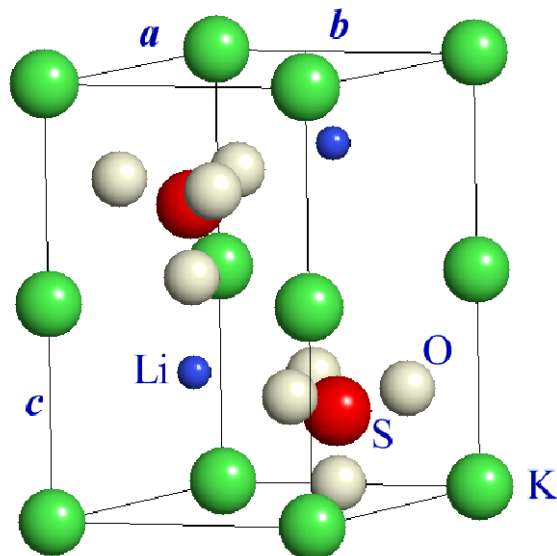
where the temperatures, given in Kelvin, are averaged over the published values in the cooling runs.

Despite the extensive effort in researching  $\text{LiKSO}_4$ , only the structures of phase I and phase III are well established. Above 943 K, the phase is hexagonal with space group  $D_{6h}^4$  ( $P6_3/mmc$ ) (Chung and Hahn 1972, Li 1984). It is characterized by orientational disorder of the sulphate group which is associated with the mobility of cations (Pimenta *et al* 1989).

The structure of the phase between 708 K and 943 K is not well known. An orthorhombic symmetry of phase II was proposed by Chung and Hahn (1972) while Li (1984) and Xie *et al* (1984) suggested the existence of a modulated structure in this phase, which would be commensurate between 708 and 743 K and incommensurate between 743 and 943 K. In their studies, Borisov *et al* (1994) observed an acoustic anomaly at 743 K. The existence of three kinds of ferroelastic domains in phase II which are oriented at  $120^\circ$  one to another was shown by some authors (Krajewski *et al* 1985, Sorge and Hempel 1986). The results were incompatible with the hexagonal symmetry suggested by Li (1984). An x-ray diffraction study (Sankaran *et al* 1988) showed that this phase could be described as a normal phase with orthorhombic symmetry, space group  $Pnma$ , containing  $Z = 4$  formula units. In their Brillouin-scattering measurements, Pimenta *et al* (1987) have shown an anisotropy in the velocity of the longitudinal acoustic waves propagating in the basal plane, which indicates that the symmetry of phase II could be lower than hexagonal.

The room-temperature structure of  $\text{LiKSO}_4$  belongs to space group  $P6_3$  ( $C_6^2$ ) with two formula units per unit cell (Bradley 1925, Schulz *et al* 1985) (figure 1). The lattice parameters of the unit cell are  $a = 5.147 \text{ \AA}$  and  $c = 8.635 \text{ \AA}$ .

Below room temperature, several phases have been reported and there is some disagreement about the nature of structures, the transition temperatures and the number of the transitions. With decreasing temperature  $\text{LiKSO}_4$  undergoes a reconstructive phase transition (without group to subgroup relation) around 205 K (240 K on heating). A trigonal structure with space group  $C_{3v}^4$  ( $P31c$ ) was proposed by Bansal and Roy (1984) based on their Raman spectra. On the other hand, a  $C_{6v}^4$  ( $P6_3mc$ ) hexagonal structure was suggested for phase IV (Tomaszewski and Lucaszewicz 1982, Kleemann *et al* 1987). The coexistence of these two different structures was observed over a broad temperature range (Perpétuo *et al* 1992). More recent measurements (Rajagopal *et al* 1991, Bhakay-Tamhane *et al* 1991) seem to support the trigonal  $P31c$  phase below room temperature. In their neutron-diffraction study, Zhang *et al* (1988) showed that disorder in the orientation of the sulphate groups persists in this phase. Bansal and Roy (1984) proposed that this phase transition is due to the reorientation of one sulphate group in each unit cell (there are two formula units per unit cell in the trigonal and hexagonal structures). Based on their study of anharmonic thermal vibrations, Schulz *et al* (1985) proposed a rotation of  $\text{SO}_4$  about an axis parallel



**Figure 1.** The hexagonal structure of LiKSO<sub>4</sub> at room temperature.

to the [120] direction, i.e. along the K–O bond. Results of Raman spectroscopy (Bansal and Roy 1984, Oliveira *et al* 1988) indicated a flip of the sulphate group about a basal axis as the mechanism for transition, although lattice dynamical calculations (Chaplot *et al* 1984) suggested a higher probability for flipping about the *c*-axis and Bhakay-Tamhane *et al* (1991) suggested that one SO<sub>4</sub> group rotates through 45° about the S–O bond along the *c*-axis.

On further cooling through 190 K, LiKSO<sub>4</sub> undergoes a ferroelastic phase transition which is related to the freezing of the orientational disorder of SO<sub>4</sub> groups. It is not clear what is the crystalline structure of the phase below 190 K. A monoclinic structure with the space group C<sub>s</sub><sup>4</sup> (*Cc*) (Kleemann *et al* 1987) and an orthorhombic structure belonging to the space group C<sub>2v</sub><sup>12</sup> (*Cmc2<sub>1</sub>*) (Cach *et al* 1985) have been proposed and the presence of ferroelastic domains in this phase has been reported (Breczewski *et al* 1981).

Very little is known about the structure of the lower temperature phases. Tomaszewski and Lukaszewicz (1983) reported the existence of a phase transition around 165 K while Bhakay-Tamhane *et al* (Bhakay-Tamhane and Sequeira 1986, Bhakay-Tamhane *et al* 1991), based on their neutron-diffraction results, proposed a phase transition at 135 K. In their optical birefringence study, Sorge and Hempel (1986) reported a phase transition to monoclinic symmetry at 83 K.

Two anomalies at 65 K and 38 K respectively were reported in a DSC study (Abello *et al* 1985). An EPS investigation by Bill *et al* (1988) showed weak anomalies in line profiles at 65 K and 38 K. The temperature dependence of electric properties of LiKSO<sub>4</sub> (Cach *et al* 1984, Oliveira *et al* 1988, Desousa *et al* 1993) showed anomalous changes near 30 K suggesting the existence of an additional low-temperature phase.

The aim of this study is to investigate the sequences of the transitions in LiKSO<sub>4</sub> for which controversies remain concerning even the number of phase transitions, their structural properties and the transition mechanisms. We shall argue that we identified six transition temperatures and that each mechanism corresponds to well defined phonon anomalies.

## 2. Experimental

The LiKSO<sub>4</sub> crystals were grown by slow evaporation of aqueous solution at 40 °C. The structure of the crystals at room temperature was confirmed by powder x-ray diffraction analysis.

The infrared powder technique was used. The powder for this IR work was obtained by ball-milling the sample in an agate mortar in a Spex microball mill for 25 minutes. KBr was used as matrix material for high temperature measurements (350–1500 cm<sup>-1</sup>) and low-temperature MIR measurements while CsI and polyethylene were used for far-infrared measurements at low temperatures.

Using a Bruker 113v FT-IR spectrometer, the absorption spectra were recorded under vacuum to avoid absorption from water and carbon oxides in the air at temperatures between 2 K and 830 K. Experiments were performed in both the mid-infrared, in the region of ~500–1500 cm<sup>-1</sup> using an HgCdTe detector cooled with liquid nitrogen, and the far-infrared, the region of ~20–700 cm<sup>-1</sup> using a room-temperature DTGS detector. Instrumental resolution of 0.5, 1 and 2 cm<sup>-1</sup> was used between 300 and 1500 cm<sup>-1</sup> and 2 cm<sup>-1</sup> between 50 and 350 cm<sup>-1</sup>. A cylindrical Pt-wound furnace coupled with a Eurotherm type 815 temperature controller was used for high-temperature experiments and a continuous flow liquid-He cryostat (Oxford Instruments) and a closed cycle liquid-nitrogen cryostat (Leybold), both equipped with KRS5 and polyethylene windows, were used for low-temperature experiments.

## 3. Analysis and results

### 3.1. Band assignment

Group theory (Hiraishi *et al* 1976) gives the irreducible representations for the C<sub>6</sub><sup>h</sup> space group as follows:

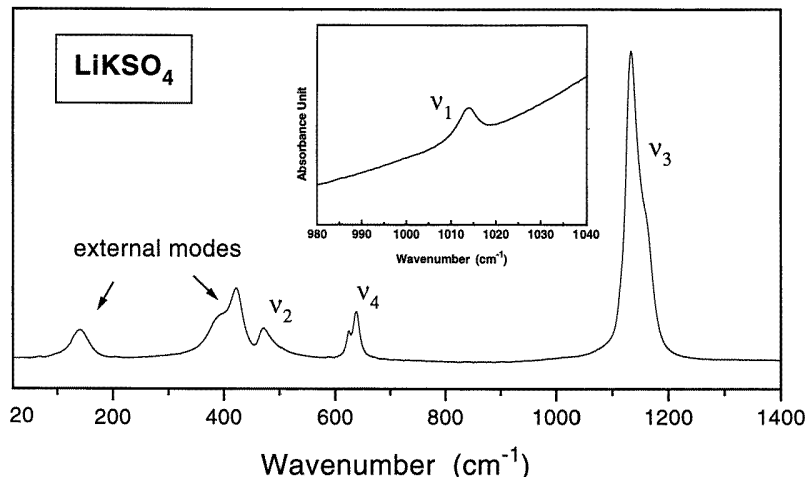
$$\Gamma = 7A + 7B + 7E_1 + 7E_2$$

among them acoustic modes (A + E<sub>1</sub>), optical transitional modes (2A + 3B + 2E<sub>1</sub> + 3E<sub>2</sub>), optical librational modes (A + B + E<sub>1</sub> + E<sub>2</sub>) and internal modes (3A + 3B + 3E<sub>1</sub> + 3E<sub>2</sub>). A, E<sub>1</sub> and E<sub>2</sub> are Raman active, and A and E<sub>1</sub> are infrared active while B modes are optically silent.

The room-temperature infrared spectrum of LiKSO<sub>4</sub> is shown in figure 2. Altogether 10 modes of the predicted 12 infrared modes are observed in the frequency region between 85 and 1500 cm<sup>-1</sup> at room temperature. They are located at 128, 202, 396, 422, 471, 624, 638, 1014, 1136 and 1165 cm<sup>-1</sup>. The vibrational modes in LiKSO<sub>4</sub> can be described by internal modes of the SO<sub>4</sub> group and external modes. The IR spectrum of the SO<sub>4</sub> group in LiKSO<sub>4</sub> is characterized by four types of internal mode: S–O symmetrical stretching  $\nu_1$  (1013 cm<sup>-1</sup>), O–S–O symmetrical bending  $\nu_2$  (471 cm<sup>-1</sup>), S–O antisymmetrical stretching  $\nu_3$  (1136 and 1165 cm<sup>-1</sup>) and O–S–O antisymmetrical bending  $\nu_4$  (624 and 638 cm<sup>-1</sup>). For the C<sub>6</sub><sup>h</sup> space group all the predicted six internal modes of SO<sub>4</sub> tetrahedra were observed in this study.

The modes below 420 cm<sup>-1</sup> are external modes (transitional and librational modes). The A mode at 396 cm<sup>-1</sup> and the E<sub>1</sub> modes at 422 cm<sup>-1</sup> are mainly due to Li motion according to the IR study on <sup>6</sup>LiKSO<sub>4</sub> and <sup>7</sup>LiKSO<sub>4</sub> by Teeters and Frech (1982).

The A mode at 202 cm<sup>-1</sup> is assigned as SO<sub>4</sub> rotation. According to Chaplot *et al* (1984), it corresponds to libration of SO<sub>4</sub> around the *c*-axis.



**Figure 2.** Infrared spectrum of LiKSO<sub>4</sub> between 20 cm and 1400 cm<sup>-1</sup> at room temperature.

A broad absorption feature occurs near 128 cm<sup>-1</sup>. It in fact consists of two modes which have very close frequencies: 133 cm<sup>-1</sup> (E<sub>1</sub>) and 134 cm<sup>-1</sup> (A) (Hiraishi *et al* 1976). As K<sub>2</sub>SeO<sub>4</sub> (Petzelt *et al* 1979) and K<sub>2</sub>SO<sub>4</sub> (a spectrum measured in this study) have bands between 100 and 150 cm<sup>-1</sup> which are mainly related to O–K motions, the band near 128 cm<sup>-1</sup> in LiKSO<sub>4</sub> could result from a similar origin. The lattice-dynamical calculation by Chaplot *et al* (1984) also showed that these modes are both mainly due to K translation and SO<sub>4</sub> translation.

The E<sub>1</sub>(TO) mode near 40 cm<sup>-1</sup> observed by Raman spectroscopy (Bansal and Roy 1984) was not recorded in this study due to its weak infrared absorption. It was assigned to the rotation of SO<sub>4</sub> around an axis perpendicular to the *c*-axis (Chaplot *et al* 1984).

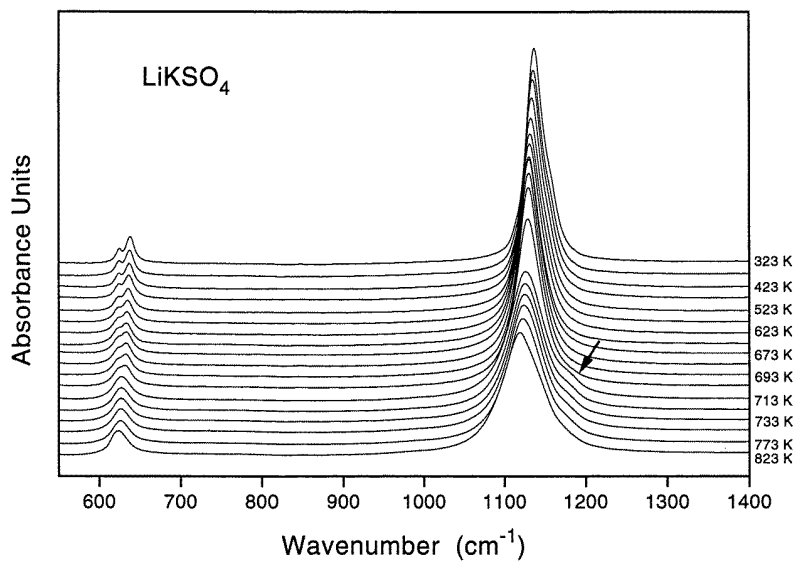
### 3.2. Temperature dependence of IR spectra at high temperatures

The temperature evolution of the infrared spectra at high temperatures is shown in figure 3. The effects of temperature on the spectra can be seen as a gradual decrease in band intensities, broadening in width and shifts of phonon frequencies.

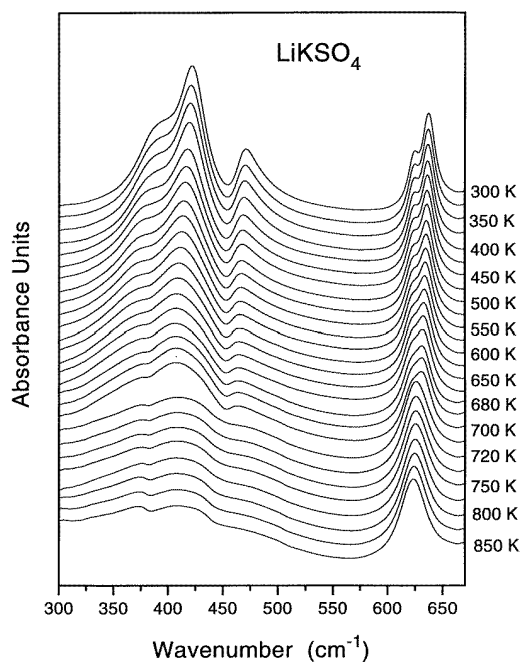
The transition from phase III to phase II at 708 K is characterized by discontinuous changes in frequencies, linewidths (FWHM) and integrated intensities of infrared bands. The changes can be seen as follows:

(1) Anomalous changes of S–O stretching modes were observed. The S–O antisymmetrical stretching  $\nu_3$  at 1136 and 1165 cm<sup>-1</sup> exhibit sudden decreases of their frequencies near 708 K (figure 3(A)), which implies that the transition is of first order. The width of the 1136 cm<sup>-1</sup> phonon mode shows a sudden increase of about 30% of its value at the transition temperature, suggesting that phase II is more disordered. An extra mode at 1180 cm<sup>-1</sup> appears at phase II (figure 3(A)). The intensity of this band decreases with increasing temperature and seems to vanish at phase I. The observation of this absorption is consistent with previous infrared reflection work by Pimenta *et al* (1986).

(2) The internal S–O bending modes show significant variations. With increasing temperature the two  $\nu_4$  modes—the A mode near 636 cm<sup>-1</sup> and the E<sub>1</sub> mode at 623 cm<sup>-1</sup>—exhibit a gradual decrease in frequency and a change of the spectral profile near 708 K



(A)



(B)

**Figure 3.** (A) Temperature evolution of infrared spectra of  $\text{LiKSO}_4$  between 550 and  $1400\text{ cm}^{-1}$  at temperatures between 323 K and 823 K. (B) The temperature evolution of infrared spectra of  $\text{LiKSO}_4$  between 300 and  $680\text{ cm}^{-1}$  between 300 K and 850 K.

(figures 3(B) and 4(C)). This transition is also seen in the internal  $\nu_2$  mode. It shows a decrease in intensity with increasing temperature and a sudden broadening and discontinuous drop of intensity near 708 K.

(3) Li bands exhibit anomalous variations. With increasing temperature, the Li modes at  $396$  and  $422\text{ cm}^{-1}$  exhibit pronounced broadening and decrease in intensity. This may mainly result from the onset of Li mobility at high temperatures. The integrated intensity between  $310$  and  $560\text{ cm}^{-1}$  as a function of temperature exhibits a discontinuity near  $708\text{ K}$  (figure 4(D)).

Anomalies of frequencies as a function of temperature for  $1135$  and  $623\text{ cm}^{-1}$  modes around  $740\text{ K}$  were observed. As Borisov *et al* (1994) observed an anomaly in the transverse-acoustic phonon frequency near  $740\text{ K}$ , it is reasonable to consider that the anomalies in IR and transverse-acoustic phonons stem from the same origin. At temperatures near  $740\text{ K}$ , a lock-in transition was reported (Xie *et al* 1984, Li 1984), but a recent x-ray study at high temperatures ( $708\text{ K} < T < 943\text{ K}$ ) (Ventura *et al* 1996) suggested an incommensurate structure in this temperature region. The nature of this anomaly is unclear and more structural investigations are necessary to understand the nature of the anomalies near  $740\text{ K}$ .

### 3.3. Temperature dependence of IR spectra at low temperatures

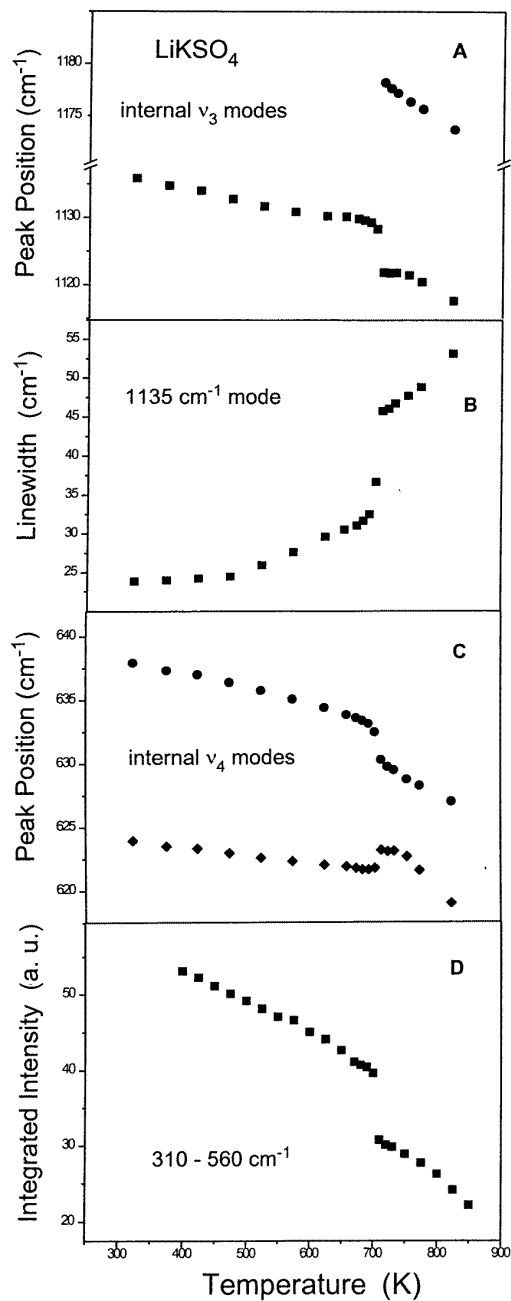
With decreasing temperature from  $300\text{ K}$ ,  $\text{LiKSO}_4$  undergoes several more phase transitions. As shown in figure 5, the most significant variations with decreasing temperature occur in the frequency range between  $85$  and  $500\text{ cm}^{-1}$ . The S–O bending between  $600$  and  $660\text{ cm}^{-1}$  and the S–O stretching between  $1000$  and  $1250\text{ cm}^{-1}$  exhibit weak changes through the transitions. In order to display the weak variations of those spectral features, the absorption spectrum of  $\text{LiKSO}_4$  recorded at  $300\text{ K}$  or  $100\text{ K}$  were subtracted from those measured at different temperatures (figure 6).

Between  $200\text{ K}$  and  $300\text{ K}$ , the infrared spectrum of  $\text{LiKSO}_4$  does not exhibit significant variations, in contrast to marked variations observed by Raman spectroscopy (Mendes *et al* 1986, Oliveira *et al* 1988), acoustic properties (Borisov *et al* 1997) and elastic constant measurements (Willis *et al* 1996). The reported reconstructive phase transition from phase III to phase IV at  $210\text{ K}$  on cooling ( $240\text{ K}$  on heating) (Tomaszewski and Lukaszewicz 1982) was characterized by weak changes of the spectral profiles of the infrared modes at  $429$  and  $1135\text{ cm}^{-1}$  (figures 7(B) and 8(B)). At the transition temperature, the width of the Li mode at  $429\text{ cm}^{-1}$  showed a discontinuity of the temperature dependence and the frequency of the  $1135\text{ cm}^{-1}$  absorption displayed a weak discontinuity as a function of temperature (figure 7(B)). A weak break in the temperature dependence of the infrared signals at  $1013$  and  $204\text{ cm}^{-1}$  was also observed (figures 5(A) and 5(C)). No additional changes of the infrared absorption was detected through the transition from phase II to phase III.

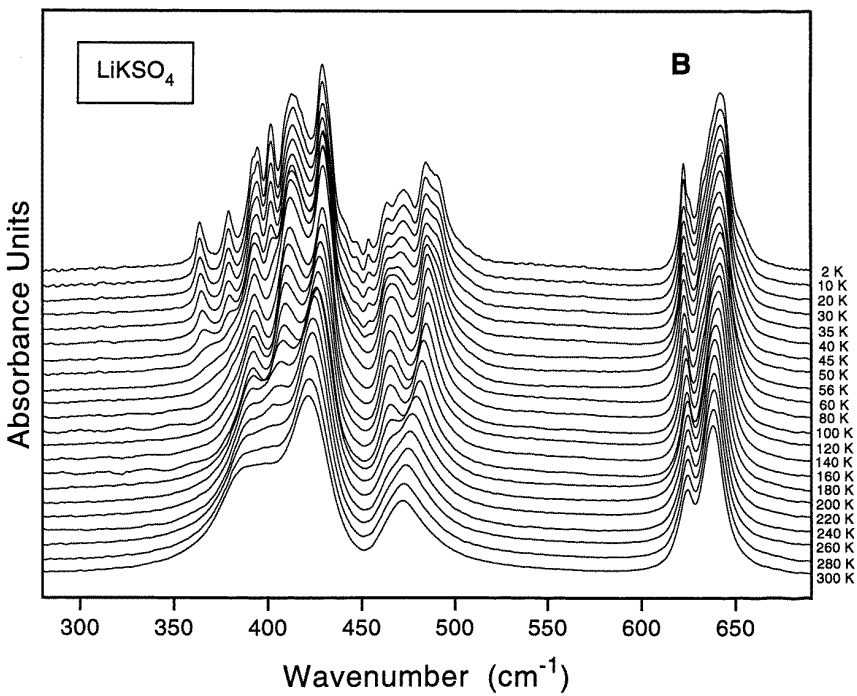
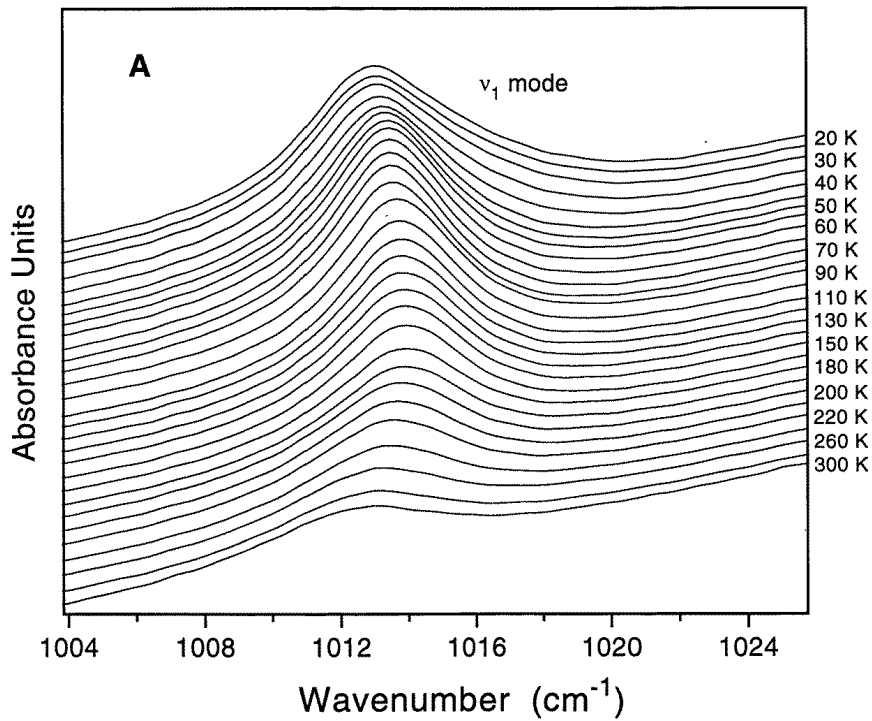
Significant spectral changes were observed through the transition from phase IV to phase V (figure 5(B)). The most important feature is that the  $\text{SO}_4$   $\nu_2$  mode at  $471\text{ cm}^{-1}$  shows a splitting as the sample is cooled through  $180\text{ K}$  (figure 5(B)) and an extra mode appears at  $632\text{ cm}^{-1}$  which may be a splitting of the  $638\text{ cm}^{-1}$  mode (figure 6(B)). Apart from this, the  $\nu_4$  modes near  $624\text{ cm}^{-1}$  and  $638\text{ cm}^{-1}$  both exhibit a break in temperature dependence and the Li modes at  $390$  and  $410\text{ cm}^{-1}$  become rather infrared active near  $190\text{ K}$ . These changes suggest the occurrence of a new phase with a lower symmetry below  $190\text{ K}$ . An absorption near  $1202\text{ cm}^{-1}$  was recorded in phase IV (figure 6(A)). Although this absorption is weak, it appears clearly in the spectra measured below  $190\text{ K}$  on heating. The emergence of the new internal modes at  $471$ ,  $632$  and  $1202\text{ cm}^{-1}$  in phase IV is an indication of breaking symmetry for the  $\text{SO}_4$  ion.

At temperature between  $180$  and  $140\text{ K}$ , no clear anomalies in the infrared spectra of  $\text{LiKSO}_4$  were detected. Two bands near  $128$  and  $165\text{ cm}^{-1}$  appeared in the spectra





**Figure 4.** (A) Peak positions of the S–O stretching modes as a function of temperature. The  $\nu_3$  mode at  $1135 \text{ cm}^{-1}$  shows a sudden decrease of frequency at 708 K with increasing temperature. An infrared mode at  $1180 \text{ cm}^{-1}$  becomes infrared active in phase II. In addition, the frequency of the  $1135 \text{ cm}^{-1}$  mode exhibits a break in the temperature dependence near 740 K. (B) Temperature dependence of the width of the  $1135 \text{ cm}^{-1}$  S–O stretching mode. With increasing temperature the discontinuous gradient indicates a typical order–disorder transition at 708 K. (C) Temperature dependence of the peak positions of the S–O bending  $\nu_4$  modes. (D) Integrated intensity in the far-infrared region between  $310$  and  $560 \text{ cm}^{-1}$ .



**Figure 5.** Temperature evolution of infrared spectra of  $\text{LiKSO}_4$  at low temperatures: (A) between 1004 and 1025  $\text{cm}^{-1}$ ; (B) between 280 and 690  $\text{cm}^{-1}$  and (C) between 85 and 250  $\text{cm}^{-1}$ .

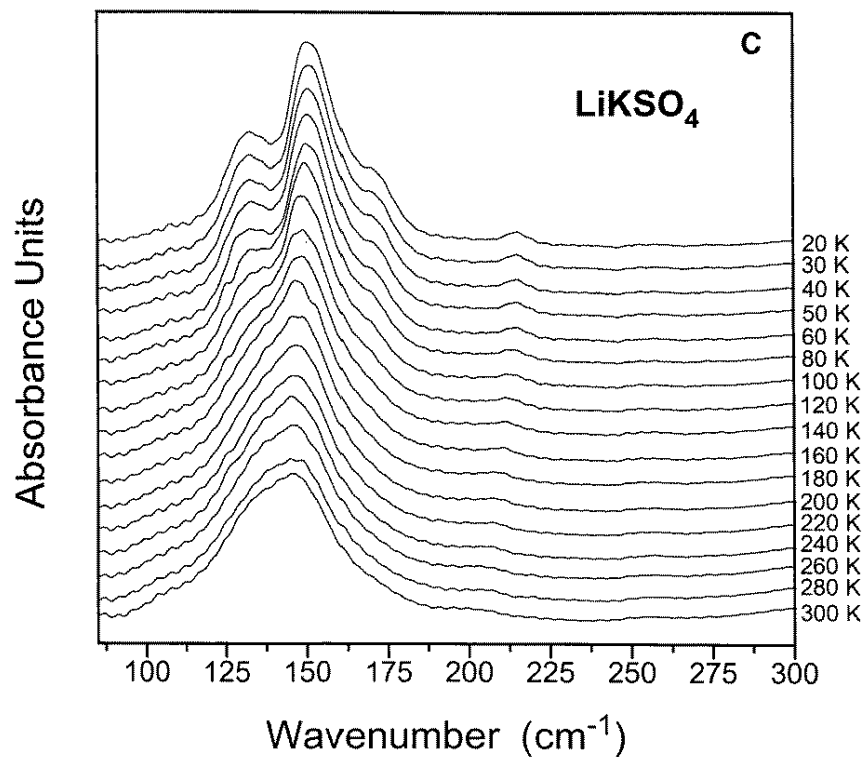
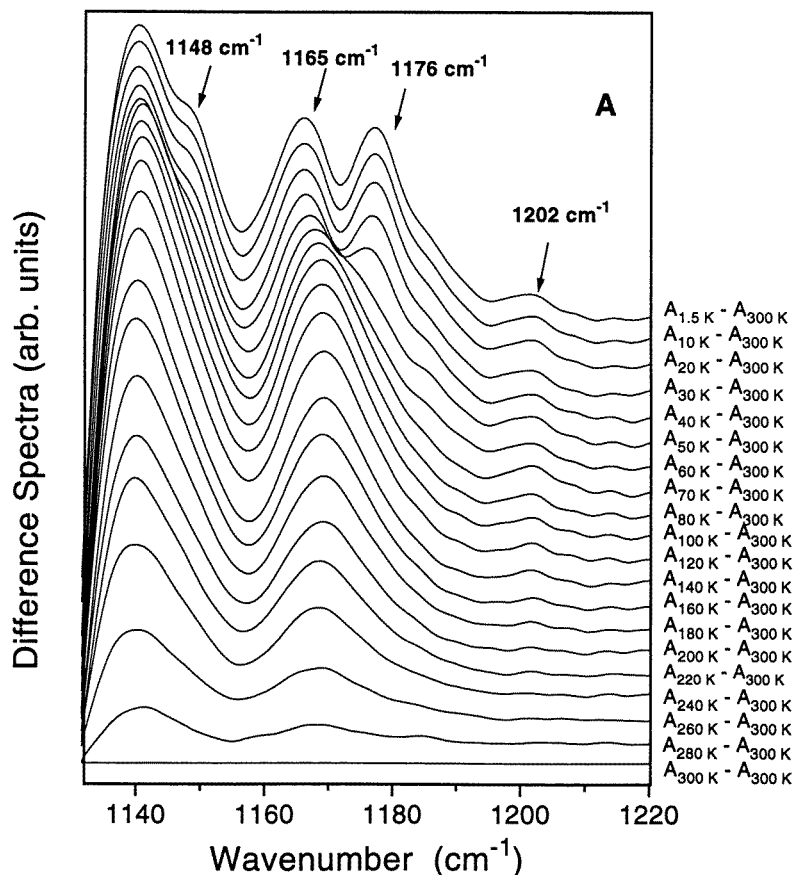


Figure 5. (Continued)

measured below 135 K (figure 5(C)) and an anomaly was seen in the width of the  $420\text{ cm}^{-1}$  band as a function of temperature (figure 8(B)), while the high frequency  $\text{SO}_4$  internal modes showed no discernible changes. It is believed that the occurrence of extra bands at  $128$  and  $165\text{ cm}^{-1}$  corresponds to the reported transition at 135 K (Bhakay-Tamhane *et al* 1991). These low-wavenumber bands are mainly due to K–O and S–O translations. Their significant changes through the transition may offer a clue to the mechanism of this transition.

No clear spectral anomalies were recorded between 60 K and 135 K.

At temperatures lower than 60 K, significant spectral changes were observed. Infrared absorption signals at  $364$ ,  $379$ ,  $402$ ,  $442$ ,  $448$  and  $454\text{ cm}^{-1}$  occur in the spectra below 60 K (figure 5(B)). They become more infrared active on further cooling. The appearance of these new bands is accompanied by an intensity discontinuity for the Li band near  $406$  and  $429\text{ cm}^{-1}$  (figure 5(B)). The frequency of the  $429\text{ cm}^{-1}$  mode starts to harden rather than to soften on cooling below 60 K and its width also exhibits a change in its temperature dependence near 60 K (figure 8). Across 60 K, the S–O bending modes between  $600$  and  $660\text{ cm}^{-1}$  exhibit a change of spectral features (figure 6(C)). In addition, spectral anomalies are also observed for S–O stretching modes. The main absorption near  $1135\text{ cm}^{-1}$  exhibits a change in temperature dependence near 60 K (figure 7(B)). Surprisingly, it also softens with decreasing temperature like the  $364$ ,  $379$  and  $429\text{ cm}^{-1}$  modes (figures 9(A) and 8(A)). This transition may be related to the weak anomalies observed by Abello *et al* (1985) and Bill *et al* (1988) near 65 K.



**Figure 6.** Temperature evolution of difference spectra: (A) the spectra in the region 1130–1220  $\text{cm}^{-1}$  between 1.5 K and 300 K; (B) the spectra between 600 and 680  $\text{cm}^{-1}$  at temperatures between 100 K and 300 K; (C) the spectra in the frequency range of 600–680  $\text{cm}^{-1}$  at temperatures between 2 K and 80 K.

A transition was recorded near 35 K on heating since band-splitting was observed for the internal  $\nu_2$  bands at 464 and 486  $\text{cm}^{-1}$  (figure 5(B)), the internal  $\nu_1$  mode at 1012  $\text{cm}^{-1}$  (figure 7(A)) and the internal  $\nu_3$  modes at 1170  $\text{cm}^{-1}$  (figures 6(A) and 7(A)). In fact, the split of these bands may start at a higher temperature, but the bands at 463 and 473  $\text{cm}^{-1}$  become clearly separated from the bands at 464  $\text{cm}^{-1}$  near 35 K. Similar behaviour was also observed for the 490, 1165 and 1176  $\text{cm}^{-1}$  bands. The S–O bending bands between 600 and 660  $\text{cm}^{-1}$  also showed an anomalous change of spectral feature through this transition (figure 6(C)). A band at 626  $\text{cm}^{-1}$  was observed in the spectra measured at 1.5 K and 10 K (figure 5(B)) and the difference spectra (figure 6(C)) show about six signals in this frequency region below 35 K. But it is difficult to determine at which temperature they first occur because of their weak intensity and overlay with each other. It is also surprising to note that at a temperature of around 35 K the external bands at 364, 379, 429  $\text{cm}^{-1}$  and the main absorption near 1135  $\text{cm}^{-1}$  show another change of frequency as a function of temperature (figures 7(B), 8(A) and 9(A)). The frequency and width of the bands at 363 and 429  $\text{cm}^{-1}$  become almost temperature independent below 35 K (figures 8 and 9). This

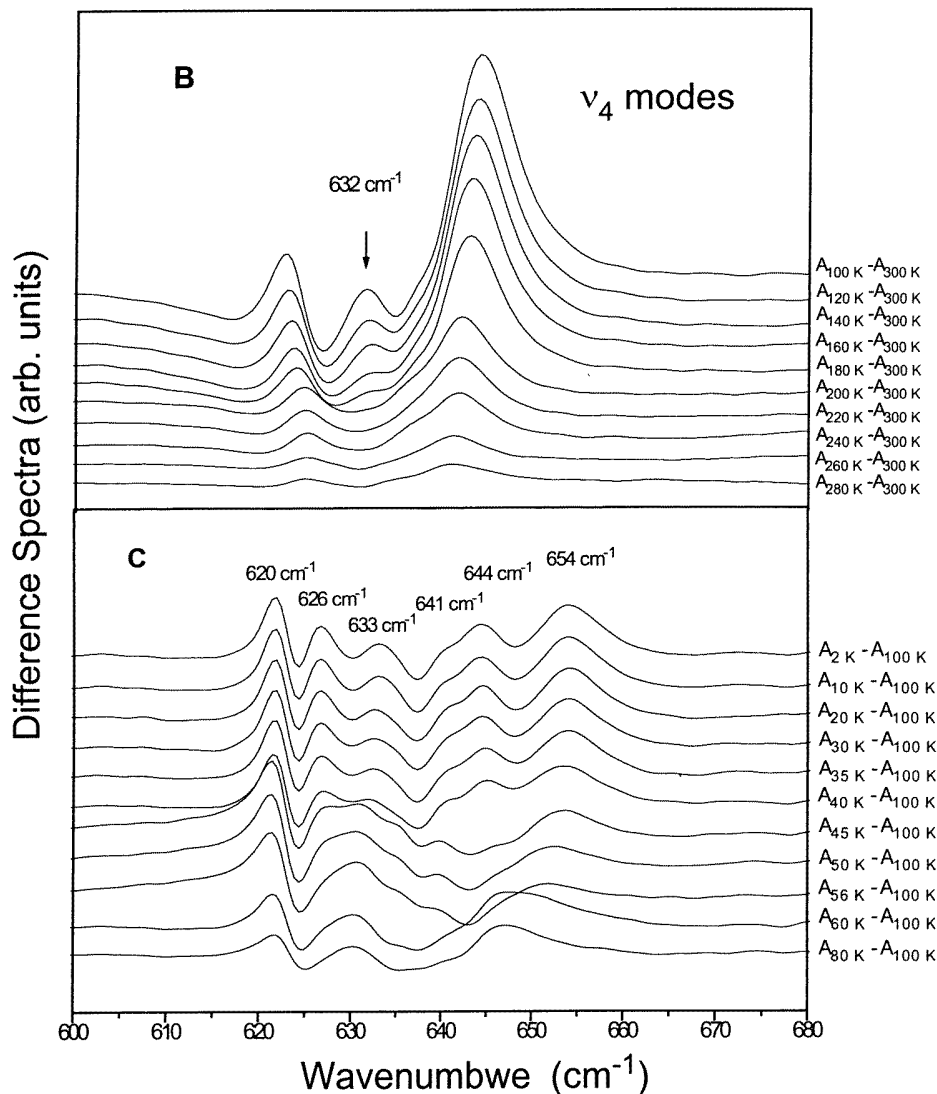
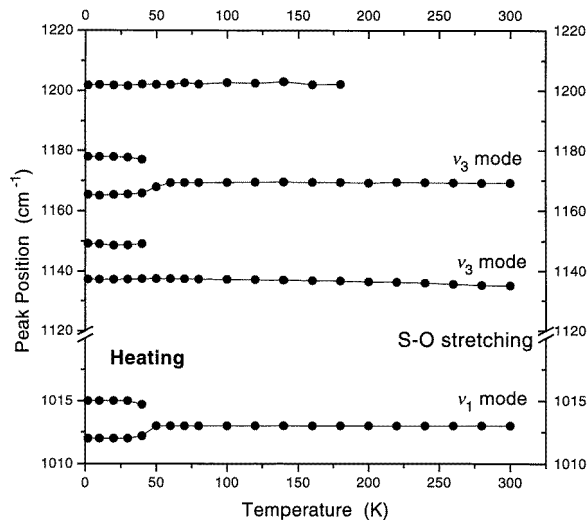


Figure 6. (Continued)

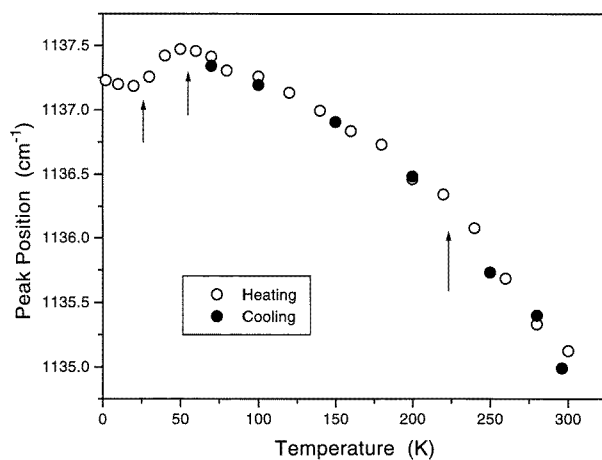
transition may correspond to the anomalies observed by electric properties measurements (Cach *et al* 1984, Oliveira *et al* 1988, Desousa *et al* 1993) near 30 K and EPS (Bill *et al* 1988) near 38 K.

#### 4. Discussion

Heating through 708 K, the appearance of the mode at  $1180\text{ cm}^{-1}$  reveals an unusual behaviour: a phase transition appears to happen towards a structure with lower symmetry at higher temperature. Our data are consistent with an orthorhombic symmetry phase above



(A)

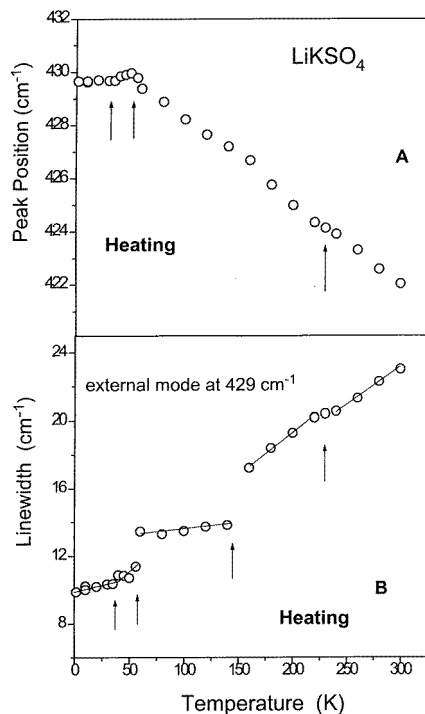


(B)

**Figure 7.** (A) Peak positions of S–O stretching bands as a function of temperature. (B) Temperature dependence of the peak position near  $1135\text{ cm}^{-1}$  at low temperatures.

708 K as suggested by Chung and Hahn (1972), but also with multiplication of the unit cell by a factor of four (Li 1984). However, it is puzzling that only one additional infrared active mode is observed in this phase. Raman spectroscopy (Bansal *et al* 1983) showed no additional mode.

The low-temperature neutron diffraction results by Bhakay-Tamhane *et al* (1991) showed that the cell parameters are  $a = b = 5.138\text{ \AA}$  and  $c = 8.655\text{ \AA}$  with  $Z = 2$  for phase IV and no evidence of cell doubling was observed. No extra infrared internal mode was observed across the transition near 205 K on cooling, suggesting that the number of the infrared internal modes is unchanged, i.e. there are still six internal IR modes. The observation of the existence of these modes is consistent with  $P31c$  ( $C_{3v}^4$ ) symmetry for the phase IV, as

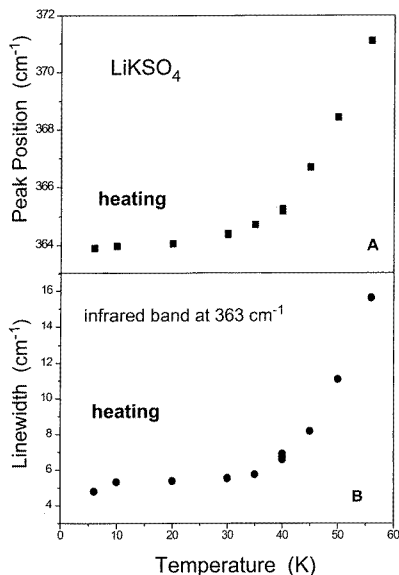


**Figure 8.** Temperature dependence of spectral parameters of the Li mode at  $429\text{ cm}^{-1}$  at low temperatures: (A) peak position and (B) width.

one  $\nu_1$  ( $A_1$ ), one  $\nu_2$  (E), two  $\nu_3$  ( $A_1 + E$ ) and two  $\nu_3$  ( $A_1 + E$ ) internal modes are expected for a  $P31c$  ( $C_{3v}^4$ ) phase.

For the case of phase V, the observation of the additional modes at  $471\text{ cm}^{-1}$  does not support the idea of an orthorhombic structure belonging to the space group  $C_{2v}^{12}$  ( $Cmc2_1$ ) as suggested by Cach *et al* (1985) since group theory gives vibrations of  $4A_1 + A_2 + 2B_1 + 2B_2$  for internal modes. Among these,  $A_1$ ,  $B_1$  and  $B_2$  are infrared and Raman active while  $A_2$  is only Raman active. There is one  $\nu_1$  ( $A_1$ ) infrared mode, one  $\nu_2$  ( $A_1$ ), three  $\nu_3$  ( $A_1 + B_1 + B_2$ ) and three  $\nu_4$  ( $A_1 + B_1 + B_2$ ) modes for the space group  $C_{2v}^{12}$ . If the transition was from  $C_{3v}^4$  to  $C_{2v}^{12}$ , one would expect to see only one new infrared internal mode (one extra  $\nu_3$  mode) become infrared active in phase IV. However, the fact that two  $\nu_2$  infrared modes exist in phase V rules out the structure of  $C_{2v}^{12}$  ( $Cmc2_1$ ). The infrared experimental results of this study are consistent with a monoclinic structure with the space group  $C_s^4$  ( $Cc$ ) (Kleemann *et al* 1987). For  $C_s^4$  symmetry, one expects to see nine infrared internal modes—one  $\nu_1$  ( $A'$ ), two  $\nu_2$  ( $A' + A'$ ), three  $\nu_3$  ( $2A' + A''$ ) and three  $\nu_4$  ( $2A' + A''$ ) modes (the number of infrared vibrational modes of  $SO_4$  groups as a function of molecular symmetry was discussed by Adler and Kerr (1965) and Ross (1974)). The observation of all these nine internal modes supports the  $C_s^4$  structure.

A transition was observed at 135 K, which is characterized by the appearance of infrared bands at  $126$  and  $165\text{ cm}^{-1}$  in the spectra recorded below 135 K while no anomalous variations were detected for the internal modes. As there are little structural information is available for the phases below 135 K, it is difficult to propose symmetries of these



**Figure 9.** Temperature dependence of the spectral parameters of the  $363\text{ cm}^{-1}$  band: (A) peak position and (B) width.

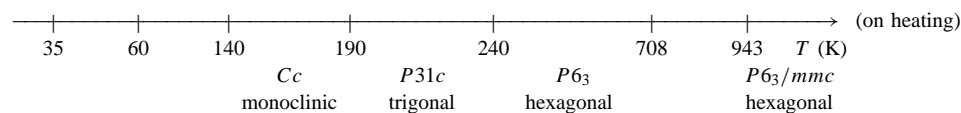
phases. However, based on our data and Raman spectroscopic work (Oliveira *et al* 1988), the space group of phase V could be  $C_1$ , because space group  $C_1$  also has nine infrared internal modes ( $3A_1 + 2A + 2B_1 + 2B_2$ ), like that of the  $C_s^4$  ( $Cc$ ) structure. Among them are one  $\nu_1$  ( $A_1$ ), two  $\nu_2$  (A), three  $\nu_3$  ( $A_1 + B_1 + B_2$ ) and three  $\nu_4$  ( $A_1 + B_1 + B_2$ ). In this infrared study, the emergence of bands at  $126$  and  $169\text{ cm}^{-1}$  was observed and it was accompanied by a discontinuous change in the width of the  $429\text{ cm}^{-1}$  Li band while no significant variations were detected for the internal S–O bands. It is rather puzzling why only these low-frequency bands show strong variations near  $135\text{ K}$ . These low-wavenumber bands are mainly due to K–O and S–O translations. The lattice-dynamical calculation by Chaplot *et al* (1984) showed that the A and E modes near  $130\text{ cm}^{-1}$  at room temperature consisted of about 70% K translation. As it is these modes which exhibited the most significant changes through the transition, it is reasonable to consider that the nature of the transition may be somewhat associated with those K–O and S–O translations.

The phase transition around  $60\text{ K}$  apparently involves symmetry breaking as a few additional external bands appear at  $T < 60\text{ K}$ . It could be mainly related to the Li atoms because the frequencies of these extra modes ( $364, 379, 402, 442, 448$  and  $454\text{ cm}^{-1}$ ) are in the frequency region where Li modes are usually located.

The splitting of  $\text{SO}_4$  internal modes through the transition near  $35\text{ K}$  may indicate that the transition is probably associated with a further rotation of the  $\text{SO}_4$  tetrahedra although no direct experimental observations exist so far which could identify the exact crystal structure of the low temperature phase.

In conclusion, our IR study of  $\text{LiKSO}_4$  shows six phase transitions ( $35\text{ K}, 60\text{ K}, 140\text{ K}, 190\text{ K}, 240\text{ K}$  and  $708\text{ K}$  on heating) between  $1.5$  and  $850\text{ K}$  as indicated below. The transition at  $708\text{ K}$  is evidenced by sudden changes in band positions, widths and integrated intensity as a function of





temperature, accompanied by an additional  $\nu_3$  band near  $1180\text{ cm}^{-1}$  in the high-temperature phase. The transition at 240 K is seen as a change of the temperature dependence of peak positions for the internal  $\nu_1$  band near  $1013\text{ cm}^{-1}$  and the  $\nu_3$  band near  $1135\text{ cm}^{-1}$ . Appearance of a  $\nu_3$  band near  $1202\text{ cm}^{-1}$  and splitting of the  $\nu_2$  band near  $471\text{ cm}^{-1}$  are observed at the phase below 190 K. The low-temperature results show that the structures in the temperature regions of 140–190 K and 190–240 K are consistent with *Cc* and *P31c*, respectively. As two extra bands near 126 and  $165\text{ cm}^{-1}$  appear below 140 K, probably the transition near 140 K is mainly associated to K–O and S–O translations. Below 60 K the appearance of six additional peaks between 350 and  $460\text{ cm}^{-1}$  suggests that the transition near 60 K may be mainly related to variations of Li and  $\text{SO}_4$  local environment configurations. A spectral anomaly is recorded near 740 K without symmetry changes while the reported transitions near 80 K and 165 K were not observed in this study.

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