Brillouin spectroscopic investigations of LiKSO$_4$ in the temperature range from 20 to 150 K

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Abstract
Brillouin spectroscopy has been used to determine the temperature dependence
of the velocity of longitudinal acoustic modes in a lithium–potassium sulphate
single crystal in the temperature range from 20 to 150 K. Small anomalies
were recorded for the modes propagating in [101] and [011] directions. The
frequency of the [100] mode is practically temperature independent. The
velocity of the [001] mode shows a minimum (relative change, 4.5%) at 52 K
which corresponds to the known phase transition temperature in this crystal.
The results of two sequential runs performed on the same sample (thermal
cycling) are compared and discussed.

1. Introduction

Lithium–potassium sulphate (LiKSO₄, sometimes referred to as LKS) belongs to a large
family of materials with the general formula ABXY₄ where A, B = {Li, Na, K, Rb, Cs,
NH₄, N(CH₃)₄, etc} and XY₄ = {SO₄, SeO₄, ZnCl₄, ZnBr₄, BeF₄, MoO₄, SO₄, WO₄, etc}.
It is the most interesting member of the group because it undergoes several phase transitions
in the temperature range from 10 K to its melting point at about $T_m = 1005$ K. Some of
its interesting physical properties which have attracted the attention of many researchers over
past years include: ferroelectricity [1,2], ferroelasticity [3,4], pyro- and piezo-electricity [5,6],
structural incommensuration [7] and optical activity [8]. The high value of its ionic conductivity
in the highest temperature hexagonal phase is also of interest from an application point of view.
However, there are controversies in the existing literature with respect to the phase transition
temperatures and the symmetry of the phases, particularly those below room temperature. Even
the mere existence of some of the phases is controversial. Some of the possible causes of those
controversies have already been identified and include merohedral twinning [9], coexistence
of phases [10], thermal history of the sample, impurities and internal stresses.

At room temperature the crystal possesses a hexagonal symmetry and belongs to the space
group $P6_3$ (C_6^6) with $Z = 2$ molecular units per unit cell of dimensions $a = b = 5.146(1)$ Å
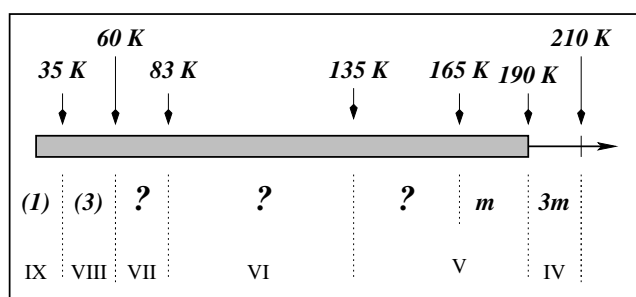
Figure 1. Schematic diagram of the sequence of low temperature phase transitions in LiKSO$_4$ (shaded area designates ferroelastic phases).

and $c = 8.638(2)$ Å [11]. The sequence of phase transitions below room temperature is schematically shown in figure 1. The most probable phase transition temperatures and symmetries of different phases are also indicated.

As the temperature is decreased from room temperature the first phase transition occurs at approximately 210 K. Large thermal hysteresis ($\sim$40 K) and discontinuous changes of physical properties suggest that this is a first order phase transition. Upon further cooling LiKSO$_4$ becomes ferroelastic below 190 K [6, 12–14]. The existence of ferroelastic domains [4, 15, 16] and crystallographic twins, as well as very slow kinetics of the phase transitions in that temperature region (which results in simultaneous presence of two or more phases at temperatures below 210 K) seems to be the cause of the controversies [17]. It is generally believed, however, that between 190 and 210 K this material posseses trigonal symmetry as indicated on figure 1.

Several other phase changes were reported in the literature below 250 K. The first one at around 165 K was reported as arising from microdomain reorientation [18] accompanied by small changes in the lattice parameter, c [19]. The complete disappearance of phase IV was also inferred from observed changes in EPR spectra [20] at that temperature.

At even lower temperatures changes of neutron diffraction peaks [10, 17, 18] and the appearance of two IR active bands [21] suggested a new phase transition probably to a triclinic system at 135 K. Some anomalies were found in the dielectric constant [22] and Raman spectra [23] in that temperature region as well. Moreover, Abello [24] reported small anomalies in the specific heat at 83, 65 and 38 K which were consistent with the anomalies in the dielectric constant mentioned earlier [22]. The results of other experiments have also confirmed the appearance of these phase transitions [21, 25–31]. However, there is a considerable lack of structural data and large inconsistencies in the reported phase transition temperatures in the region below 150 K.

The present work was undertaken because of the almost complete lack of information about the thermal behaviour of the elastic properties of LiKSO$_4$ at temperatures below 150 K. Moreover, measurements of thermal conductivity [31] in this material at low temperatures revealed an anomalous change at around 38 K. The work presents the results of Brillouin spectroscopy investigations in the temperature range from 20 to 150 K with particular emphasis on the occurrence of phase transitions in that temperature region. In order to confirm that the crystals transformed into the ferroelastic phase at around 190 K, the results for acoustic waves propagating along the [001] direction in this higher temperature range are also included.

2. Experimental details

To achieve temperatures in the range from 20 to 150 K a two-stage, closed cycle helium refrigeration system by *Air Products* was used. The sample holder, which was designed to minimize the vertical temperature gradient within the sample, was surrounded by a highly polished copper radiation shield and a brass vacuum shroud with four glass windows. A cryogenic temperature controller (LakeShore Cryotronics, model DTC 500) was used together with a silicon diode (DT-470) mounted in the base of the sample holder to maintain constant temperature during data accumulation. A separate miniature silicon diode (DT-420) was also used for sample temperature reading. It was placed about 3 mm away from the sample. This arrangement maintained the temperature at a constant level with an accuracy no worse than 0.05 K throughout the whole temperature range.

The experiment was performed using a back-scattering geometry because cracking of samples at around 50 K in preliminary experiments prevented the collection of spectra below that temperature with 90° geometry. The light of wavelength 514.5 nm from a single mode argon-ion laser (spectra physics series 2000) was used as an excitation source. Its intensity was adjusted to be between 20 and 50 mW, so as to minimize heating of the sample.

The back-scattered light collected from the sample was analysed by a piezoelectrically-scanned Fabry–Perot interferometer (Burleigh RC 110) operating in five-pass mode equipped with two quartz plates with 88% reflectivity dielectric coatings and flat to $\lambda/200$. Its intensity was detected by a thermoelectrically cooled photomultiplier tube (ITT FW 130) used in photon counting mode. A narrow band pass filter (band width = ±5 nm) was inserted into the beam to block all light other than that in the range of the Brillouin spectrum. The tube's output was then sent to a computerized data acquisition and stabilization system via an amplifier–discriminator (Princeton Applied Research, SSR 1120). Accumulation time for the spectra ranged from 2 to 12 h. The system was allowed to equilibrate for 20–30 min at each temperature before the beginning of accumulation.

The lithium–potassium sulphate single crystals used in the experiment were grown from aqueous solution (dynamic method) in the Crystal Physics Division, Faculty of Physics at Adam Mickiewicz University in Poznan (Poland). The solution contained an equimolar mixture of the initial salts: Li$_2$SO$_4$, K$_2$SO$_4$. The crystals were grown under isothermal conditions at 315 K and were in the form of hexagonal bi-prisms or parallelepipeds. Samples in the shape of rectangular parallelepipeds ($5 \times 6 \times 7$ mm^3) were cut from as-grown, untwinned parts of the crystal and were not treated thermally prior to experiment. They were then ground and manually polished to minimize losses due to surface scattering. All of the samples were colorless and of good optical quality. Their orientations were determined on the basis of single crystal morphology and the uncertainity is estimated to be no greater than 1°.

3. Results and discussion

Several hundred spectra were collected from LiKSO$_4$ samples for four different acoustic wavevector directions: [100], [101], [011] and [001]. Measurements for different orientations were performed using previously uncooled samples to assure their similar thermal history. Moreover, as mentioned earlier, sample cracking at around 50 K practically excluded the repeated use of any given sample (with one exception).

Brillouin shifts ($\Delta\nu$) for all the modes investigated in this work are shown in figure 2. One can see that the frequency of the light scattered by longitudinal elastic waves propagating along [100] is practically temperature independent. The sound velocity along the yz diagonal increases with decreasing temperature and in the temperature range from 150 down to 55 K it
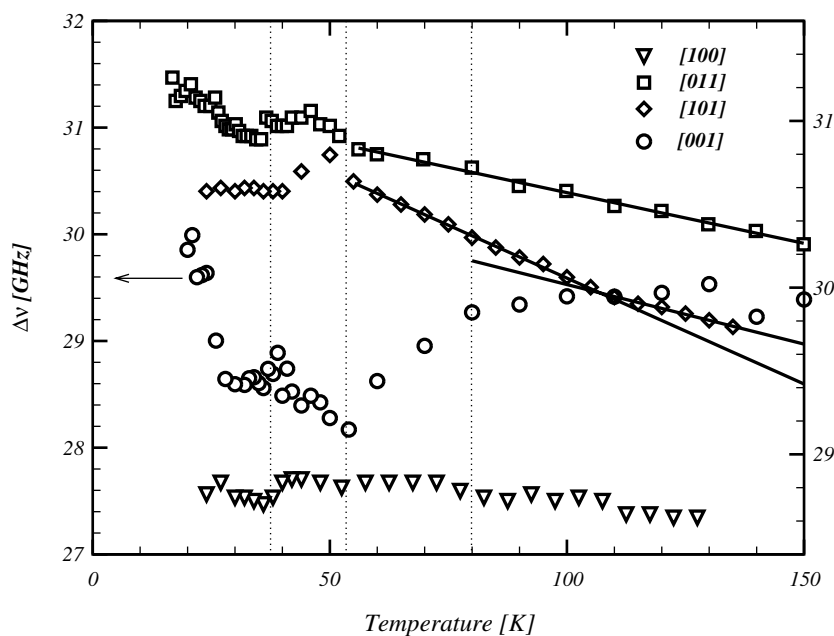
Figure 2. Brillouin shift of longitudinal modes in LiKSO$_4$ for decreasing temperature. Vertical lines are positioned approximately at the phase transition temperatures. The left hand vertical scale applies to the open circles only.

can be approximated by a straight line with the formula $\Delta \nu = -0.006T + 31.17$. The relative change of Brillouin shift was estimated to be approximately 1.6% in this temperature range.

In the same temperature range the velocity of the sound wave propagating along the [101] direction also increases with decreasing temperature. However, it shows a slight change of slope at around 105 K and can be again approximated by straight-line equations of the form $\Delta \nu = -0.013T + 31.33$ for $T < 105$ K, and $\Delta \nu = -0.007T + 30.73$ for $T > 105$ K. The total change of Brillouin shift for that mode is approximately 3%. The temperature at which the change of slope occurred has not been reported previously as a temperature for anomalous behaviour of any of the physical quantities. On the basis of results presented in this work it cannot be decided unequivocally if it is due to a phase transition.

Below 55 K the longitudinal modes propagating along [011] and [101] directions show some small anomalous changes. For example, the velocity of acoustic waves propagating along the yz diagonal show small local maxima and minima at approximately 46 and 34 K, respectively. The shift of the other mode displays a small local maximum at around 49 K and then levels off at 40 K and stays constant below that temperature. Due to the very small changes of elastic properties displayed by these modes in that temperature range one cannot accurately deduce the phase transition temperatures. However, the fact that both of the modes show anomalous behaviour suggests the presence of structural changes occurring in LiKSO$_4$ in that temperature range. Moreover, special attention should be paid to transverse acoustic modes propagating in these directions, which were not observed in our experiment because for the scattering geometry used most of them are forbidden.

The temperature dependence of the [001] mode is the most interesting of all the results presented in this work. Small anomalies between 130 and 150 K will be discussed later. Between 80 and 130 K the frequency of this mode decreases linearly with decreasing
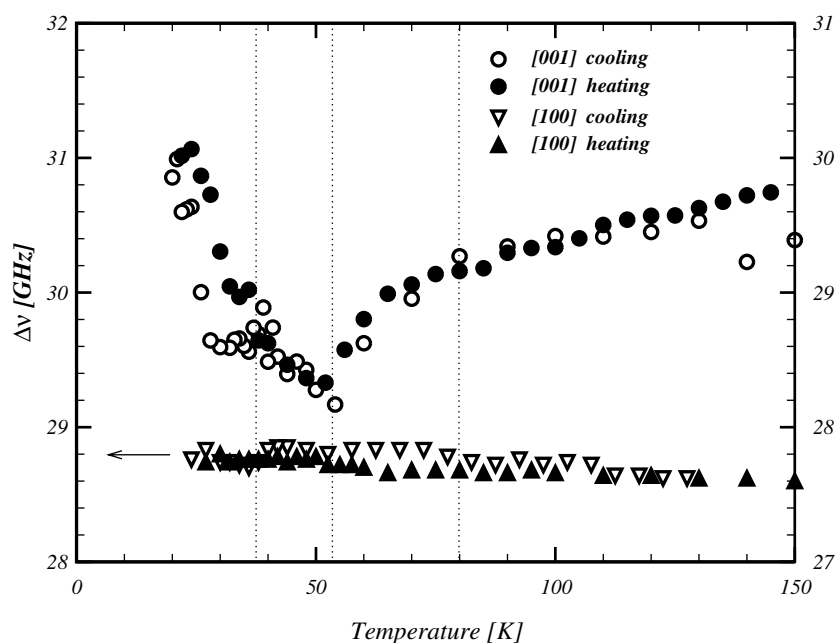
Figure 3. Brillouin shift as a function of decreasing and increasing temperature. The left hand vertical scale applies to triangular points (open and closed) only.

temperature, then it starts to decrease faster as it approaches its minimum at approximately 54 K. This minimum is most probably associated with the phase transition reported in this temperature range [22, 30]. The relative change of Brillouin shift between 130 and 54 K is approximately 4.6%. The shift increases with further decrease of temperature. Its value reaches a small local maximum at 39 K then slightly decreases and displays a very sharp increase between 21 and 28 K. The latter change is most probably related to the phase transition that has been observed at around 20 K (during cooling) in this material where an abrupt decrease of dielectric constant [26, 28], an anomalous behaviour of pyroelectric coefficient, and spontaneous polarization [2] were observed. However, the phase transition temperatures do not correspond to those presented in this work, suggesting that different results can be obtained from different single crystals. The relative change of Brillouin shift at 20 K is 4.7%. It should be noted however that a similar temperature dependence of the c_{33} elastic constant has been reported earlier by Ganot [32].

To obtain information about thermal hysteresis of the phase transitions (if any) an attempt has been made to collect results for decreasing and increasing temperature. However, for the reasons mentioned earlier, this was possible only in two cases. The results are shown on figure 3. For increasing temperature the Brillouin shift for the [100] mode stays approximately constant for the whole temperature range studied. For the [001] direction the sound velocity decreases with increasing temperature and exhibits a 6 K thermal hysteresis for the lowest anomaly observed. This, together with rather sharp changes of the Brillouin shift, suggests that the phase transition is of first order, in agreement with an abrupt change of dielectric constant reported in the literature [26, 28]. Upon further increase of temperature the Brillouin shift reaches its minimum value at approximately 52 K and then starts to increase following the curve recorded for decreasing temperature. The local maximum of the sound velocity observed at 39 K during cooling is not clearly seen for increasing temperature. It is probably
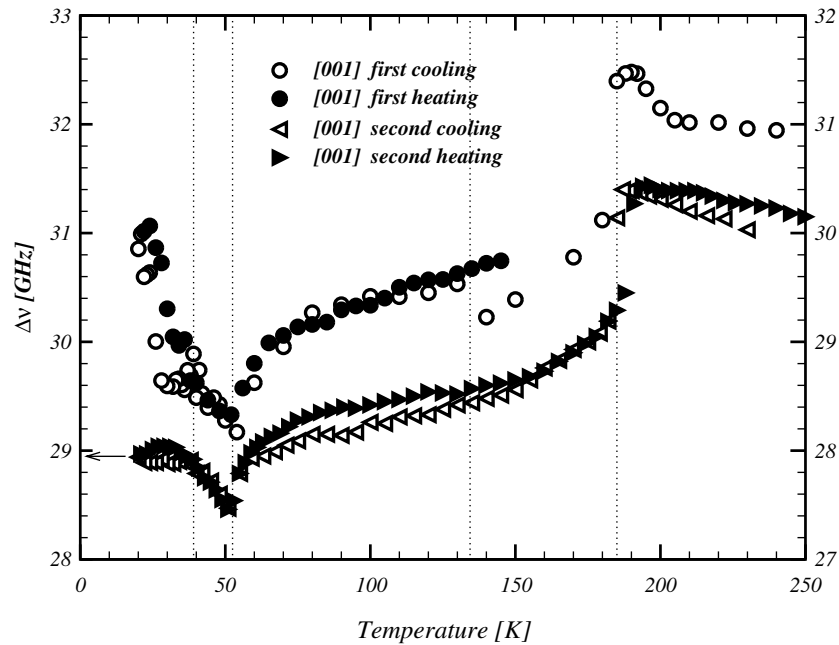
Figure 4. Brillouin shift versus temperature for the longitudinal acoustic mode propagating along [001] direction. Comparison between first and second measurements performed on the same sample. The left hand vertical scale applies to triangular points (open and closed) only.

hidden under the lower anomaly shifted towards higher temperatures due to hysteretic effects. From the changes of Brillouin shift reported here it cannot be determined if the phase transition observed at 52 K is of first or second order. However, very small thermal hysteresis associated with it suggests the latter.

In order to confirm the anomalous behaviour of the elastic properties discussed above, the experiment was repeated using the same sample and the results are shown on figure 4. More experimental points were collected and the measurements were extended towards higher temperatures to include the ferroelastic phase transition at approximately 190 K.

As can be seen from figure 4 the data recorded in the first experiment in the temperature range from 250 down to 130 K clearly confirm the existence of a first order phase transition at 185 K (during cooling). No multiple Brillouin peaks, due to the existence of ferroelastic domains, were observed below that temperature because it is most probable that the scattering volume was contained entirely within one orientational state of the sample. Moreover, an unusual increase of the Brillouin shift was observed at 204 K. In addition, a small local minimum of the sound velocity was observed at 140 K. Unfortunately no data are available for the first heating in that temperature range.

No anomaly was observed at 204 K in the second run. The Brillouin shift increased linearly with decreasing temperature reaching the same value as in the first experiment shortly before the ferroelastic phase transition at 185 K. The minimum in the sound velocity corresponding to the phase transition from phase VII–VIII occurred at 52 K a slightly lower temperature than during the first experiment. Also the relative changes of the Brillouin shift are smaller. Below that temperature no rapid increase of Brillouin shift was observed, in contrast to the first experiment, but the sound velocity remained constant from 38 down to 20 K. It should

be noted that the temperature at which the Brillouin shift levels off corresponds well with the small local maximum of the sound velocity observed at 39 K during first cooling.

Finally, the second experiment permitted determination of the phase transition temperatures more accurately. The ferroelastic phase transition occurs at 185 K during cooling and at 191 K during heating. The jump-like changes and the 6 K thermal hysteresis suggest the phase transition to be of the first order. These results are in good agreement with those reported in the literature [6].

The differences between thermal behaviour of the velocity of the acoustic wave propagating in the [001] direction discussed above can have a two-fold origin. Firstly they can be explained by assuming coexistence of different phases in the whole temperature range studied. This phenomenon was experimentally confirmed at temperatures between 150 K and room temperature for LiKSO$_4$ [10]. Secondly a presence of impurities or defects can, in general, have a profound effect on the thermal characteristic of many thermodynamic quantities in the vicinity of a phase transition [33] when the structure becomes 'soft'. Moreover, in the immediate vicinity of any defects in an otherwise perfect crystallographic structure one would expect modification of its elastic properties. Therefore, since Brillouin spectroscopy probes the elastic properties of the sample locally (information obtained results from scattering of an incident radiation within small volume of the sample), a possibility that the scattering volume was not in the same region of the sample during both runs can serve as a reasonably qualitative explanation of the differences observed. No attempt was made to confirm this hypothesis by changing the position of the laser beam inside the sample.

It should also be mentioned that one experiment was performed with stronger clamping springs. This resulted in an application of higher compressional stress to the sample as compared to all other cases. These results are not included because the sample fractured around 50 K to such a degree that measurements could not be continued (i.e. no Brillouin lines appeared in the spectra after 24 h of accumulation). This suggests that uniaxial stress can have a significant influence on the phase transition at 52 K. This also led us to conclude that cracking of our samples could be due to stresses resulting from different thermal expansion coefficients of the sample and the grease which was placed between the crystal and the sample holder to improve thermal contact.

4. Conclusions

From the experimental results presented and discussed in the previous section the following conclusions can be drawn:

  (i) LiKSO$_4$ undergoes a phase transition at 52 K. It is associated with a 4.5% decrease in the sound velocity of the acoustic wave propagating in the [001] direction. The temperature of the phase transition is independent of thermal cycling.
 (ii) The coexistence of different phases in the temperature range from 20 K to room temperature, and the interaction of phase transitions with the spatial distribution of defects provides a reasonable explanation for the differences in the thermal behaviour of elastic properties observed in subsequent experiments performed on the same sample.
(iii) The ferroelastic phase transition occurred at 185 K and is characterized by 6 K thermal hysteresis. Its general characteristics do not depend on thermal cycling.
(iv) The possibility of the existence of other phase transitions at temperatures below 40 K, associated with anomalous changes of elastic properties, is supported by our results. However, further work in this temperature region is needed to determine their character and exact transition temperatures.

Acknowledgments

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