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# ANOMALOUS CHANGES IN THE SPECIFIC HEAT AND THERMAL CONDUCTIVITY OF LiKSO$_4$ CRYSTALS AROUND THE HIGH-TEMPERATURE PHASE

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## Abstract

The thermophysical properties of LiKSO$_4$ crystals were studied around the high-temperature phase, at $T_{c_2}$ = 943 K. A Heraeus (DSC) technique was used to measure the specific heat, $c_p$, while the thermal conductivity, $K$, was measured by the linear heat flow steady-state method. The measured parameters showed an anomaly in the temperature dependence of both $c_p$ and $K$. Anisotropy in the thermal conductivity coefficient was also observed in the different crystallographic axes.

**Keywords:** high-temperature phase, LiKSO$_4$ crystals, specific heat, thermal conductivity

## Introduction

Lithium potassium sulphate (LiKSO$_4$) crystals are known to exhibit an interesting sequence of structural phase transitions [1]. The discovery of ferroelasticity [2, 3] and an incommensurate phase [4, 5] in LiKSO$_4$ crystals has recently made this material the subject of extensive experimental investigations. Above room temperature, crystalline LiKSO$_4$ undergoes two phase transitions, at about $T_{c_1}$ = 708 and $T_{c_2}$ = 943 K [6–9]. At room temperature, LiKSO$_4$ has a hexagonal structure with space group $C_6^6$ (P6$_3$) with two formula units per unit cell [10].

Extensive studies on the physical and thermal properties of LiKSO$_4$ crystals have been reported, and some of these properties show anomalous behaviour, indicating a phase transition at 708 K [3, 11].

Xie *et al.* [12] and Li [4] proposed an incommensurate (IC) phase between 743 and 943 K, and a commensurate phase between 708 and 734 K, belonging to a hexagonal space group similar to the space group at room temperature, but with a unit cell four times larger.

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The aim of the present investigations is to study the phase transition in $LiKSO_4$ crystals in the vicinity of the IC phase, by means of specific heat, $C_p$, and thermal conductivity, $K$, measurements.

## Experimental

$LiKSO_4$ crystals were grown isothermally at 331 K from aqueous solution by a dynamic method. The crystals obtained were large, colourless and of good optical quality.

The samples to be studied were cut out of the untwinned crystal and were prepared in the form of rectangular rods (3 mm×3 mm×30 mm) such that the longer parts of the rods were oriented along the principal crystallographic axes [100], [010] and [001]. The crystallographic axes for the $LiKSO_4$ crystals were assumed in accordance with the directions previously proposed.

The thermal conductivity $K_{ij}$ ($i = j$ = 1, 2 and 3) was measured by using a linear heat flow steady-state method [14]. The details of the experimental arrangement and the precautions required have been described elsewhere [15].

The specific heat at constant pressure, $C_p$, was determined by using a differential scanning calorimeter (DSC) technique, a Heraeus (DSC) cell being connected to a Heraeus DTA 500 thermal analyser. Measurements were performed by applying the base line method [16]. Lidded pans made of Pt were used to eliminate the slope of the base line. At Pt 100 thermocouple was used as temperature sensor and heating at 2 deg·min$^{-1}$ was applied.

## Results and discussion

Figure 1 shows the temperature dependence of $C_p$ for $LiKSO_4$ crystals, measured around the high-temperature phase, at $T_{c_2}$ = 943 K.

It is clear from Fig. 1 that $C_p$ exhibits anomalous behaviour at t $T_{c_2}$ = 943 K. The anomaly extends between 938 and 953 K.

In order to study the critical behaviour in the IC phase (between 743 and 943 K), the excess specific heat ($\Delta C_p$) was assumed to be expressed as

$$\Delta C_p = A\,\tau^{-\alpha} \tag{1}$$

where $\tau = T - T_c /T_c$ $\alpha$ is the critical exponent and $A$ is a constant. Figure 2 presents this dependence. Figure 2 gave $\alpha$ = 0.25, more than twice the value expected for the 3d Ising model ($\alpha = 0.1$) [17].

The anomalous part of $C_p$ mainly originates directly from the spontaneous strain fluctuations due to interaction.

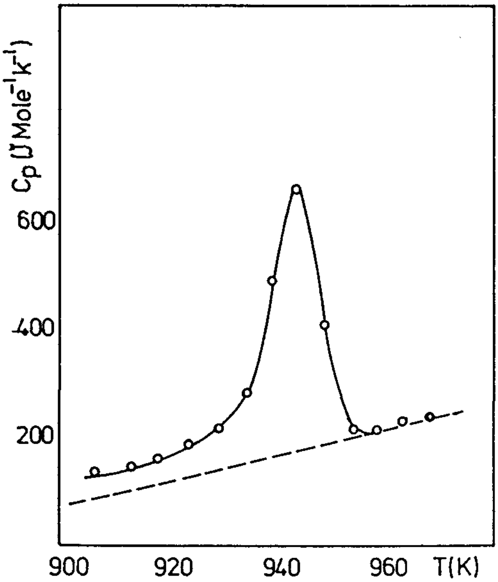

**Fig. 1** Specific heat $C_p$ of LIKSO$_4$ as function of temperature $T$ in the region of high temperature incommensurate phase

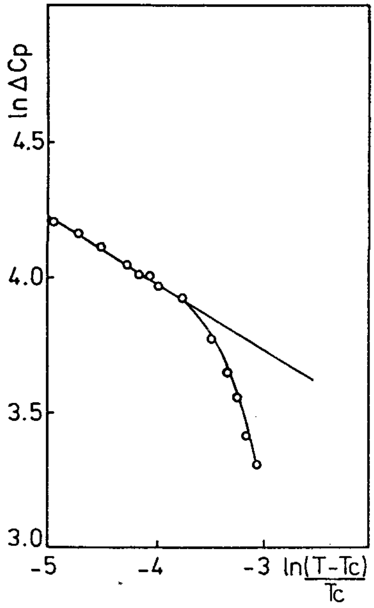

**Fig. 2** Variation of the specific heat excess against $(T-T_c)/T_c$ near the transition of 940 K

The contributions to $C_p$ in the IC phase could arise from the critical fluctuations, which were examined by fitting $C_p$ according to the power laws.

$$C_p = A\,(T - T_c)^{-\beta} \qquad \text{for } T < T_c \tag{2}$$

$$C_p = A'(T - T_c)^{-\beta'} \qquad \text{for } T > T_c \tag{3}$$

where $\beta$ and $\beta'$ are the critical exponents which depend on incommensurability, while $A$ and $A'$ are constants.

Figure 3 shows the relation of $\ln C_p$ *vs.* $\ln(T - T_c)$ for $LiKSO_4$ crystals in the vicinity of the IC temperature.

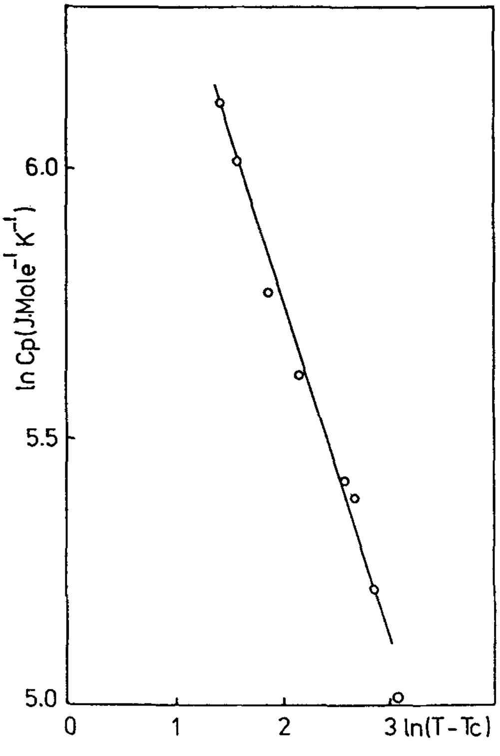

**Fig. 3** Specific heat critical behaviour for commensurate- incommensurate phase transition

According to the data reported by Larkin [18] and Imry and Ma [19], the IC phase tails should be sharper and the heat capacity tail should be $C_p \approx (T–T_c)^{-2/3}$ at $T > T_c$ and $C_p \approx (T - T_c)^{-5/2}$ at $T < T_c$. However, from Fig. 3 it was found that $C_p \approx (T - T_c)^{-0.6}$ at $T > T_c$, and we therefore presume that the IC phase is not completely pure [20].

Larkin [18] and Imry and Ma [19] showed that there is no long-range order of interaction in the IC phase with any concentration of point defects which fix the phase.

This means that the critical indices for the IC phase transition are pointless, because of the smearing of the transition.

Figures 4–6 present the measured $K_{ij}$, ($i = j = 1$, 2 and 3 ) of a $LiKSO_4$ single-crystal as a function of temperature $T$ along the three fundamental axes [100], [010], [001], respectively. The order of magnitude of K is about one and a half that measured for the same crystal in the ferroelastic phase at $T_c = 705$ K [15]. This means that the defects in the IC phase are effective. The thermal conductivity along each of the three directions shows a sharp peak at 943 K, indicating that there is a structural phase transition, which agrees with the results of Brillouin scattering by Pimenta *et al.* [17].

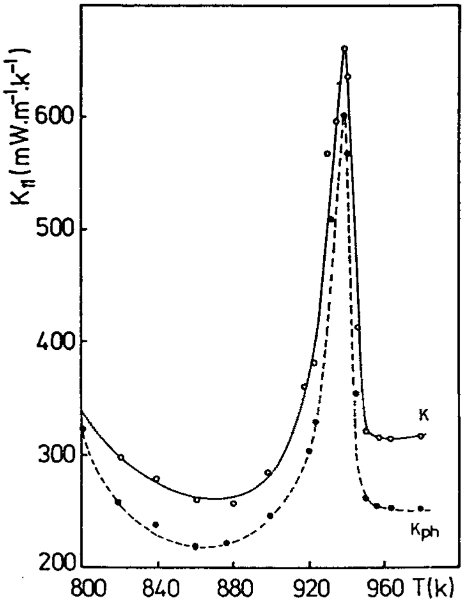

**Fig. 4** Thermal conductivity component $K_{11}$ (along X-axis) of $LiKSO_4$ *vs.* temperature together with phonon contribution $K_p$

In order to understand the role played by lattice vibration (phonons) in transporting an expression has to be found for the lattice (phonon) contribution ($K_{ph}$) in relation to heat along the different directions, the radiative thermal conductivity ($K_r$) and the electronic contribution ($K_e$) to the thermal conductivity.

This is

$$K_{ph} = K - K_r - K_e \tag{4}$$

where $K_{ph}$ is the lattice (phonon) contribution term. The radiative thermal conductivity is given by

$$K_r = \frac{16}{3}\sigma_R n^2 T^3 < \alpha_{ij}^{-1} > \tag{5}$$

where $\sigma_R$ is the Stefan–Boltzmann constant, $T$ is the absolute temperature, $n$ is the refractive index and $\alpha_{ij}^{-1}$ is the average of the inverse of the optical absorption coefficient $\alpha_{ij}$. Since the optical absorption due to free carriers is absent in dielectrics [21, 22] and the $LiKSO_4$ crystals were found to be optically homogeneous from 300 K up to about 700 K [2], the measured values of $\alpha_{ij}$ at room temperature in different directions were used as constants in Eq. 5. Our measurements at room temperature revealed $\alpha_{11} = \alpha_{22} = 962\ m^{-1}$ and $\alpha_{33} = 1380\ m^{-1}$. The calculated radiative contribution to the conductivity is given in

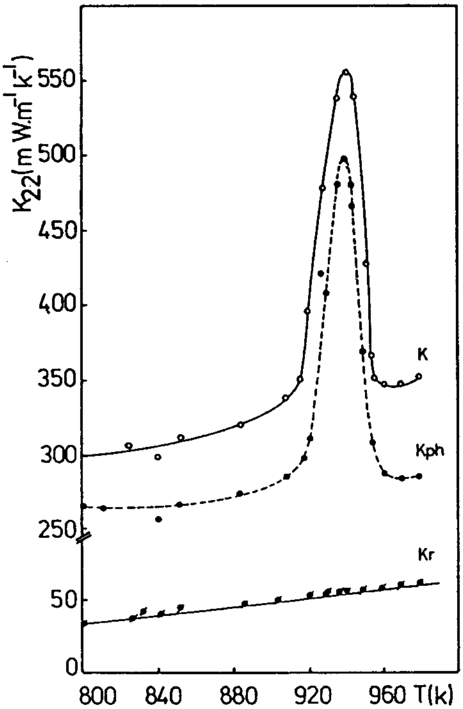

Fig. 5 Thermal conductivity component $K_{22}$ (along y-axis) vs. temperature together with radiative (photon) term $K_r$ and $K_{ph}$

Figs 5 and 6 for the [010] and [001] axes, respectively. The electronic contribution $K_e$ was calculated by using the published data on the electrical conductivity [23] from the relation

$$K_e = L_o \sigma T \tag{6}$$

where $L_o$ is the normal Lorentz number ($=2.45\times10^{-8}$ V$^2$K$^{-2}$) and $\sigma$ is the electrical conductivity.

These calculations revealed that the electronic part of the thermal conductivity may be considered negligible. According to the above argument, the thermal conductivity for $LiKSO_4$ in the IC phase (743–943), due to the phonon contribution to the conductivity $K_{ph}$ along each direction, is represented in the corresponding Figs 4–6.

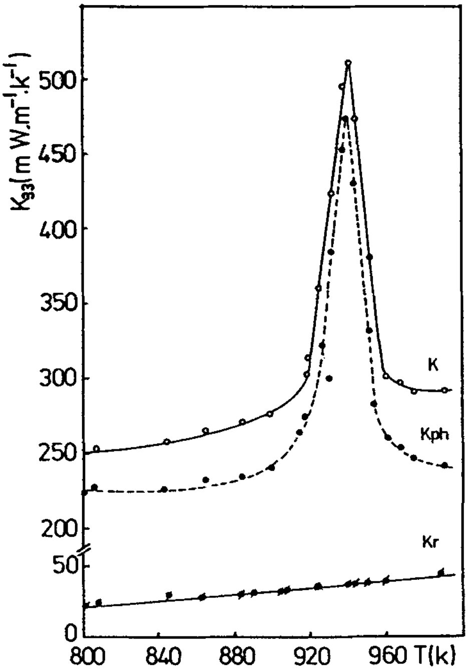

**Fig. 6** Thermal conductivity component $K_{33}$ (along Z-axis) *vs.* temperature together with $K_r$ and $K_{ph}$

It is well known that the thermal (or electrical) conductivity in ionic crystals is a defect-controlled property; such defects cause a static strain field and again anharmonicity results in a vibration of the sound velocity in the neighbourhood of the lattice defects which scatter the phonons. There may also be additional scattering mechanisms, e.g. vibrations of atoms, groups of molecules and or domain walls in the phase below $T_c$. Due to this enhanced phonon scattering mechanism, the lattice thermal conductivity decreases with increasing temperature up to $T_c$. At $T = T_c$, the frequency of the corresponding mode (a so-called soft mode) goes to zero. This means that at this temperature the crystal is unstable.

$LiKSO_4$ crystals display a ferroelastic phase [2] between 700 K and 940 K, with a spontaneous strain associated with it. In order to explain the strong anomaly (the sharp maximum at the transition), we relate this anomaly to the freezing-in of optic and/or acoustic modes in the near vicinity of the phase transition temperature $T_c$. The atomic displacements associated with the ordering are governed by the vibrational mode which has softened. As the system approaches $T_c$, the amplitude of vibration corresponding to the softening mode gradually increases and finally this vibration is frozen in at $T = T_c$.

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**Zusammenfassung** — In der Nähe der Hochtemperaturphase wurden bei $T_{c2}$ = 943 K die thermophysikalischen Eigenschaften von $LiKSO_4$-Kristallen untersucht. Zur Messung der spezifischen Wärme $c_p$ wurde eine Heraeus (DSC)-Technik eingesetzt, die Wärmeleitfähigkeit $K$ mit Hilfe der linearen Wärmefluß Steady-state Methode. Die gemessenen Parameter zeigten sowohl für $c_p$ als auch für $K$ eine Anomalie der Temperaturabhängigkeit. Für die drei verschiedenen kristallografischen Achsen wurde auch eine Anisotropie des Wärmeleitfähigkeitskoeffizienten festgestellt.