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Thermal conductivity of $LiKSO_4$ near its high-temperature phase transition

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The thermal conductivity of $LiKSO_4$ ferroelastic crystals was measured along the three principal crystallographic axes in the vicinity of its high-temperature phase transition at 705 K. The data showed an anomalous behaviour in the temperature dependence of the thermal conductivity in the transition region of width about 25 K. The anomaly in the phonon contribution to the conductivity was referred to the freezing-in of either optic and/or acoustic modes of lattice vibrations in the near vicinity of the phase transition. The results are discussed in terms of the scattering mechanisms of energy carriers.

1. Introduction

Lithium potassium sulphate ($LiKSO_4$) crystals are pyroelectric [1] with a hexagonal symmetry at room temperature. The system is associated with the space group $P6_3$ and there are two molecules in the hexagonal unit cell. Extensive studies on the physical properties of $LiKSO_4$, in different temperature ranges, have been reported [2–6].

These studies have shown that the crystal undergoes several phase transitions at low as well as high temperatures. In the high-temperature region, the crystal exhibits a structural phase transition from hexagonal to orthorhombic system [7] at about 705 K. The next and last high-temperature phase transition, probably back to the hexagonal system, was observed near 940 K [2]. These high-temperature phase transitions have been the subject of several experimental investigations [4, 8–10] of their electrical and optical properties. The phase between 700 and 940 K was found to be ferroelastic [10].

No thermal conductivity data for $LiKSO_4$ have been reported in the literature except those of Mahmoud *et al.* [11] who measured the thermal conductivity in the low-temperature range 77 to 220 K. It is the aim of this work to report on thermal conductivity measurements in the near vicinity of the high-temperature phase transition, around 700 K, and to investigate the possible influence of the ferroelastic phase transition on the thermal conductivity.

2. Experimental procedure

Single crystals of $LiKSO_4$ were grown isothermally at 315 K by the dynamical method from aqueous solutions containing the initial salts in stoichiometric ratio. The samples were cut from the untwinned crystal and were prepared in the form of rectangular rods with dimensions of 3 mm × 3 mm × 30 mm such that the longer parts of the rods were oriented along the principal crystallographic axes: (1 0 0), (0 1 0) and (0 0 1).

The thermal conductivity K was measured using a linear heat-flow steady-state method [12]. A heater made of manganin wire was cemented to one end of the sample. By means of air-drying silver paste the other end of the sample was in a good thermal contact with a metallic heat sink. A cylindrical guard shield was placed between the sample and the furnace, which had a temperature gradient matched roughly to that of the guard. The shield was heated independently of the sample such that the temperatures along the shield should be matched with those of the sample at the top as well as the bottom part. A further heated guard was placed over the sample to ensure that all its heat flowed downward through the sample. In order to minimize heat loss by radiation, the sample and the guards were surrounded with an insulating, highly porous powder. The temperature gradient along the sample was measured by connecting two fine Pt/Pt–13% Rh thermocouples back to back. The differential e.m.f. was measured using a precise potentiometer with an accuracy of $\pm 1\,\mu V$. The mean measuring error in K was of the order of ±6%. The measurements were performed on samples oriented along the three fundamental crystallographic axes in the temperature range between 500 and 800 K.

3. Results and discussion

In Figs 1 to 3 are given the measured thermal conductivity K_{ij}, ($i = j = 1, 2$ and 3) of $LiKSO_4$ single crystal as a function of absolute temperature T along the three fundamental axes x, y, and z, respectively. The order of magnitude of K_{ij} is about half that measured for the same crystal in the low-temperature range [11]. This means that the crystal becomes more insulating on going upward in temperature. The thermal conductivity along each of the three directions

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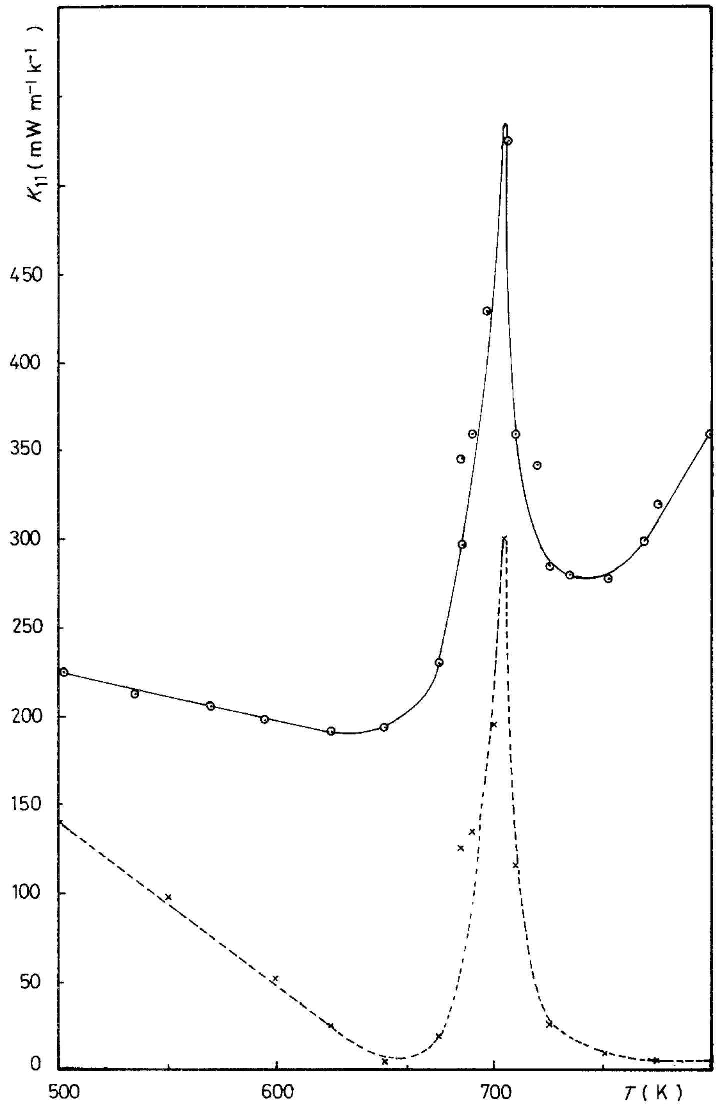

Figure 1 Thermal conductivity of $LiKSO_4$ single crystals along the x axis: (——) K, (– – –) K_{ph}.

shows a sharp maximum between 700 and 710 K, indicating clearly a structural phase transition in agreement with the optical measurements on $LiKSO_4$ reported by Krajewski *et al.* [10] and with the specific heat and thermal expansion data [7].

In order to understand the role played by lattice vibrations (phonons) in transporting heat along the different directions, the radiative thermal conductivity K_r and the electronic contribution K_e must be first subtracted from the total (measured) thermal conductivity K, i.e.

$$K_{ph} = K - K_r - K_e \qquad (1)$$

where K_{ph} is the lattice (phonon) contribution term. The electronic contribution K_e was calculated by assuming a normal Lorenz number L_0 ($= 2.45 \times 10^{-8}\,V^2K^{-2}$) and using the published data on the electrical conductivity (δ) of $LiKSO_4$ [9] and the relation

$$K_e = L_0 \delta T \qquad (2)$$

K_e was found to be vanishingly small so it is completely neglected, in what follows.

Following Men' and Sergeev [13] and Parrot and Stuckes [14], the theoretical expression for the radiative thermal conductivity is given by

$$K_r = \tfrac{16}{3}\sigma_R n^2 T^3 \langle \alpha_{ij}^{-1} \rangle \qquad (3)$$

where σ_R is the Stefan–Boltzmann constant, T is the absolute temperature, n is the refractive index and $\langle \alpha_{ij}^{-1} \rangle$ is the average of the inverse of the optical absorption coefficients (α_{ij}). Since in insulators the optical absorption due to free carriers is absent [14] and since $LiKSO_4$ crystals were found to be optically homogeneous from 300 up to about 700 K [10], the measured values of α_{ij} at room temperature, in different directions, were used as constant values in Equation 3. 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 illustrated in Figs 2 and 3 for the y and z axes, respectively.

On subtracting the radiative thermal conductivity K_r from the experimental data, the phonon contribution to the conductivity (K_{ph}) along each direction is represented in the corresponding figure. It has been recognized that lattice vibrations set up dynamic strain fields which, due to anharmonicity, modulate the sound velocity and cause interactions between phonons. Also, it is well known that the thermal (or electrical) conductivity in ionic crystals is a defect-controlled property. Such defects cause static strain fields and, again, anharmonicity results in a variation of the sound velocity in the neighbourhood of the lattice defects which scatter the phonons. There may be

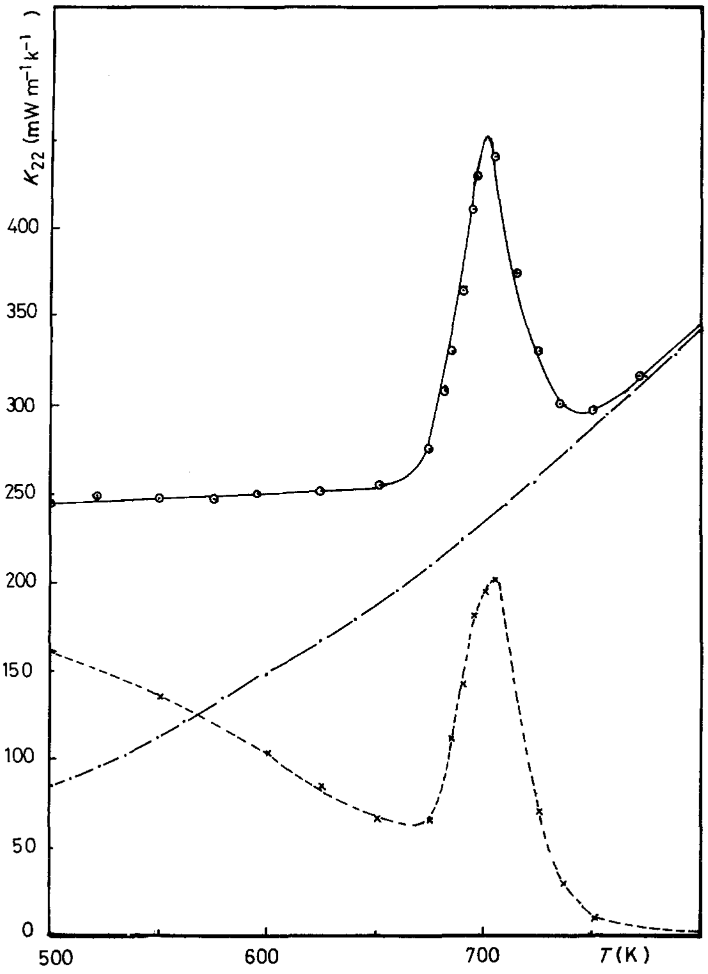

Figure 2 Thermal conductivity of LiKSO$_4$ single crystals along the y axis: (——) K, (– – –) K_{ph}, (–·–) K_r.

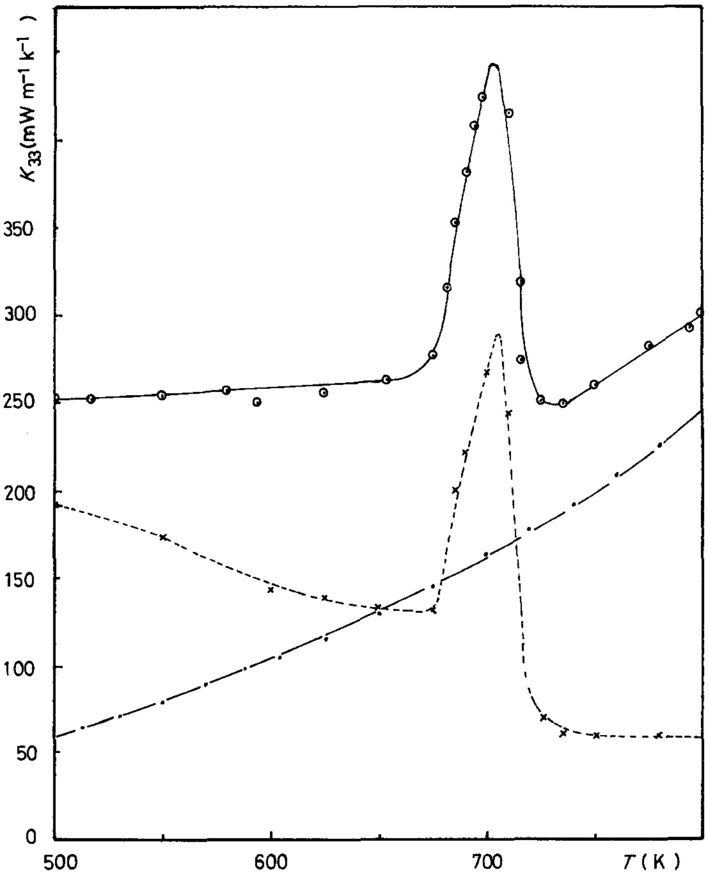

Figure 3 Thermal conductivity of LiKSO$_4$ single crystals along the z axis: (——) K, (– – –) K_{ph}, (–·–) K_r.

also additional scattering mechanisms, e.g. vibrations of atoms, groups of molecules, and/or domain walls (if they exist) in the phase below T_c. We may conclude that, due to these enhanced phonon scattering mechanisms, the lattice thermal conductivity decreases with increasing temperature up to near T_c from below.

Krajewski *et al.* [10] have reported that the high-temperature phase between 700 and 940 K is a ferroelastic one with a spontaneous strain associated with it. This low-symmetry ferroelastic phase is characterized by a stress–strain hysteresis loop which discloses the occurrence of several strain-differing stable states or what are called "ferroelastic domains" [15]. 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. Wadhawan [16] has established the equivalence between the order-parameter and the soft-mode descriptions. An optic mode is a lattice vibration of frequency $\omega(T)$ such that $|\omega(T)|^2 \rightarrow 0$ as $T \rightarrow T_c$ for a second-order phase transition. 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 gets frozen-in at $T = T_c$.

David [17] has described a number of structural relationships between the spontaneous strain and acoustic properties of ferroelastic materials. The spontaneous strain is associated with the freezing-in of the displacements of mutually perpendicular pairs of pure transverse acoustic modes, which propagate with zero velocity along acoustic symmetry axes at the ferroelastic phase transition temperature T_c. As the temperature gets further above T_c (purely ferroelastic phase), the phonon scattering by the well-organized domain walls will cause the phonon contribution K_{ph} to decrease rapidly to a very small value. Chaplot *et al.* [18] have derived phonon dispersion relations for $LiKSO_4$ in the room- and low-temperature phases, but no theoretical phonon study has been yet made of the high-temperature phases. No firm theoretical confirmation of our conclusion can therefore be made at the moment.

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