

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 750 K. The data showed an anomalous behaviour in the temperature dependence of the thermal conductivity in the transition region of width of about 25 degrees. 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 scattering mechanisms of energy carriers.

Lithium potassium sulphate, LiKSO_4 , crystal is pyroelectric [1] with a hexagonal symmetry at room temperature. The system corresponds to 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 [2-5].

These studies have shown that the crystal undergoes several phase transitions. 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 the last high temperature phase transition, probably back to hexagonal system, was observed near 940 K [2]. These high temperature phase transitions were so far the subject of several experimental investigations [4, 8-10] of electrical and optical properties. The phase between 700 and 940 K was found to be ferroelastic [10].

No thermal conductivity data of LiKSO_4 have been reported in the literature except the one due to 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 close 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.

Experimental

Single crystals of LiKSO_4 were grown isothermally at 315 K by the dynamical method from an aqueous solutions containing the initial salts at stoichiometric ratio. The samples were cut from the untwinned crystal and were prepared in the form of rectangular rods with dimensions of $3 \times 3 \times 30 \text{ mm}^3$ such that the longer parts of the rods were oriented along the principal crystallographic axes: (100), (010) and (001).

The thermal conductivity (K) was measured using a linear heat-flow steady state method [12]. A heater made of manganin wire was cemented onto 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 has a temperature gradient matched roughly to that of the guard. The shield was heated independently of the sample such that the temperature 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 all its heat flow downward through the sample. In order to minimize heat loss by radiation, the sample and the guards were surrounded with a highly porous insulating 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 ($\pm 1 \mu\text{V}$). The mean measuring error was of the order of $\pm 6\%$. The measurements were performed on samples oriented along the three fundamental crystallographic axes in the temperature range between 500 and 800 K.

Results and discussion

In Figs (1–3) are given the measured thermal conductivity (K_{i-j} , $i=j=1, 2$ and 3), of a 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 gets more insulating on going upward in temperature. The thermal conductivity along each of the three directions shows a sharp maximum between 700 and 710 K clearly indicating the 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.,

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

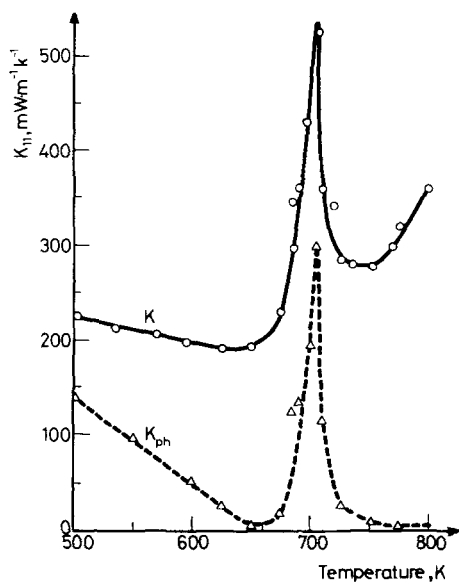


Fig. 1 Thermal conductivity of a LiKSO_4 single crystal vs. T along axes x

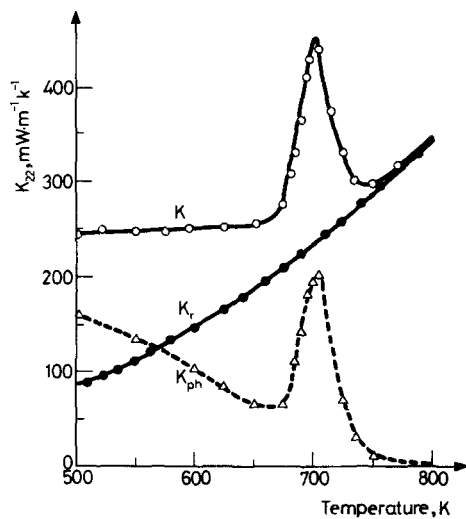


Fig. 2 Thermal conductivity of a LiKSO_4 single crystal vs. T along axes y

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

$$K_e = L_0 \sigma T \quad (2)$$

This was found to be negligibly small.

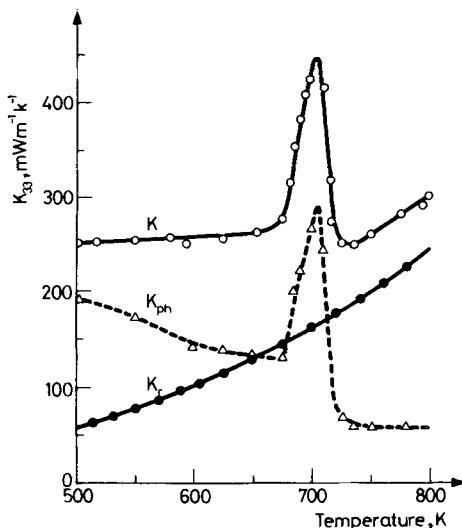


Fig. 3 Thermal conductivity of a LiKSO_4 single crystal vs. T along axes z

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

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

where σ_R is the Stefan-Boltzmann constant, n is the refractive index, and $\langle \alpha_{ij}^{-1} \rangle$ is the average of the inverse of the optical absorption coefficient (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 temperatures, revealed: $\alpha_{11} = \alpha_{22} = 962 \text{ m}^{-1}$ and $\alpha_{33} = 1380 \text{ m}^{-1}$. The calculated radiative contribution to the conductivity is illustrated in Figs (2) and (3) for 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 causes 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 field and, again, anharmonicity results in a variation of the sound velocity in the neighbourhood of the lattice defect which scatters the phonons. There may be 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-deferring stable states or what is called ferroelastic domains [15]. In order to explain the strong anomaly (the sharp maximum at the transition), we are referring this anomaly to the freezing—in of either optic—and/or acoustic-modes in the close vicinity of the phase transition temperature T_c . Wadham [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 gone soft. 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 in the high-temperature phases. So no firm theoretical confirmation of our conclusion can be made at the moment.

References

- 1 R. Ando, *J. Phys. Soc. Japan*, 17 (1962) 937.
- 2 S. J. Chung and T. Hahn, *Acta Cryst.*, A 28 (1972) 557.
- 3 P. Sharma, *Pramana*, 13 (1979) 223.
- 4 M. L. Bansal, S. K. Deb, A. P. Roy and V. C. Sahni, *Solid State Commun.*, 36 (1980) 1047.
- 5 T. Breczewski, T. K. Krajewski and B. Mroz, *Ferroelectrics*, 37 (1980) 744.
- 6 B. Maroz, T. Krajewski and T. Breczewski, *Ferroelectrics*, 42 (1982) 71.
- 7 M. E. Kassem, E. E.-Wahidy, S. H. Kandil and M. A. El-Gamal, *J. Thermal Anal.*, 29 (1984) 325.
- 8 R. Cach, P. Tomaszewski, P. Bastle and J. Bornarel, *Ferroelectrics*, 53 (1984) 1.
- 9 M. E. Kassem, E. F. El-Wahidy, M. El-Hawary and N. A. Ibrahim, *Egypt J. Solids*, 7. 1. (1985) 48.
- 10 T. Krajewski, T. Breczewski, P. Piskunowicz and B. Mroz, *Ferroelectrics Letters*, 4 (1983) 95.
- 11 S. Mahmoud, M. E. Kassem, H. Muller and E. Hegenarth, *Phys. Stat. Sol.*, (a), 90, K (1985) 135.
- 12 D. A. Ditmar and D. C. Ginnings, *J. Res. Nat. Bur. Stand.*, 59 (1957) 93.
- 13 A. A. Men' and O. A. Sergeev, *High Temperatures-High Pressures*, 5 (1973) 19.
- 14 J. E. Parrott and Audrey Stuckes, *Thermal Conductivity of Solids*, Pion Limited, London 1975.
- 15 Jean-Claude Toledano and Pierre Toledano, *Phys. Rev. B*, 21, 3 (1980) 1139.
- 16 Vinod K. Wadhawan, *Phase Transition*, 3 (1983) 3.
- 17 William I. F. David, *J. Phys. C. Solid State Phys.*, 16 (1983) 2455.
- 18 S. L. Chaplot, K. R. Rao and A. P. Roy, *Phys. Rev. B*, 29, 8 (1984) 4747.

Zusammenfassung — Entlang der drei grundlegenden kristallografischen Achsen der ferroelastischen Kristalle von LiKSO_4 wurde in der Nähe dessen Hochtemperaturphasenübergangs bei 705 K deren Wärmeleitfähigkeit gemessen. Die Messungen zeigen ein anomales Verhalten der Temperaturabhängigkeit der Wärmeleitfähigkeit in der Nähe der Übergangstemperatur mit einer Intervallbreite von ca. 25 K. Die Anomalie des Phononenbeitrages zur Leitfähigkeit wird dem Einfrieren optischer und oder akustischer Repräsentanten von Gittervibrationen in unmittelbarer Nähe des Phasenübergangs zugeschrieben. Die Ergebnisse wurden an Hand von Streuungsmechanismen der Energieträger diskutiert.

Резюме — Термопроводимость ферроэластических кристаллов LiKSO_4 вдоль его трех главных кристаллографических осей была измерена вблизи его высокотемпературного фазового перехода при 705 К. Данные показали anomальное поведение температурной зависимости термопроводимости в области фазового перехода в пределах около 25°. Аномалия фонового вклада в проводимость была отнесена за счет замораживания оптических и (или) акустических мод решеточных колебаний вблизи фазового перехода. Результаты обсуждены на основе механизмов рассеяния носителей энергии.