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Anomaly in Thermal Conductivity of SbSI

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Abstract. The thermal conductivity of materials with soft optical lattice vibrations was recently found to exhibit interesting effects which are in close connection with the phenomenon of ferroelectricity. This work presents results obtained for SbSI, a material which is ferroelectric with a Curie point at 292 °K. The thermal conductivity of SbSI has been measured between 6 °K and 316 °K, with heat flow parallel to the needle shaped crystals. Below 200 °K a behaviour typical for insulators is found. However, at the Curie point a lambda type anomaly occurs: The thermal conductivity increases by a factor of 1.5 above the 'background'. This behaviour is unique, as indentations are observed instead for other ferroelectrics. An interpretation of these effects is given in terms of specific heat, sound velocity and mean free path. It is suggested that the occurrence of a first order phase transition is a probable condition for a lambda type thermal conductivity anomaly. Measurements of the effect of a *dc* electric field applied in the *c*-axis of the crystal and parallel to the heat flow were made; an electric field of 3 kV/cm was found to increase the thermal conductivity close to the Curie point by 19%. This is ascribed to a shift of the soft mode with electric field as in $SrTiO_3$ and $KTaO_3$.

Introduction

Materials with soft optical lattice vibrations have drawn much attention in the recent past because of the close connection of their occurrence with the effect of ferroelectricity. In particular, the thermal conductivity of such materials was found to exhibit interesting effects which were shown to originate from the temperature dependent soft lattice modes [1].

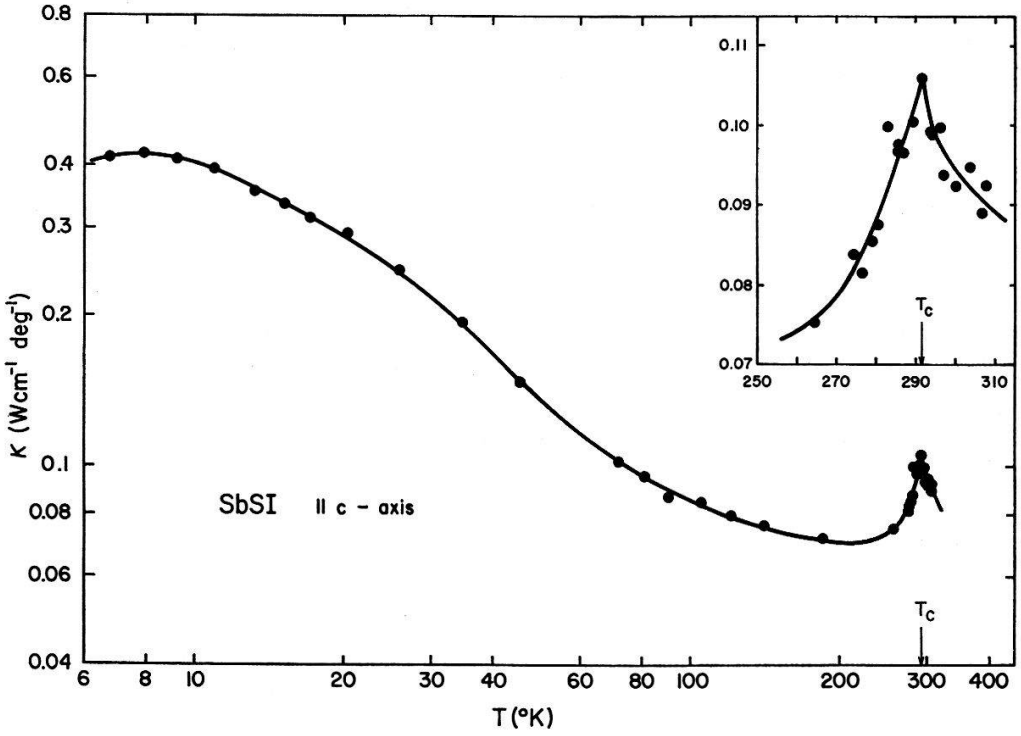
Motivated by these results, studies have been undertaken on SbSI, a material which, because of its strong anisotropy, is a very interesting ferroelectric [2]. To the authors knowledge, thermal conductivity measurements on crystalline ferroelectrics were reported to date only for $BaTiO_3$ [3], KH_2PO_4 [4, 5] and KH_2AsO_4 [5]. All of these show pronounced conductivity minima at their Curie points. It seems attractive to investigate whether this is necessarily so for all ferroelectrics or whether an anomaly of different type is observable in some cases. Another interesting point is the question as to whether a field effect is observed in SbSI which might provide evidence that this material is a ferroelectric of the Cochran type.

The needle shaped SbSI single crystal was grown by sublimation at Laboratories RCA. It is highly resistive in the dark ($\varrho > 10^{10}\,\Omega$ cm). For the thermal conductivity measurements the crystal was used in its grown habitus form with a cross section of 1.3 mm^2 in the shape of a hexagon. It was cut to a length of 13 mm by melting off the ends with a hot wire. Care was taken in mounting the crystal to avoid the application of strain as much as possible, since the material is extremely soft, and splits

easily into many small needles. The crystal was fixed to the sample holder at its lower end, while the upper end, carrying the small heater, could move freely. Electrodes were applied at the top of the crystal and at the base, in order to study the effect of an applied electric field. For all measurements with no applied field, these electrodes where shorted to avoid any buildup of electric charges. The details of the thermal conductivity apparatus have been described elsewhere [1]. The thermocouples where placed 8.7 mm apart, and the temperature gradients were about 0.4 deg/cm. The heat flow was parallel to the crystallographic c-axis which coincides with the needle axis. It should be mentioned that the absolute accuracy of the measurement is somewhat reduced due to the smallness and the shape of the crystal; it may be of the order of 20%. The relative accuracy, however, is of the order of a few percent. Measurements close to the Curie temperature were made only after the sample had been kept each temperature for several hours to allow for full equilibrium.

Results and Discussion

The results are shown in the Figure as a function of the absolute temperature. The thermal conductivity maximum at the lowest temperatures is typical for high purity single crystal insulators, although a peak temperature of only 8 °K is rather unusual. It is believed to be a consequence of the comparatively low Debye temperature ($\theta \leqq 150$ °K) of the material [6]. At medium temperatures the conductivity decreases with about T^{-1}, which is according to theory [7]. At 292 °K, however, the material undergoes a phase transition from C_{2v} ferroelectric, at low temperatures, to D_{2h} paraelectric, at high temperatures. At this temperature, a lambda type anomaly is seen to occur. The thermal conductivity rises by a factor of about 1.5 above the 'background', as the inset in the Figure demonstrates. Such a behaviour is unique for



The thermal conductivity of SbSI as a function of the absolute temperature. Inset: enlarged scale in the region of the Curie point.

crystalline ferroelectrics [8], pronounced indentations are reported instead for $BaTiO_3$ [4], KH_2PO_4 [4, 5] and KH_2AsO_4 [5]. In fact it is extremely rare to find lambda type thermal conductivity anomalies at all in solids [9], and the question arises as to what this is due to.

At first, it should be pointed out that the thermal conductivity in SbSI is purely lattice conductivity, as the material is highly insulating in the dark. In a most simple theory, the lattice conductivity K can be expressed as [7]

$$K = \frac{1}{3} c v l$$

where c is the specific heat, v the sound velocity, and l the mean free path of the lattice vibrations. If the expression is valid in this simple form at the Curie temperature as well, the behaviour of the thermal conductivity at this point will depend on the exact analytical form in which these three quantities depend on temperature. This obviously is a very difficult question, since the mean free path is not easily amenable to measurement. It appears to be generally true, though, that the sound velocity will be greatly reduced at the phase transition. The same behaviour is presumed to take place for the mean free path due to critical fluctuations causing additional phonon scattering. It is well known, on the other hand, that the specific heat is enhanced at the transition. The occurrence of a lambda type anomaly in K thus seems to require a very sharp peak in the specific heat at the Curie point, overcompensating the reduction in v and l. In the light of this, it is worthwhile to compare the ferroelectrics for which thermal conductivity results are available: SbSI, $BaTiO_3$ and KH_2PO_4. The specific heat peaks of these materials [10–12] are found to be of quite different sharpness. In SbSI, which shows a lambda type anomaly in K, the rise in specific heat is appreciably steeper than in crystalline $BaTiO_3$, exhibiting a pronounced minimum in K. (The differences partly may be due to inhomogeneities and internal strains for which a needle shaped crystal like SbSI might be less susceptible than a cubic one.) It is remarkable that *ceramic* $BaTiO_3$ behaves differently from the crystalline material; the specific heat rises much steeper [11, 13] and at the same time the thermal conductivity shows a slight increase [14] at the Curie point (by a factor of 1.05 to 1.12 above the 'background') instead of an indentation. In KH_2PO_4 the sitation is different; the specific heat rise is comparable in steepness to SbSI, but the thermal conductivity shows no indication of a lambda type anomaly [4, 5]. This implies that the specific heat alone is unable to explain all features, and the behaviour of v and l at the Curie point has to be considered as well in comparing different materials.

One other interesting point, however, is the question as to whether a correlation exists between the thermal conductivity anomaly and the order of the phase transition. SbSI [2, 15] as well as $BaTiO_3$ [16] is of first order, while KH_2PO_4 [15] is of second order. (The evidence for this, which is based on measurements of dielectric constants, spontaneous polarisation and x-ray diffraction, is rather conclusive, although a latent heat has never been observed experimentally in ferroelectrics [15].) Considering the results mentioned above, such a correlation is indeed suggested.

To establish the matter further it is of interest to search for thermal conductivity anomalies as well in non-ferroelectric phase transitions: According to BAER et al. [9]

a peak in the thermal conductivity marks the transition from the semiconducting β-phase to the metallic α-phase in Ag_2Se, which occurs at 133 °C. In this case, the change in electronic structure was shown to be responsible for the peak; the major part to the thermal conductivity is contributed by the electrons, unlike in SbSI. It is interesting to note, though, that BAER et al. calculated a peak at 133 °C as well for the minor lattice contribution. They also found this transition to be of first order with a latent heat of 1.68 Kcal/mol. At 90 °C they observed another phase transition with no latent heat involved in it (within their experimental error of about 100 cal/mol); no peak in the lattice conductivity seems to be correlated with it.

Thermal conductivity anomalies have been found also at the magnetic transitions in MnO, CoO, MnF_2, CoF_2 [17], UO_2 [4]. All these materials show indentations in K at their Néel temperatures, and the transitions are known to be of second order.

Considering all these results on ferroelectrics, on Ag_2Se, and on magnetic materials, the experimental fact seems to be established that a lambda type thermal conductivity anomaly is correlated with the occurence of a first order transition; (a further requirement appears to be a certain sharpness of the specific heat peak). Whether these are the necessary and sufficient conditions for a lambda type anomaly in K is an attractive goal for further experimental and theoretical studies.

The discussion of the present results on SbSI is of course rather qualitative in nature, and the detailed mechanism for the thermal conductivity anomaly still has to be evaluated. In order to get some more insight into it, measurements of the effect of an electric field on the thermal conductivity of SbSI were also made. These were carried out in the paraelectric phase, but in close neighbourhood of the Curie temperature. It was found that a dc electric field of 3 kV/cm, applied parallel to the heat flow, increases the thermal conductivity at 297 °K and at 308 °K by 19 and 15%, respectively. Such a behaviour is similar to one reproted for the pseudo-ferroelectric materials $SrTiO_3$ and $KTaO_3$ [1]. It is ascribed to a shift of the soft lattice mode under an applied electric field, and suggests that SbSI is a ferroelectric of the Cochran type.

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[8] It should be mentioned that a weak indication for a peak was reported for the almost ferroelectric material $SrTiO_3$ at 113 °K by E. HEGENBARTH, in Proceedings of the International Meeting on Ferroelectricity, Prague 1966, edited by V. DVORAK et al. (Institute of Physics and the Czeckoslovak Academy of Science, Prague 1966), p. 104. This observation, however, was not confirmed by three other authors (see Reference [1]).
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Einkristallines Galliumarsenid ohne Versetzungen

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Abstract. Big doped and undoped crystals of GaAs (ca. 100 g) can be pulled completely dislocation free. The minimum concentration of charge carriers in undoped crystals is $n, p \gtrapprox 10^{15}$ cm^{-3}, the total acceptor and donor concentration being, however, as high as 10^{17} cm^{-3}, limiting the room temperature electron mobility to ca. 5000 cm^2/Vs. Doping limits are $n, p < 5 \cdot 10^{19}$ cm^{-3}. Epitaxial dislocation free GaAs layers can only be grown on dislocation free substrates. For undoped layers, the type and concentration of the substrate are irrelevant, as long as it is dislocation free.

There is no measurable direct interaction between electronic transport phenomena and individual dislocations, dislocation free GaAs having the same electrical parameters as GaAs with dislocations. Under special conditions, however, the dislocations, the primary distribution and precipitations of foreign atoms affect the diffusion processes. The important problem of dislocation free diffusion into dislocation free GaAs has been solved. Some important perturbing local effects can be explained.

Einleitung

Der Übergang der Halbleitertechnologie vom Germanium auf Silizium war in erster Linie durch die höheren zulässigen Betriebstemperaturen begünstigt. Dioden und Transistoren aus Ge sind auf den Temperaturbereich unterhalb etwa 70 °C beschränkt, während bei Si bis 150 °C gegangen werden kann. Damit lässt sich der grösste Teil der industriell wichtigen Anwendungen realisieren – und der Aufwand zur Beherrschung der schwierigeren Si-Technologie war gerechtfertigt. Industriell von grösster Bedeutung war zudem, dass mit (durch thermische Oxydation erreichbarem) SiO_2 als Isolator und Deckschicht ein chemisch stabiles und relativ leicht bearbeitbares Dielektrikum sich anbot. Trotz der reichhaltigen Varietät der Halbleitereigen-