

THERMAL CONDUCTIVITY OF NaCl SINGLE CRYSTALS DOPED BY Ca^{++} AND OH^-

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In the present paper the results of thermal conductivity measurements in an NaCl single crystal doped by Ca^{++} and OH^- within the temperature range of 5 K to 190 K are presented. Some anomalies have been found in the temperature dependence of the thermal conductivity. Contrary to earlier works, a detailed analysis of the measured results has shown that the "dips" in thermal conductivity are caused by localized modes on larger aggregates due to impurities. In the past the "dips" were interpreted by localized modes on vacancy — bivalent impurity complexes.

УДЕЛЬНАЯ ТЕПЛОПРОВОДНОСТЬ МОНОКРИСТАЛЛОВ NaCl С ПРИМЕСЯМИ ИОНОВ Ca^{++} И OH^-

В настоящей работе приводятся результаты измерений удельной теплопроводности в монокристаллах NaCl с примесями ионов Ca^{++} и OH^- в области температур 5°—190° К. Были обнаружены некоторые аномалии в зависимости удельной теплопроводности от температуры. В отличие от прежних работ, детальный анализ результатов измерений показал, что «спады» в удельной теплопроводности вызваны локализованными модами на больших агрегациях, которые обусловлены примесями. Раньше эти «спады» интерпретировались локализованными модами на свободных двухвалентных комплексах образованных примесями.

1. INTRODUCTION

In ionic crystals the heat flow is provided by the transport of phonons. The value of thermal conductivity is then limited by phonon scattering. At high temperatures the thermal conductivity is given by multiphonon scattering. With decreasing temperature the efficiency of the phonon-phonon scattering decreases whilst the thermal conductivity increases within the limit given by phonon scattering on lattice defects.

The influence of lattice defects on thermal conductivity was investigated both theoretically and experimentally by many authors. A qualitative agreement bet-

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When experimental results and theory were found. The influence of bivalent impurity ions on thermal conductivity of ionic crystals within the temperature range 1 K to 100 K was investigated by Klein, Schwartz and Walker, Pohl and Slack [1—5]. They found that, in agreement with theory, the thermal conductivity maximum decreases with an increasing impurity concentration. Moreover, the "dips" in the temperature dependence of thermal conductivity were measured by many authors [2, 4, 5]. For bivalent impurities in NaCl the anomaly occurs at temperatures from 30 K to 40 K. The anomaly of thermal conductivity was theoretically interpreted by Wagner [6] as an influence of localized modes on the thermal conductivity of crystals. Almost in all works in which the "dips" in thermal conductivity were measured, the interpretation by means of the localized modes was employed.

In the present work the influence of Ca^{++} and OH^- ions on thermal conductivity of single crystals was investigated in order to elucidate the origin of the anomalous course of thermal conductivity in the range of low temperatures.

II. EXPERIMENTAL PROCEDURE

The thermal conductivity was measured using the stationary method of Klein and Caldwell [7] with certain modifications (cf. Fig. 1). When measuring thermal conductivity by this method, the size of the samples presents one of the most important problems. From the accuracy and measurement sensitivity viewpoints, long samples are preferable. In the used crystal lengths a homogeneity in the concentration of defects must be ensured. In our work 2 cm long samples were used. The distance between thermometers was about 1.5 cm. For measurement of temperature the Allen Bradley resistors with a resistance of 220 Ω at room temperature were used. Resistivity was measured by the potentiometric method using the TETTEX compensator. The temperature of the sample was set by the heater (H1). The heater (H2) sets the temperature gradient in the sample. The gradient ranged from 0.1 K to 0.2 K. The radiation influence during measurement was eliminated by the shieldings (S1) and (S2). In order to improve thermal contacts vacuum seal was used.

The described arrangement enables measurements within a temperature region from 2 K to 190 K with the help of a properly applied liquid medium (He, N_2), a suitable construction of the thermal bridge (TB) and heater (H1). In order to decrease the temperature of liquid helium or nitrogen, the vapour was removed using the helium or nitrogen vapour pressure regulator, respectively. Before each measurement the thermometers (T1) and (T2) were calibrated relatively to each other so that the measured temperature difference between them was smaller than 0.005 K. From these calibrated points the temperature scale for the thermometers

was obtained using the three-point least squares smoothing. After this procedure the measurement itself was performed. The temperature gradient 0.1 K was set by the heater H2 with the help of the upper heater H1 the thermal conductivity of the single crystal was measured successively, point by point.

For our measurements a single crystal made by MONOKRYSTALY Co. in Turnov containing bivalent Ca^{++} impurities (in a concentration of several hundreds ppm) and OH^- anions was employed. The sample was cut in the 100 direction. Its size was $0.5 \times 0.5 \times 2 \text{ cm}^3$. The surface of the sample was ground by abrasive paper.

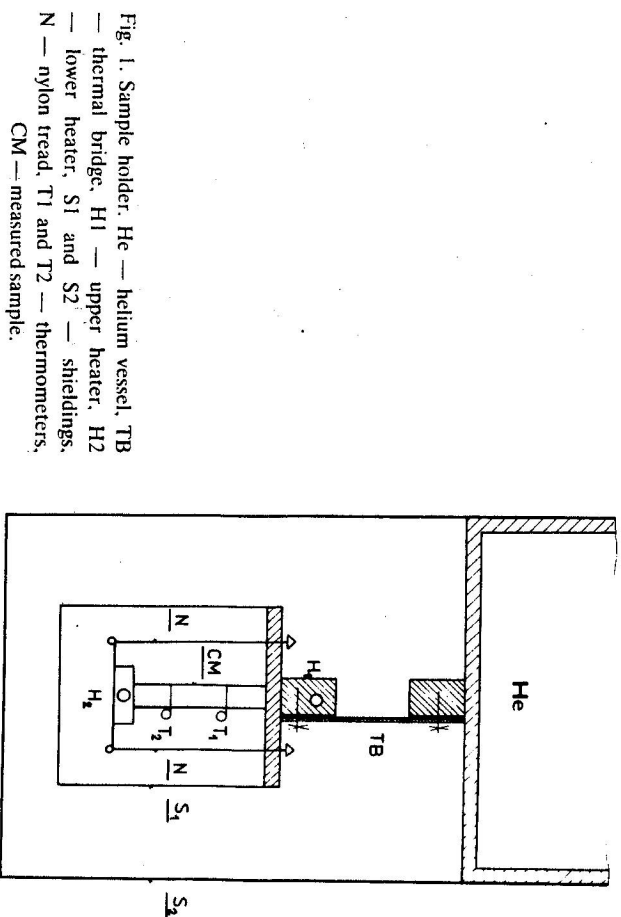


Fig. 1. Sample holder. He — helium vessel, TB — thermal bridge, H1 — upper heater, H2 — lower heater, S1 and S2 — shieldings, N — nylon tread, T1 and T2 — thermometers, CM — measured sample.

III. RESULTS AND DISCUSSION

The measured thermal conductivity course as a function of temperature shown in Fig. 2 is similar to that measured by Klein [2] in a crystal made by the HARSAW Company. Thus, we may judge that both crystals have similar properties. The curve (a) corresponds to the cut crystal. The curve (b) corresponds to the crystal treated thermally for 12 hours at 750 °C and cooled slowly for 5 hours to room temperature. By this procedure the impurities built in the crystal were allowed to form aggregates of a greater size [8]. Comparing the curves (a) and (b) one can see that by the heat treatment the "dips" in thermal conductivity at a temperature range 30

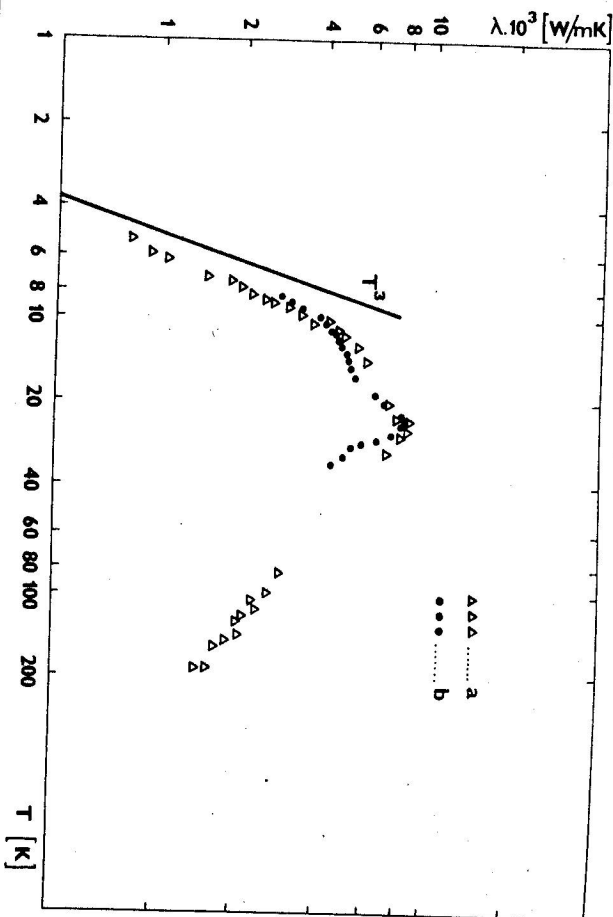


Fig. 2. Thermal conductivity of NaCl (a) cut crystal, (b) crystal thermally treated for 12 hours at 750 °C and then slowly cooled to room temperature.

to 40 K became substantially more pronounced. From this it follows that the anomaly is caused by the influence of localized (or quasilocalized) modes on larger aggregates.

The influence of bivalent ions on the thermal conductivity of NaCl, KCl, and KBr, was measured by Schwartz and Walker [4]. They interpret the thermal conductivity anomaly by the formation of quasilocalized modes in such regions where a vacancy is in the neighbourhood of the bivalent ion. The concentration of impurities in the investigated crystals was over 500 ppm. They studied the influence of Sr^{2+} and Ca^{2+} on the thermal conductivity of NaCl. Slack studied the influence of Ca^{2+} on the thermal conductivity of KCl. The concentration of impurities varied from 60 to 200 ppm. In all these works the thermal conductivity "dips" were measured in the temperature range 20 K to 40 K. As follows from electrical, dielectric, and ITC measurements [9] the solubility limit for impurities is substantially lower. It is clear that in measuring the thermal conductivity of the mentioned crystals there was, in fact, measured the influence of localized and quasilocalized modes on larger aggregates — and not on the vacancy-impurity ion complexes. This is also confirmed by concentration measurements done by Schwartz and Walker [5]. By increasing the concentration far over the solubility

limit, the anomaly becomes more pronounced. This fact is supported also by measurements presented in this paper (Fig. 2).

Another anomaly in the thermal conductivity occurs at a temperature of about 18 K. Klein [2] found in some HARSAW Co. crystals a deviation of the measured points from the T^3 rule. It was interpreted by a scatter of the measured values. From electrical measurements it follows that the OH^- groups greatly favour the formation of precipitates [10]. The HARSAW Co. crystals as well as the crystals measured in this work contain OH^- groups. It is clear that the heat treatment in our work accelerated the formation of precipitates. This can be seen in Fig. 2, where already in the cut crystal some indication of a "dip" is present.

IV. CONCLUSION

The value of the thermal conductivity of single crystals in the low temperature region is dependent on the lattice defects. The interpretation of the thermal conductivity dependence on temperature is not always unambiguous, since many scattering mechanisms may overlap. A detailed interpretation of thermal conductivity may be discussed only after taking into account other measurements such as the ITC measurement of electrical conductivity, dielectric losses, mechanical properties, etc. Another important factor for the interpretation of measurement is the thermal treatment of the sample prior to the measurement. In this paper, the interpretation was based on the electrical measurement results. Contrary to previous works, it was observed that after the thermal treatment of an NaCl single crystal the anomaly in thermal conductivity was caused by larger aggregates formed by impurity atoms. Naturally, the form of aggregates at present cannot be predicted from the shape of the "dips".

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