“Anomalous” Thermal Conductivity of Crystalline Alkali Halides Close to Their Melting Point

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The thermal conductivity of crystalline alkali halides MX (M = Li, Na, K, Rb, and Cs; X = Cl, Br, and I) close to their melting point has been measured by the steady-state coaxial-cylinders method. It was found to change anomalously as the temperature varied. A minimum of the thermal conductivity at a characteristic temperature depends on the ionic composition of the crystal. This effect is ascribed to the formation of cooperating defects in the melting lattice. An expression relating the thermal conductivity of the ionic crystal near the melting point to the concentration of these defects is proposed.

Key words: Thermal conductivity, High temperature, Melting point, Ionic crystal, Alkali halide.

Introduction

Data on the thermal conductivity (λ) of crystalline alkali halides at high temperature are scarce. Those of solid lithium fluoride, natrium chloride and potassium chloride measured up to the melting point are in disagreement [1–3]. The thermal conductivity exhibits appreciable deviations from that calculated on the basis of the phonon theory of energy exchange [4–7]. It has been conjectured that these deviations from the law $\lambda \sim T^{-n}$ result either from the contribution of radiation or a redistribution of the optical and acoustic modes at elevated temperatures. In order to elucidate this problem we have measured the thermal conductivity of alkali chlorides, bromides and iodides as a function of temperature close to their melting point.

Experimental

The steady-state method of coaxial-cylinders was used. The design of the experimental device was described in [8]. Platinum was selected as the most suitable material for the cylinders. The gap between the cylinders was 1 mm wide and the temperature difference over it did not exceed 1.5 K to diminish heat transfer by radiation. The low emissivity of platinum and the transparency of alkali halides in the spectral range of maximum heat absorption enabled to reduce the contribution of heat transfer by radiation to 3–5%.

Special attention was paid to preparing anhydrous pure salts since adsorption of any impurities could affect the reflectivity of the platinum surface. High-purity alkali halides were heated under vacuum. Possible contaminants were removed by zone melting. The experiments were carried out in an atmosphere of high-purity inert gas.

λ was measured when the temperature difference (ΔT) through the gap filled with salt and the heat flow (Q) became constant. It was calculated by the equation $\lambda = \ln(R/r) \cdot Q/(2\pi l \cdot \Delta T)$, where R and r are the outer and inner radii of the annular salt layer while l is the axial extent of the gap.

The error or our results did not exceed 6%.

Particular attention was paid to the experimental procedure. First the device was immersed in the fused salt so that the gap between the cylinders was filled with it. Then salt was slowly cooled until a temperature slightly lower than the melting point was reached. Then λ of the crystalline salts was measured in accordance with [8].

Since molten salts wet the noble metals there occurred no scaling of the crystallizing salts from the platinum walls. Cracs in the crystalline salt layer would impair the experimental data. When the formation of cracks occurred, the thermal conductivity droped quickly. In this case the run was interrupted, the salt was again fused and the previous experimental procedure was repeated. The temperature of the initial

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formation of cracks decreases as the molecular mass of the salt increases, going from lithium to caesium halides. The short-time evolution of the heat of crystallization and additional infrared radiation [9] at the melting point could not influence the thermal conductivity of the crystalline alkali halides measured at lower temperatures. The same thermal conductivity determined both with heating and cooling the salt was found within the experimental error.

Results and Discussion

In [10, 11] the thermal conductivity of molten alkali halides was found to increase sharply when the melting point was reached. On further cooling, however, λ of the solid salt decreased and reached a minimum ($\lambda_{\min}$) at a characteristic temperature ($T_{\min}$). Then the thermal conductivity increased with decreasing temperature, in good agreement with the phonon theory of heat transfer.

λ of crystalline alkali halides varies with temperature according to empirical equation

$$\lambda = a + b \cdot T + c \cdot T^2 \pm \Delta\lambda \, .$$

The values *a*, *b*, and *c* calculated from experimental data by a least-squares fitting are given in Table 1. $T_{\min}$, $\lambda_{\min}$ and temperature ranges of the measurements are also tabulated there.

The experimental thermal conductivity, λ_{exp}, differs greatly from λ_{id} estimated on the basis of the phonon theory of energy exchange in ionic crystals at temperatures higher than the Debye temperature [4]. In terms of this theory we attributed the premelting effect observed to the peculiarities of the defective crystal near the melting point.

Under heating the number of the thermal defects rises and so the thermal conductivity connected with the phonon mean free path [4, 6] decreases. When the concentration of the defects is low, the interaction between them is so weak that one could expect a linear decrease of log λ with rising log T. A deviation from this dependence is only observed close to the melting point (T_{m}) and for most salts a change in the sign of this dependence takes place. This can be explained with a cooperation of the defects near T_{m}, resulting in a decrease of the number of phonon scattering centres. $\Delta\lambda_{\text{def}}$ is the difference between the experimental and the "classical" phonon thermal conductivity:

$$\Delta\lambda_{\text{def}} = \lambda_{\text{exp}} - \lambda_{\text{id}} \, . \tag{1}$$

In a wide temperature range lower than $T_{\min}$ the thermal conductivity is described by the equation

$$\log \lambda_{\text{exp}} = n \log T \, .$$

where n is constant, that is in accordance with the phonon theory of heat transfer. At higher temperatures up to the melting point λ_{id} can be estimated by extrapolation of this relation.

The value of $\Delta\lambda_{\text{def}}$ is related to the concentration (N) of the cooperating defects. There exist reliable data on the lattice parameter (α) as a function of temperature for various crystalline alkali halides up to the melting point [12]. The experimental values of α show positive

Table 1. Thermal conductivity of crystalline alkali halides.

Salt	$T_{\min}$ K	$\lambda_{\min}$ $W/(\text{m} \cdot \text{K})$	Temperature interval K	$\alpha \cdot 10$ $W/(\text{m} \cdot \text{K})$	$-b \cdot 10^4$ $W/(\text{m} \cdot \text{K}^2)$	$c \cdot 10^7$ $W/(\text{m} \cdot \text{K}^3)$	$\Delta\lambda$ $W/(\text{m} \cdot \text{K})$
LiCl	839	0.688	886– 800	898.410	2124.730	1265.940	0.049
NaCl	1059	0.898	1073–1010	191.491	344.092	162.750	0.008
KCl	1038	0.804	1040–1010	438.131	828.131	399.071	0.016
RbCl	973	0.464	983– 950	962.742	1969.270	1011.900	0.010
CsCl	882	0.341	910– 875	338.623	759.759	430.504	0.013
LiBr	811	0.781	820– 790	1983.100	4868.970	300.042	0.026
NaBr	–	–	1021– 980	95.882	158.573	68.522	0.004
KBr	991	0.541	1005– 960	1782.810	3585.620	1808.350	0.014
RbBr	935	0.528	957– 910	847.219	1800.930	963.062	0.010
CsBr	883	0.359	905– 860	517.750	1164.990	659.907	0.009
NaI	841	0.390	930– 760	41.132	88.488	52.585	0.018
KI	898	0.373	952– 810	50.651	104.384	58.062	0.040
RbI	902	0.438	919– 790	34.378	66.491	36.849	0.040
CsI	763	0.264	887– 380	12.633	26.266	17.216	0.040

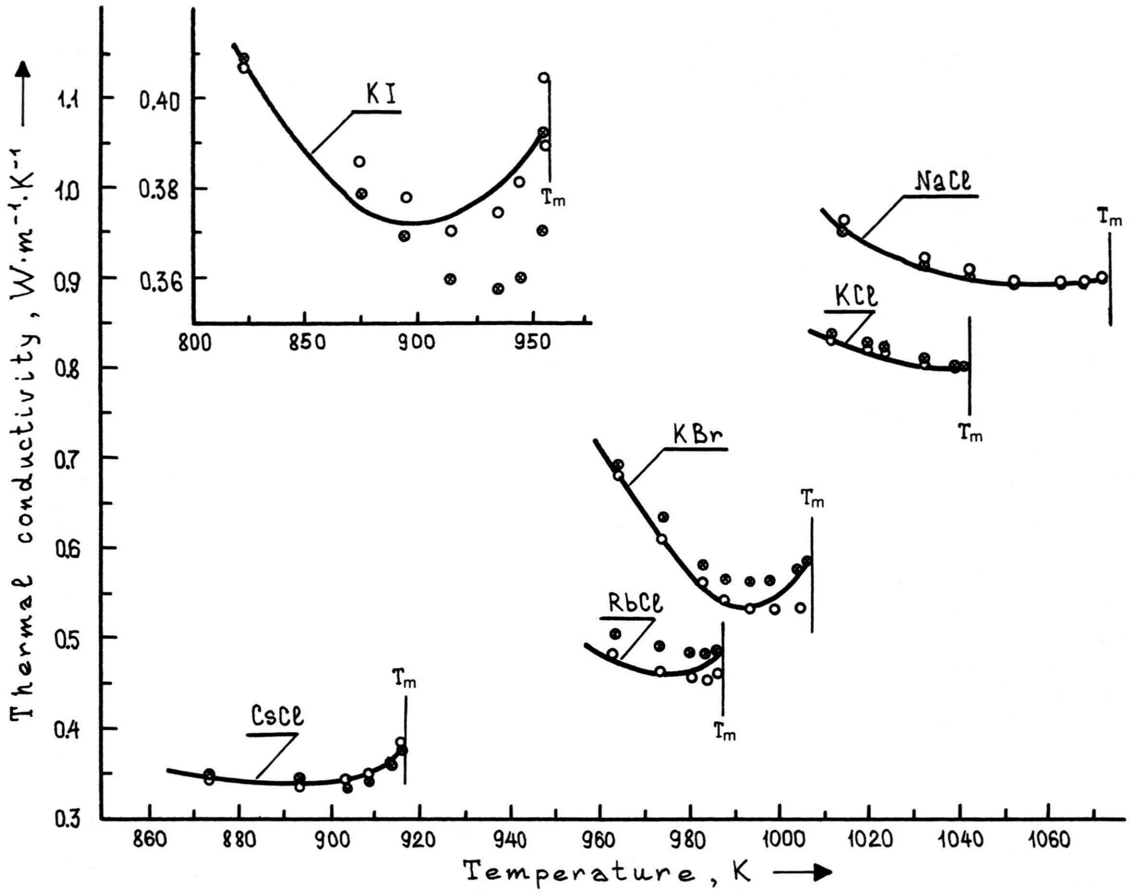

Fig. 1. Thermal conductivity of crystalline alkali halides close to their melting point (T_m): experimental values (——); values calculated according to model I (⊗) or model II (○).

deviations ($\varDelta\alpha$) from those calculated by the relation $\log \alpha = \mathrm{const}\,(1/T)$ over the same temperature range, the "anomalous" thermal conductivity is observed. These deviations are also connected with the lattice imperfections close to T_m. So the ratio of $\varDelta\alpha$ at a given temperature to that at the characteristic temperature (T_m or $T_{\min}$) can be used as a measure of the concentration of the cooperating defects.

If the melting point is taken as the reference temperature (model I) one can derive

$$N_{\mathrm{I}} = \varDelta\alpha_T / \varDelta\alpha_{T_m} \tag{2}$$

and

$$\varDelta\lambda_{\mathrm{def\,(I)}} = N_{\mathrm{I}}(\lambda_{\mathrm{exp}} - \lambda_{\mathrm{id}})_{T_m}\,. \tag{3}$$

If $T_{\min}$ is taken (model II):

$$N_{\mathrm{II}} = \varDelta\alpha_T / \varDelta\alpha_{T_{\min}} \tag{4}$$

and

$$\varDelta\lambda_{\mathrm{def\,(II)}} = N_{\mathrm{II}}(\lambda_{\mathrm{exp}} - \lambda_{\mathrm{id}})_{T_{\min}}\,. \tag{5}$$

The thermal conductivity of the crystalline alkali halides calculated in terms of above models with the Eqs. (1)–(5) are jaxtaposed with that measured in Figure 1. The model and experimental values of λ are found to be in reasonably good agreement. Nevertheless, model II provides a better fit to the experimental data than Model I. This is due to some uncertainty of the values of N_{I} and $\varDelta\lambda_{\mathrm{def\,(I)}}$ evaluated from the extrapolated magnitudes of the latticed parameter and the termal conductivity. In model II only directly measured values are used.

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