THERMAL CONDUCTIVITY OF 1,2-DICHLOROETHANE AND 1,2-DIBROMOETHANE

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This paper gives the thermal conductivities of 1,2-dichloroethane and 1,2-dibromoethane between liquid nitrogen temperature and room temperature.

Questions relating to the effect of "rotational excitations" of molecules on heat transfer in molecular crystals have not been well investigated either theoretically or experimentally. Yet the available data indicate that such excitations affect the thermal conductivity in a number of cases [1].

For a further study of this question we measured the thermal conductivities of two similar organic substances between liquid nitrogen temperature and room temperature. The substances used for the measurements were cp.

A characteristic feature of the investigated compounds is the considerable rotational mobility of the molecules in the crystal lattice: the pronounced molecular liberations make an appreciable contribution to the specific heat even at very low temperatures [2]. The two compounds also show interesting phase transitions. At T = 249.5°K ethylene dibromide undergoes a first-order nonisothermal transition with an anomalous increase in specific heat in the low-temperature modification. Ethylene dichloride undergoes a gradual transition, probably of the second order, in a wider temperature interval, with a maximum at T = 177°K.

The temperature dependence of the thermal resistance of 1,2-dibromoethane is shown in Fig. 1a, and that of 1,2-dichloroethane in Fig. 1b. Solid ethylene dibromide shows the usual relationship: the experimental values lie satisfactorily on a straight line beginning at 0°K. In the region of the phase transition, due to a polymorphic transformation, there is a sharp reduction of thermal conductivity, as distinct from ethylene dibromide, which conforms with the law

$$W_1 = \frac{1}{B_1} T, \tag{1}$$

crystalline ethylene dichloride between liquid nitrogen temperature and 140-145°K obeys the relationship

$$W_2 = \frac{1}{B_2} T - C, \tag{2}$$

where the constant C is 370 cm · sec · deg/cal. Above 140-145°K the thermal resistance follows a more complex law. Since the Debye temperatures of these compounds have not been determined we cannot calculate the constants B_1 and B_2 theoretically from the well-known formula given in [3]:

$$B = \frac{2K_B^2 \Theta_D T_m}{(6\pi^2)^{1/3} V_0^{1/3} \hbar}. \tag{3}$$

According to the Lindemann theory, we have:

$$\Theta_D = \text{const}\, T_m^{1/2} \rho^{1/3} M^{-5/6}. \tag{4}$$

In view of the similarity of the crystal lattices of ethylene dibromide and ethylene dichloride we can obtain from expressions (3) and (4) a relationship between the constants B_1 and B_2:

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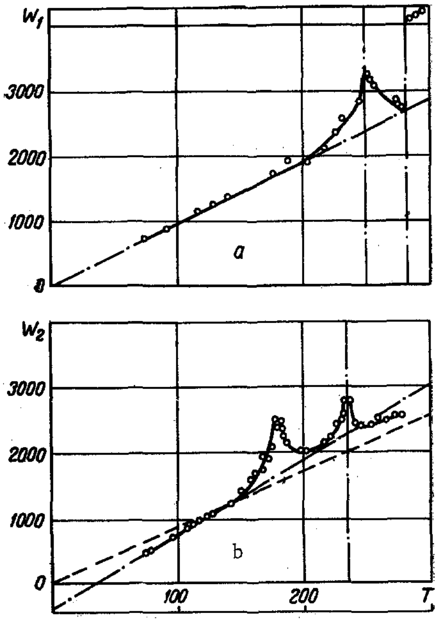

Fig. 1. Temperature dependence of thermal resistance of: a) 1,2-dibromoethane; b) 1,2-dichloroethane. W_1 and W_2 in cm · sec · deg /cal; T in °K.

$$B_2 = B_1 \frac{T_m \rho_2^{2/3} M_1^{7/6}}{T_m \rho_1^{2/3} M_2^{7/6}} . \tag{5}$$

The constant B_1 is determined from the slope of the linear part in Fig. 1a. All the other quantities on the right side of (5) are known.

The theoretical dependence of the thermal resistance of ethylene dichloride, obtained from (5), is shown by the dashed line Fig. 1b. At low temperatures there is additional heat transfer, and above 140-145°K additional scattering predominates. This behavior can be attributed to rotation of the molecules in the lattice sites. At low temperatures the molecular liberations are partially frozen and for this reason, probably, their interaction with acoustic phonons is greatly reduced. The liberations of the molecules make a contribution to the thermal conductivity, which decreases with temperature increase. At high temperatures, above the region of the phase transition right up to the melting point, the enhancement of the interaction is the reason for the intense scattering of acoustic phonons and reduction of the thermal conductivity below the expected value.

Rotation of the molecules is probably more restricted in the dibromide than in the dichloride, which leads not only to later onset of the phase transition, but also prevents the heat transfer at low temperatures due to the waves associated with these rotations. The small change in the thermal resistance of crystalline ethylene dichloride on transition to the liquid state indicates a high degree of orientational disorder of the solid phase above the phase transition temperature.

The great difference in the behavior of the thermal conductivity of crystals of such similar structure is difficult to understand and requires further investigation. The reasons for the anomalies in the thermal resistance in the region of the transitions, and also near the melting point in ethylene dichloride, are also obscure.

NOTATION

W_1, W_2	are the thermal resistances of ethylene dibromide and ethylene dichloride, respectively;
C, B, B_1, B_2	are the constants;
T	is the absolute temperature;
M	is the molecular weight;
ρ	is the density;
T_m	is the melting point;
T_{m1}, T_{m2}	are the melting points of ethylene dichloride and ethylene dibromide, respectively;
T_{tr}	is the phase transition temperature;

Θ_D is the Debye temperature;
V_0 is the molar volume;
K_B is the Boltzmann constant;
$\bar{h}$ is the Planck constant.

LITERATURE CITED

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