INVESTIGATION OF THE THERMAL CONDUCTIVITY OF MOLECULAR CRYSTALS

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The nonsteady-state heated-wire method was used to measure the coefficients of thermal conductivity of benzene and cyclohexane over the temperature range from −196°C to +30°C. We have attempted to explain the heat-transfer mechanism in these substances.

The thermal conductivity of molecular crystals is an area of physics in which little research has been done. As in other poorly conductive substances, a phonon heat-transfer mechanism is apparently dominant in all molecular crystals; the curve representing thermal conductivity as a function of temperature has a characteristic maximum in a very narrow temperature region and the characteristic dependence

$$\lambda = B/T \quad \text{at} \quad T \gtrsim \frac{\theta_D}{3-4}. \tag{1}$$

According to the theory in [1], heat transfer by optical phonons is possible in molecular crystals, being associated with vibratory excitation of the molecules at the lattice points. Thermal conductivity is also inhibited as a result of the scattering of acoustic phonons at these excitation sites. Moreover, phase transitions and the effects related to melting and the premelting stage further complicate the temperature function of thermal conductivity. All these phenomena require careful study, but few experimental investigations have been conducted [2]. The present article describes an experiment that made it possible to plot thermal conductivity as a function of temperature for two typical molecular crystals, benzene and cyclohexane, over the temperature range from −196°C to +30°C. Analysis of the experimental data is used as the basis for an attempt to explain the heat-transfer mechanism in these substances.

The coefficient of thermal conductivity was measured by the non-steady-state heated-wire probe method [3]. The constant-power probe was a molybdenum wire about 0.1 mm in diameter soldered into a glass ampule. In contrast to other studies [4], the temperature was not measured with a thermocouple but directly from the wire resistance, the wire simultaneously serving as the heating element. During passage of a known current, the change in probe temperature with time was recorded by automatic milliammeters with the aid of a bridge circuit. This change in temperature depends on the thermal conductivity of the medium in which the probe is immersed. The coefficient of thermal conductivity was calculated from the formula

$$\lambda = \frac{I^2 r}{4\pi L \gamma}. \tag{2}$$

The substance to be investigated was poured into a measuring ampule and crystallized by the method described below.

Polycrystalline benzene (t_m = 5.5°C) was produced by two methods: 1) rapid chilling to 0°C and slow heating for 24 h; 2) initiation of crystallization at the tip of the ampule by very rapid chilling, e.g., with dry ice, after which the measuring ampule was slowly inserted into a Dewar flask containing an ice–water mixture with the aid of a timing mechanism. No marked differences were detected in the thermal conductivities of the specimens produced by these methods.

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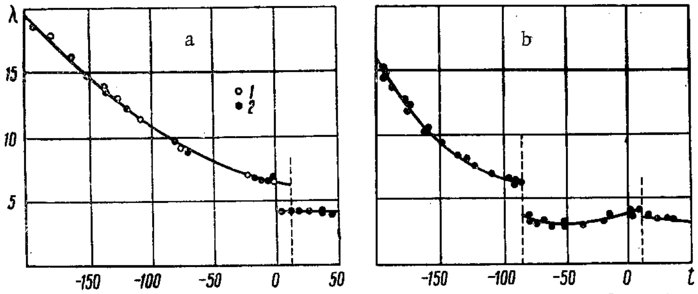

Fig. 1. Coefficient of thermal conductivity as a function of temperature for benzene (a) and cyclohexane (b). 1) Data from [5]; 2) data from present article; λ, cal/cm · sec · deg · 10^{-4}; t, °C.

TABLE 1. Certain Thermodynamic Characteristics of Benzene and Cyclohexane

Compound	t_m, °C	t_{vap} °C	ΔS_{tra}	ΔS_m	$\Delta S_{tra}+\Delta S_m$
Benzene	5,5	80,1	—	8,4	8,4
Cyclohexane	6,5	80,7	8,6	2,3	10,9

Polycrystalline cyclohexane (t_m = 6.5°C) was produced by slowly immersing the measuring ampule in a Dewar flask containing an ice–water mixture.

In order to avoid formation of air bubbles, cavities, and hollows in the crystals, the rate of solidified-zone motion was kept quite small (selected experimentally). In some cases, repeated recrystallization was necessary. The quality of the specimens obtained was checked visually. In order to measure thermal conductivity as a function of temperature, the ampule containing the crystallized substance was clamped in a special holder, which was wrapped with constantan wire that served as the heating element and was embedded in a massive copper tube. The measurement temperature was regulated by the depth to which the tube was immersed in the liquid nitrogen or inserted into the heating furnace. The actual measurement process, i.e., determination of the coefficient of thermal conductivity at one point on the temperature scale, required an average of 5-7 sec, so that there was no need to use a special cryostat or other complicated equipment to maintain a constant temperature over a long period of time, as is necessary in measurements made by the steady-state method.

The temperature dependence of the thermal conductivity of benzene is shown in Fig. 1a, in which are also shown the data of Euken [5] who used a steady-method for his measurements. Our data were in good agreement with Euken's curve. The rule $\lambda = B/T$, where B_{exp} = 0.17 cal/cm · sec was satisfied over the entire solid-state temperature range, which corresponds to thermal conductivity produced principally by anharmonic transfer processes. The decrease in thermal conductivity during the solid–liquid phase transition was $(\lambda_{so}/\lambda_l)_{tm} = 1.6$. According to the theory of Leibfried and Schlomann [6],

$$\lambda \sim \theta_D \frac{c_v^2}{c_p - c_v}. \tag{3}$$

The change in λ during fusion can be evaluated by Mott's method [7]. It can be shown that the ratio of the coefficients of thermal conductivity for the solid and liquid phases equals:

$$\left(\frac{\lambda_{so}}{\lambda_l}\right)_{t_m} = \left[\left(\frac{c_v^2}{c_p - c_v}\right)_{so} \Big/ \left(\frac{c_v^2}{c_p - c_v}\right)_l\right] \exp\frac{H_m}{3RT_m}. \tag{4}$$

The first term in Eq. (4) varies little and the second is decisive. This formula yields $(\lambda_{so}/\lambda_l)_{tm} = 2$.

The change in the thermal conductivity of cyclohexane with temperature is considerably more interesting (Fig. 1b). The current literature contains no data on the thermal conductivity of this compound in the solid state. Here the rule $\lambda = B/T$, where B_{exp} = 0.12 cal/cm · sec, was satisfied only for the low-temperature modification. The phase-transition point is –87°C. It is a type I transition and leads to a lattice rearrangement, being accompanied by a relatively large latent heat of transition and an increase in volume. Anomalies in heat capacity [8] and dielectric loss [9] have been observed in the transition region and there is an abrupt drop in the second moment of the proton-resonance line [10]. The subsequent behavior of the thermal conductivity of solid cyclohexane follows the change in heat capacity. The very small decrease in the coefficient of thermal conductivity on melting, $(\lambda_{so}/\lambda_l)_{tm} = 1.07$, is noteworthy. During the phase transition, $(\lambda_{so}^{I}/\lambda_{so}^{II})_{tm} = 1.6$.

Both benzene and cyclohexane are nonpolar hydrocarbons with similar molecular weights and differ little (by less than 1°) in their melting and boiling points, but they have totally different entropies of fusion [10] (Table 1).

The character of the change in thermal conductivity for the low-temperature form of cyclohexane was found to be analogous to that for benzene. In contrast to benzene, favorable conditions for molecular displacement are created in the high-temperature form of cyclohexane, as a result of the more globular form of the molecule. It has been demonstrated that the molecules in the low-temperature form of cyclohexane "rotate" in the lattice at temperatures between −123°C and −87°C, but these rotations are substantially inhibited by the large potential barrier and have the character of reorientation with respect to the third-order axis. The lattice can be regarded as essentially rigid below −123°C. A similar phenomenon occurs in crystalline benzene , which has been found to exhibit molecular reorientation with respect to the sixth-order axis at temperatures between −183°C and −153°C [10]. Moreover, we were unable to observe any effect of this molecular reorientation on thermal conductivity in either benzene or cyclohexane.

The cyclohexane lattice becomes more symmetric after the phase transition (the monoclinic modification is converted to the cubic form). Intensive reorientation of molecules around axes differing from the third-order axis apparently occurs in this "expanded" lattice (the molar volume increases by 8% during the transition) and the crystal enters a plastic (quasiliquid) state. The structural amorphization, which progresses with rising temperature, causes the centers of molecular mass to lose their fixed positions at the lattice points, a process that starts between −50°C and −30°C. The thermal conductivity has a minimum in this region and, as was already noted, varies in direct proportion to the heat capacity. The behavior of the thermal conductivity of cyclohexane is thus in complete conformity with the theory that the cyclohexane crystal is plastic [11].

The constant B in the function $\lambda = B/T$ can be evaluated by the method proposed by Slack [12], using the general formula

$$\lambda = \frac{1}{3}\,\bar{c}_v v l, \tag{5}$$

where $\bar{c}_v$, v, and l are expressed in terms of known quantities:

$$\bar{c}_v = \frac{6K_B}{V_0}, \quad V_0 = \frac{M}{\rho N}; \qquad \upsilon = \frac{K_B\theta_D}{\hbar}\left(\frac{V_0}{6\pi^2}\right)^{1/3}, \quad l = \frac{T_m}{T}\,V_0^{1/3}. \tag{6}$$

Substituting Eq. (6) into Eq. (5), we obtain

$$B_{theo} = \frac{2K_B^2\,\theta_D T_m}{(6\pi^2)^{1/3}V_0^{1/3}\hbar}. \tag{7}$$

For benzene, $B_{theo} = 0.2$ and the ratio $B_{theo}/B_{exp} = 1.18$. Better correspondence is obtained for cyclohexane if T_m is replaced by $T_{tra} = 186°K$; the crystal is converted to the plastic, highly disordered form above this temperature. The values obtained for cyclohexane are $B_{theo} = 0.13$ and $B_{theo}/B_{exp} = 1.08$.

NOTATION

λ	is the thermal conductivity;
λ_{so}, λ_l	are the thermal conductivity in solid and liquid phases respectively;
λ_{so}^{I}, λ_{so}^{II}	are the thermal conductivity of high- and low-temperature modifications, respectively;
θ_D	is the Debye temperature;
t, T	is the temperature;
t_m, T_m	is the melting point;

t_{vap}	is the boiling point;
t_{tra}, T_{tra}	is the phase-transition temperature;
S_{tra}, S_m	is the entropy of phase transition and entropy of fusion, respectively;
B	is the constant;
B_{exp}, B_{theo}	are the constants determined experimentally and theoretically, respectively;
c_v, c_p	is the heat capacity at constant volume and pressure, respectively;
H_m	is the enthalpy of fusion (per mole);
$\overline{c}_v$, v, l	are the average heat capacity per unit volume, velocity, and free phonon path length, respectively;
V_0	is the volume per molecule;
M	is the molecular weight;
e	is the density;
k_B, $\hbar$	are the Boltzmann and Planck constants, respectively;
N	is the Avogadro number;
R	is the gas constant;
I	is the current;
r	is the probe resistance;
L	is the probe length;
γ	is the slope of measuring-probe temperature versus logarithmic time curve.

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