

# HEAT TRANSFER BY “DIFFUSIVE” MODES AND PHONON SCATTERING IN $\beta$ -PHASE OF SOLID SULFUR HEXAFLUORIDE

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The isochoric thermal conductivity of  $\beta$ -SF<sub>6</sub> is described within the framework of a model, where heat is transferred by low-frequency phonons and by “diffusive” modes migrating randomly from site to site above the phonon mobility edge. The contributions of the phonon-phonon and one- and two-phonon scatterings to the total thermal resistance of solid SF<sub>6</sub> are calculated in the supposition of the additive contribution of different scattering mechanisms. The mobility edge  $\omega_0$  is found from the condition that the phonon mean-free path restricted by the examined mechanisms of scattering cannot become smaller than half the wavelength. An increase of the isochoric thermal conductivity of solid SF<sub>6</sub> at premelting temperatures is attributed to the weakening of the one-phonon scattering by the collective rotational excitations of molecules.

## 1. Introduction

The classical theoretical models of heat transfer in solid dielectrics have predicted the thermal conductivity behavior  $\Lambda \sim 1/T$  at temperatures  $T \geq \Theta_D$  ( $\Theta_D$  is the Debye temperature) [1]. Most of these models were applied to the simplest structures such as atomic crystals, and, under the pre-conditions, they did not take into account the additional mechanisms of phonon scattering in molecular crystals. One of these mechanisms affecting the temperature dependence of the thermal conductivity is the translation-rotation coupling. Experimental and theoretical data on thermal conductivity should be compared at constant densities of samples to exclude the effect of thermal expansion [1, 2]. The isochoric thermal conductivity  $\Lambda_v$  can be measured directly or recalculated from the isobaric data  $\Lambda_p$  if the volume dependence of thermal conductivity is known [3]:

$$\Lambda_v = \Lambda_p \left( \frac{V_m(T)}{V_0} \right)^g. \quad (1)$$

Here,  $V_m(T)$  is the instantaneous value of the temperature dependent molar volume of a free sample,  $V_0$  is the molar volume of a sample, for which the

recalculation is carried out, and  $g$  is the Bridgman coefficient:  $g = -(\partial \ln \Lambda / \partial \ln V)_T$ .

As temperature increases, the phonon-phonon scattering processes enhance, and the phonon mean-free path decreases, but it cannot become smaller than half the phonon wavelength  $\lambda/2$  [4]. If all vibrational modes scatter for a distance of  $\lambda/2$ , the thermal conductivity reaches its lower limit

$$\Lambda_{\min} = \left( \frac{\pi}{6} \right)^{1/3} k_B n^{2/3} \times \sum_i v_i \left\{ \left( \frac{T}{\Theta_i} \right)^2 \int_0^{\Theta_i/T} \frac{x^3 e^x}{(e^x - 1)^2} dx \right\}. \quad (2)$$

The summation is carried out over three (one longitudinal and two transverse) sound modes with the sound velocities  $v_i$ ,  $\Theta_i$  is the Debye cutoff frequency for each polarization in Kelvins ( $\Theta_i = v_i (\hbar/k_B) (6\pi^2 n)^{1/3}$ ),  $n = 1/a^3$  is the number of atoms per unit volume,  $a^3$  is the volume of a single atom (molecule), and  $k_B$  is Boltzmann's constant. The calculated values of  $\Lambda_{\min}$  were, as a rule, considerably smaller than experimental ones [5, 6]. The most obvious reason for this difference is that the site-to-site transfer of the rotational energy was not taken into account [6]. In molecular crystals, heat is transferred by mixed translation-rotation modes, whose heat capacity is saturated in proportion to the total molecular degrees of freedom:

$$\Lambda_{\min}^* = \frac{1}{2} \left( \frac{\pi}{6} \right)^{1/3} \left( 1 + \frac{z}{3} \right) k_B n^{2/3} (v_\ell + 2v_t). \quad (3)$$

Here,  $v_\ell$  and  $v_t$  are the longitudinal and transversal sound velocities, respectively, and  $z$  is the number of rotational degrees of freedom.

The isochoric thermal conductivity of molecular crystals shows considerable deviations from the  $\Lambda \sim 1/T$  dependence at  $T \geq \Theta_D$  [6, 7]. It is shown that, in orientationally ordered phases, it can be described within a model, where heat is transferred by low-frequency phonons; above the phonon mobility edge, it is transferred by “diffusive” modes migrating randomly from site to site [6]. In orientationally disordered phases, the isochoric thermal conductivity increases, as a rule; the increase is due to the weakening of phonon scattering by short-range orientational order fluctuations with increase in temperature. The expressions for the relaxation times of the one- and two-phonon scatterings under rotational excitations of molecules were derived in [8] for solid methanes.

In the present work, the isochoric thermal conductivity of SF<sub>6</sub> is calculated using both the expressions for the phonon-phonon [1] and phonon-rotation scattering [8] and taking into account the limitation of phonon mean-free path [6].

## 2. Model

This calculation was performed on the basis of the Debye’s expression for thermal conductivity [1] using the approach of Roufosse and Klemens [9] who used the idea of a lower limit for the phonon mean-free path

$$\Lambda = \frac{k_B}{2\pi^2 v^2} \int_0^{\omega_D} l(\omega) \omega^2 d\omega, \quad (4)$$

where  $\omega_D$  is the Debye frequency ( $\omega_D = (6\pi^2)^{1/3} v/a$ ), and  $l(\omega)$  is the phonon mean-free path.

At  $T \geq \Theta_D$ , heat transfer in molecular crystals is determined mainly by the phonon-phonon and phonon-rotation interactions. In this case,  $l(\omega)$  is the combined phonon mean-free path determined by all of the examined mechanisms of scattering. Therefore,

$$l_\Sigma(\omega) = \sum_i \left( l_i(\omega)^{-1} \right)^{-1}. \quad (5)$$

In turn, the phonon-rotation relaxation time is determined by the one- and two-phonon scattering processes. To explain the increase of the thermal conductivity in the orientationally disordered phases of solid methane and deuteromethane, the authors of [8] drew the analogy between molecular and spin systems [10]. In a number of magnetic crystals, the thermal conductivity was observed to increase above the magnetic phase transition. The reason for these

anomalies is the critical scattering of phonons by the critical fluctuations of the short-range magnetic order above the Neel point. In the orientationally disordered phases of molecular crystals, the increase of the isochoric thermal conductivity is due to the weakening of phonon scattering by the fluctuations of the short-range orientational order with increase in temperature. Using the equations for one- and two-phonon relaxation times in [9], the phonon mean-free path of each of the examined scattering mechanisms can be expressed as

$$l_u(\omega) = v/AT\omega^2, \quad (6.1)$$

$$l_I(\omega) = \rho v^5/B^2\Lambda_{\text{rot}}T\omega^2, \quad (6.2)$$

$$l_{II}(\omega) = \pi\rho^2v^8/C^2k_B C_{\text{rot}}T^2\omega^4, \quad (6.3)$$

$$A = \frac{18\pi^3}{\sqrt{2}} \frac{k_B\gamma^2}{ma^2\omega_D^3}, \quad (7)$$

where the Grüneisen parameter  $\gamma = -(\partial \ln \Theta_D / \partial \ln V)_T$ ,  $l_u(\omega)$  is the phonon mean-free path determined by  $U$ -processes,  $l_I(\omega)$  and  $l_{II}(\omega)$  are the phonon mean-free paths for one and two-phonon scattering,  $m$  is the average atomic (molecular) weight,  $B$  and  $C$  are the constants of noncentral intermolecular interactions,  $\Lambda_{\text{rot}}$  is the thermal conductivity of the orientational subsystem, and  $C_{\text{rot}}$  is the rotational heat capacity per unit volume. In the first approximation,  $B = C^2$  [8]. The coefficient  $B$  can be found from the pressure dependence of orientational ordering temperature:

$$B = - \left( \frac{1}{\chi_T} \right) \frac{\partial (\ln T_f)}{\partial P}. \quad (8)$$

Here,  $\chi_T$  is the isothermal compressibility,  $T_f$  is temperature of the orientational phase transition, and  $P$  is the pressure. The thermal conductivity  $\Lambda_{\text{rot}}$  can be found from the well-known gas-kinetic expression

$$\Lambda_{\text{rot}} = \frac{1}{3} C_{\text{rot}} a^2 \tau^{-1}, \quad (9)$$

where  $\tau$  is the characteristic time of the orientational excitation transfer from one lattice site to another one.

By substituting (6)–(8) in (5), the combined phonon mean-free path can be expressed as

$$l_\Sigma(\omega) = \left( \frac{AT\omega^2}{v} + \frac{B^2\Lambda_{\text{rot}}T\omega^2}{\rho v^5} + \frac{C^2k_B C_{\text{rot}}T^2\omega^4}{\pi\rho^2v^8} \right)^{-1}. \quad (10)$$

Expression (12) is not applicable if  $l(\omega)$  becomes of the order or smaller than half the phonon wavelength  $\lambda/2 = \pi v/\omega$ . A similar situation was considered previously in the case of  $U$ -processes only [6]. Let us assume that, in the general case,

$$l(\omega) = \begin{cases} l_{\Sigma}(\omega), & 0 \leq \omega \leq \omega_0, \\ \alpha \pi v/\omega = \alpha \lambda/2, & \omega_0 < \omega \leq \omega_D, \end{cases} \quad (11)$$

where  $\alpha$  is the numerical coefficient of the order of unity. The frequency  $\omega_0$  can be found from the condition

$$\left( \frac{AT\omega_0^2}{v} + \frac{B^2\Lambda_{rot}T\omega_0^2}{\rho v^5} + \frac{C^2k_B C_{rot}T^2\omega_0^4}{\pi\rho^2v^8} \right)^{-1} = \frac{\alpha \pi v}{\omega_0}. \quad (12)$$

It equals

$$\omega_0 = -\frac{u}{\left(-\eta + \sqrt{u^3 + \eta^2}\right)^{1/3}} + \left(-\eta + \sqrt{u^3 + \eta^2}\right)^{1/3}, \quad (13)$$

where the parameters  $u$  and  $\eta$  are

$$u = \frac{\pi\rho^2v^7}{3C^2k_B C_{rot}T} \left( A + \frac{B^2\Lambda_{rot}}{\rho v^4} \right), \quad (14)$$

$$\eta = -\frac{\rho^2v^7}{2\alpha C^2k_B C_{rot}T^2}.$$

Condition (14) is the well-known Ioffe-Regel criterion implying localization. We can therefore assume that the excitations, whose frequencies are above the phonon mobility edge  $\omega_0$ , are “localized” or “diffusive”. Since the completely localized modes do not contribute to the thermal conductivity, the localization is assumed to be weak, and excitations can hop from site to site diffusively, as was supposed in [4].

If  $\omega_0 > \omega_D$ , the mean-free path of all modes exceeds  $\lambda/2$ , and the thermal conductivity is determined exceptionally by the processes of phonon scattering. At  $\omega_0 \leq \omega_D$ , the thermal conductivity integral (4) is separated into two parts describing the contributions to the heat transfer from the low-frequency phonons and “diffusive” modes:

$$\Lambda = \Lambda_{ph} + \Lambda_{loc}. \quad (15)$$

In the high-temperature limit ( $T \geq \Theta_D$ ), these contributions are

$$\Lambda_{ph} = \frac{k_B}{2\pi^2v^2} \int_0^{\omega_0} \frac{\omega d\omega}{\frac{C^2k_B C_{rot}T^2\omega^3}{\pi\rho^2v^8} + \frac{AT\omega}{v} + \frac{B^2\Lambda_{rot}T\omega}{\rho v^5}}, \quad (16)$$

$$\Lambda_{loc} = \frac{\alpha k_B}{4\pi v} (\omega_D^2 - \omega_0^2), \quad (17)$$

In the case of orientationally ordered phases, Eq. (18) gives the well-known dependence  $\Lambda \sim 1/T$  at  $\omega_0 > \omega_D$ :

$$\Lambda_{ph} = \frac{k_B\omega_D}{2\pi^2vAT}. \quad (18)$$

### 3. Results and Discussion

A number of molecular crystals have several solid phases, which differ in their orientational orders. If the noncentral forces are strong, and the temperature is low, there is a long-range orientational order in the location of molecular axes. The molecules perform small vibrations around the selected axes (librations), so that the motion of neighboring molecules is correlated, and the collective orientation excitations, librations, propagate in the crystal. In the first approximation, the librational oscillations make an additional contribution to the thermal resistivity  $W = 1/\Lambda$  of the crystal [11].

If the noncentral forces are relatively weak, and the temperature is high enough, the molecules can have a considerable orientational freedom. In this case, a number of orientations are accessible to a molecule, which can pass from one orientation to another. In individual cases, the limit of such a reorientational motion can be a continuous rotation. The unfreezing of molecular rotation is accompanied by an increase of the isochoric thermal conductivity [7], and the phonon mean-free path can no longer be described by Eq. (6).

Sulphur hexafluoride is often classed as a substance that has a plastic crystalline phase. Indeed, the relative molar entropy of melting  $\Delta S_f/R$  of  $SF_6$  is 2.61 [12], which is close to Timmerman’s criterion. Here,  $R$  is the universal gas constant. However, the nature of orientational disorder in the high-temperature phase of  $SF_6$  is somewhat different from that of plastic phases in other molecular crystals, where the symmetries of a molecule and its environment do not coincide. The  $SF_6$  molecule has the octahedral symmetry. At 222.4 K, sulphur hexafluoride crystallizes into the bcc lattice of  $I_m3m (O_h^9)$  symmetry with two molecules per unit cell. As a result, the molecule and its environment have the

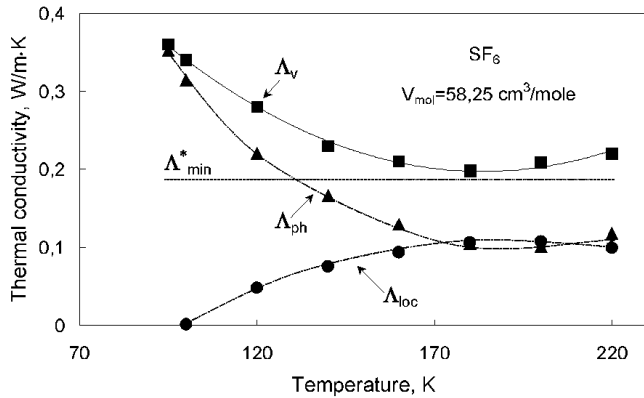


Fig. 1. Isochoric thermal conductivity  $\Lambda_v$  of solid  $\text{SF}_6$  ( $V_{\text{mol}} = 58.25 \text{ cm}^3/\text{mole}$ ) (squares). The solid line is the fitting curve for isochoric thermal conductivity.  $\Lambda_{\text{ph}}$  and  $\Lambda_{\text{loc}}$  are relative contributions of phonons and “diffusive” modes. The lower limit of the thermal conductivity  $\Lambda_{\text{min}}^*$  (3) is calculated taking into account the possibility of the site-to-site transfer of the rotational energy

same symmetry. On the further cooling to 94.3 K, a polymorphous transition occurs and suppresses the symmetry of the translational and orientational subsystem to the monoclinic one with the space group  $C2/m$  ( $C_{2h}^3$ ). The interaction between the nearest neighbors in the bcc phase is favorable for the molecular ordering caused by the S–F bonds along  $\{100\}$  direction, and the interaction with the next nearest neighbors is dominated by the repulsion between F atoms. According to X-ray and neutron diffraction data [13–15], a strict order is observed in  $\beta\text{-SF}_6$  just above the phase transition point. The structural dynamical factor  $\mathfrak{R}$  characterizing the degree of orientational order is close to unity in the interval 95–130 K.

This feature distinguishes  $\text{SF}_6$  from other plastic crystals, such as methane, carbon tetrachloride, adamantane, and others, where the long-range orientational order becomes disturbed immediately after the phase transition. The orientational disordering in  $\text{SF}_6$  starts to intensify only above 140 K. As follows from the analysis of the terms of the Debye–Waller factor derived from neutron-diffractometric data for the  $\beta$ -phase of  $\text{SF}_6$ , F atoms have large effective librational amplitudes. As temperature rises, the librational amplitudes increase to  $20^\circ$  and higher, but the F localization is still appreciable near  $\{100\}$  direction. This implies that the orientational structure of  $\text{SF}_6$  does not become completely disordered even at rather high temperatures. The disordering itself is dynamic by nature. The increasing amplitudes of librations are not the only factor responsible for the increasing

orientational disordering with dynamic reorientations which become more intensive due to the frustrations of molecular interactions.

Owing to these features,  $\text{SF}_6$  offers a considerable possibility for studying the influence of wide-range rotational states of molecules on the thermal conductivity in a monophasal one-component system, where such states can vary from nearly complete orientational ordering to frozen rotation.

Up to now, the thermal conductivity of solid  $\text{SF}_6$  has been studied for several isochores in the narrow temperature interval near the melting point [16] and in the whole region of the existence of  $\beta$ -phase under isobaric  $\Lambda_p$  conditions [17].

The isochoric thermal conductivity  $\Lambda_v$  was recalculated from the isobaric data for the molar volume of  $V_{\text{mol}} = 58.25 \text{ cm}^3/\text{mole}$ , which corresponds to the volume of  $\text{SF}_6$  just beyond the phase transition temperature (94.3 K). The recalculation was carried out using formula (1) and experimental data [13, 17]. The recalculation results are shown in Fig. 1 (black squares). The isochoric thermal conductivity  $\Lambda_v$  of solid  $\text{SF}_6$  first decreases with rising temperature, passes through a smooth minimum, and then begins to increase. Such a behaviour is in good agreement with experimental data [16].

The computer fit to the values of isochoric thermal conductivity was performed using Eqs. (14)–(19) by varying coefficients  $\alpha$ ,  $A$ ,  $B$ , and  $C$ . The integral of the thermal conductivity (18) was determined by Simpson’s method. The fitted values  $\alpha$ ,  $A$ ,  $B$ ,  $C$ , and parameters of the Debye model for thermal conductivity used for fitting are listed in Table 1. The theoretical value of the coefficient  $B_{\text{th}}$  was calculated using Eq. (10) and the data given in [13, 18]. As seen in Table 1, the fitted coefficient  $B$  is in good agreement with  $B_{\text{th}}$ , the distinction being no more than 7.5% .

Figure 1 shows the fitting results for isochoric thermal conductivity (solid line) and contributions of phonons  $\Lambda_{\text{ph}}$  (18) and “diffusive” modes  $\Lambda_{\text{loc}}$  (19) to heat transfer. It also shows the lower limit of thermal conductivity  $\Lambda_{\text{min}}^*$  (3) calculated taking into account the possibility of the site-to-site transfer of the rotational energy.

**Table 1. Parameters of the Debye model of thermal conductivity used in the fitting, and other quantities which were used in calculations**

$a$ , $10^{-8} \text{ cm}$	$v$ , $\text{m/s}$	$\gamma$	$g$	$\alpha$	$A \times 10^{-17}$ , $\text{s/K}$	$B_{\text{th}}$	$B$	$C$	$\Theta_{\text{D}}$ , $\text{K}$	$\Theta_{\text{Eins}}$ , $\text{K}$
4.6	994	2	5.2	2	9.65	7.6	7	2.6	62	49.8

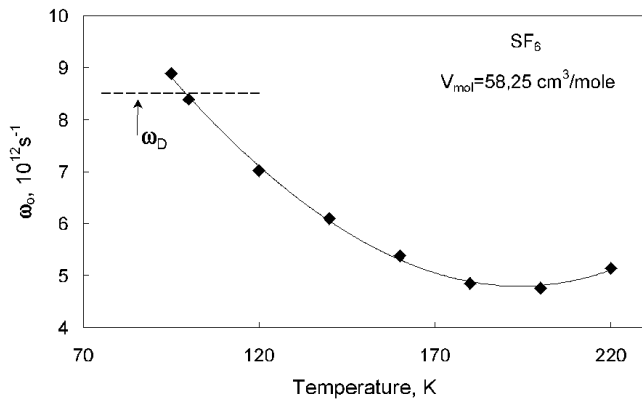


Fig. 2. Temperature dependence of the phonon mobility edge  $\omega_0$  in the  $\beta$ -phase of solid  $\text{SF}_6$ ,  $\omega_D$  is the Debye frequency

The phonon mobility edge  $\omega_0$  calculated by Eq. (15) is presented in Fig. 2. It is seen that the localization of high-frequency modes starts practically immediately after the phase transition. At 100 K, the calculated  $\omega_D$  and  $\omega_0$  are  $8.41 \times 10^{12} \text{ s}^{-1}$  and  $8.39 \times 10^{12} \text{ s}^{-1}$ , respectively.

As the temperature increases,  $\omega_0$  decreases, passes through a minimum at 190 K, and increases again.

The isochoric heat capacity  $C_v$  of a molecular crystal can be presented as a sum of contributions from the translational  $C_{tr}$  and rotational  $C_{rot}$  subsystems and the intramolecular modes  $C_{in}$ :

$$C_v = C_{tr} + C_{rot} + C_{in}. \quad (19)$$

Earlier, the components of heat capacity for  $\beta$ -phase  $\text{SF}_6$  were calculated in [13] using the heat capacity at a constant pressure  $C_p$  cited in [19]. At the premelting point temperatures, the growth of  $C_{rot}$  does not agree with the data of structural studies [12,15], where the intense growth of the orientational disordering was observed above 150 K. In our opinion, the reason for the higher calculated values of rotational heat capacity in the vicinity of premelting temperatures is the doubtful value of isobaric heat capacity [19]. We therefore recalculated the components of heat capacity. The last at a constant volume  $C_v$  is difficult to measure. In practice, it is recalculated, when the data on thermal expansion  $\beta$  [13] and the Grüneisen parameter  $\gamma$  [13] are available from the values of the heat capacity at atmospheric pressure  $C_p$  [19] by using the known thermodynamic relation

$$C_v = C_p / (1 + \gamma \beta T). \quad (20)$$

To estimate the translational, intramolecular, and rotational contributions to heat capacity, we used the

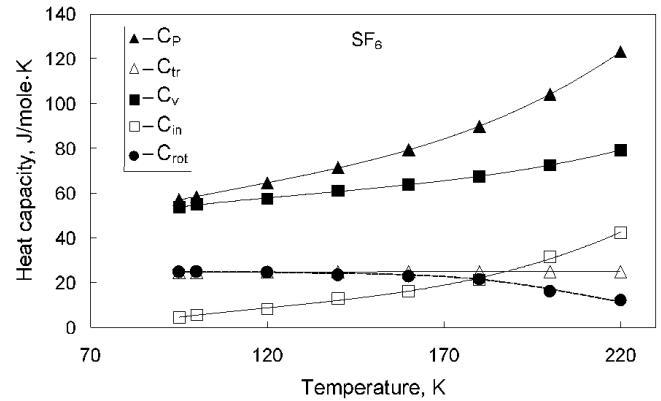


Fig. 3. Temperature dependences of  $C_p$  [19],  $C_v$ ,  $C_{tr}$ ,  $C_{in}$  and  $C_{rot}$  of solid  $\text{SF}_6$

separation method similar to that described in [13]. The calculation was carried out using the data of [12, 13, 19]. The characteristic Debye ( $\Theta_D$ ) and Einstein ( $\Theta_{Eins}$ ) temperatures (see Table 1) were determined as

$$\Theta_D = v (\hbar/k_B) (6\pi^2 n)^{1/3}, \quad (21)$$

$$\Theta_{Eins} = h\nu_i/k_B, \quad (22)$$

where  $\nu_i$  are the intramolecular frequencies [20]. The calculated components of heat capacity are shown in Fig. 3 (see also Table 2). The translational heat capacity  $C_{tr}$  was calculated in the Debye approximation and is close to  $3R$ . The contribution of intramolecular vibrations to the heat capacity  $C_{in}$  was calculated in the Einstein approximation. The rotational component  $C_{rot}$  was determined as  $C_{rot} = C_v - C_{tr} - C_{in}$ . At premelting temperatures, the heat capacity of the rotational subsystem  $C_{rot}$  approaches  $3/2R$ , which is characteristic of a free three-dimensional rotator. This is consistent with structural data [12,14], according to which there is an intense growth of the processes of

**Table 2.** Calculated values of the translational  $C_{tr}$ , intramolecular  $C_{in}$ , and rotational  $C_{rot}$  contributions to the heat capacity  $C_v$  ( $V_{mol} = 58.25 \text{ (cm}^3/\text{mole)}$ )

$T$ , K	$C_v$ , J/(mole·K)	$C_{tr}$ , J/(mole·K)	$C_{in}$ , J/(mole·K)	$C_{rot}$ , J/(mole·K)
95	53.67	24.48	4.52	24.66
100	54.97	24.53	5.57	24.88
120	57.48	24.67	8.24	24.57
140	61.01	24.76	12.81	23.44
160	63.84	24.89	16.12	22.83
180	67.39	24.74	21.14	21.51
200	72.51	24.86	31.56	16.09
220	79.20	24.93	42.28	11.99

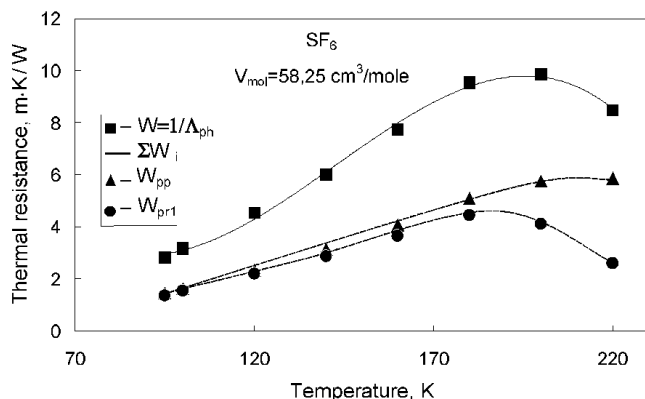


Fig. 4. Contributions of the phonon-phonon scattering  $W_{pp}$  and one-phonon scattering  $W_{pr1}$  to the total thermal resistance of solid  $SF_6$ . Square symbols indicate the total thermal resistance  $W = 1/\Lambda_{ph}$ . The solid line shows the sum of thermal resistances  $W_{pp}$ ,  $W_{pr1}$ , and  $W_{pr2}$

orientational disordering in solid  $SF_6$  at temperatures above 150 K. The fairly good agreement between the data in [13] and the present calculated values of the rotational component  $C_{rot}$  of heat capacity is obtained up to 160 K.

The increase of  $\Lambda_v$  in the premelting region is related to the increase of  $\Lambda_{ph}$ . The temperature dependence of  $\Lambda_{ph}$  is determined, as was marked above, by the phonon-phonon and phonon-rotation scattering mechanisms. We assume that the contributions of various scattering mechanisms to the thermal resistance are additive [1]:

$$\sum_i W_i = W_{pp} + W_{pr1} + W_{pr2}, \quad (23)$$

where  $W_{pp}$  is the phonon-phonon thermal resistance, and  $W_{pr1}$  and  $W_{pr2}$  are thermal resistances determined by the one- and two-phonon mechanisms of scattering, respectively.

The contributions of different mechanisms of phonon scattering to the total thermal resistance of solid  $SF_6$  were calculated within a model assuming the independence of the phonon mean-free path for each scattering mechanism. Using (4) and (6)–(8), we get

$$W_{pp} = 2\pi^2 v AT \left/ k_B \int_0^{\omega_0} d\omega, \right. \quad (24.1)$$

$$W_{pr1} = 2\pi^2 B^2 \Lambda_{rot} T \left/ k_B v^3 \rho \int_0^{\omega_0} d\omega, \right. \quad (24.2)$$

$$W_{pr2} = 2\pi C^2 T^2 C_{rot} \left/ \left( v^6 \rho^2 \int_0^{\omega_0} \frac{d\omega}{\omega^2} \right) \right. \quad (24.3)$$

The results of calculations are shown in Fig. 4. The total thermal resistance determined as  $W = 1/\Lambda_{ph}$  is marked with black squares. The solid curve is the sum of thermal resistances calculated by Eqs. (26)–(28).

The phonon-phonon component of the thermal resistance  $W_{pp}$  increases with temperature and shows the tendency to be constant above 200 K. This is in good agreement with the concept of the minimum of thermal conductivity (Fig. 1). The thermal resistance due to the rotational degrees of freedom of molecules increases initially at rising temperature. This behaviour can be attributed to the additional scattering of phonons by collective rotational excitations, whose density increases as the temperature rises [12]. The two-phonons component  $W_{pr2}$  of the total thermal resistance is practically zero and cannot be responsible for the anomalous behaviour of thermal conductivity. The thermal resistance  $W_{pr1}$  due to the one-phonon scattering upon rotational excitations of molecules passes through a maximum at 180 K and then decreases. This also agrees with the data in [12] which indicate the intense growth of orientational disordering above 150 K. A decrease of the thermal resistance caused by the one-phonon scattering relative to the maximum is around 40%. The additional contribution of  $W_{pr1}$  is about 45% of the total thermal resistance. Thus, it can be assumed that the main reason for the increase of the isochoric thermal conductivity of solid  $SF_6$  at premelting temperatures is a decrease of the one-phonon scattering.

#### 4. Conclusions

The isochoric thermal conductivity of  $\beta$ - $SF_6$  is described within the framework of a model, where heat is transferred by phonons and, above the phonon mobility edge, by “diffusive” modes migrating randomly from site to site. The total thermal resistance is determined by the phonon-phonon and phonon-rotation scattering mechanisms. In turn, the phonon-rotation relaxation time is determined by the one- and two-phonon scatterings. The mobility edge  $\omega_0$  can be found from the condition that the phonon mean-free path restricted by the examined mechanisms of scattering cannot become smaller than half the wavelength. The temperature dependences of the translational, intramolecular, and rotational components of the heat capacity of solid  $SF_6$

are calculated. The contributions of the phonon-phonon, one-, and two-phonon scatterings to the total thermal resistance of solid SF<sub>6</sub> are calculated in supposition of the additive contribution of different scattering mechanisms.

An increase of the isochoric thermal conductivity of solid SF<sub>6</sub> at premelting temperatures is attributed to the weakening of the one-phonon scattering by collective rotational excitations of molecules.

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#### ПЕРЕНОСЕННЯ ТЕПЛА “ДИФУЗНИМИ” МОДАМИ І ФОНОННЕ РОЗСІЯННЯ В $\beta$ -ФАЗИ ТВЕРДОГО ГЕКСАФТОРИДУ СІРКИ

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#### Резюме

Поведінку ізохорної теплопровідності в  $\beta$ -фазі твердого SF<sub>6</sub> описано в рамках моделі, в якій тепло переноситься низькочастотними фононами, а вище від межі рухливості фононів — “дифузними” модами, що мігрують випадковим чином з вузла на вузол. Внески фонон-фононного, одно- та двофононного розсіяння в повний тепловий опір твердого SF<sub>6</sub> розраховано у припущенні адитивності різних механізмів розсіяння фононів. Межу рухливості  $\omega_0$  знайдено із умови, що довжина вільного пробігу фонона, яка визначається всіма розглянутими механізмами розсіяння фононів, не може стати меншою за половину довжини хвилі. Зростання ізохорної теплопровідності твердого SF<sub>6</sub> в області передплавильних температур пояснюється зменшенням однофононного розсіяння колективними оберतालними збудженнями молекул.