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# THERMAL EXPANSION EFFECT ON HEAT TRANSFER PROCESSES IN ORIENTATIONALLY DISORDERED PHASES OF MOLECULAR CRYSTALS

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UDC 536.21:539.2

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The effect of thermal expansion on the processes of heat transfer in orientationally disordered phases of crystalline SF<sub>6</sub>, CCl<sub>4</sub>(Ib), and C<sub>6</sub>H<sub>6</sub> has been studied. A modified version of the reduced coordinate method is used to separate the contributions of translational and translational-rotational interactions to the total thermal resistance of crystals.

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## 1. Introduction

High-temperature ( $T \geq \Theta_D$ ) heat conductivity of simple molecular crystals is governed by both translational and rotational motions (RM) of molecules. In the general case, the vibration spectra of molecular crystals are translational-rotational, and the separation of the contribution given by every vibrational mechanism to heat conductivity is a rather challenging task. Depending on a specific substance and the temperature  $T$ , the character of the RM of molecules can vary from low-frequency vibrations with small amplitudes to almost free rotations. Very often, the change of the molecular RM character brings about a phase transition of the orientational melting type (for instance, in CCl<sub>4</sub>), whereas, in other cases, the orientational disordering processes develop without a following phase transition (for instance, in C<sub>6</sub>H<sub>6</sub>).

A reduction of correlations in the orientational subsystem, which occurs as the temperature decreases, is specifically reflected in the behavior of isochoric heat conductivity  $\Lambda_v$  of molecular crystals. A gradual transition from molecular librations to almost free rotations is accompanied by the growth of  $\Lambda_v$ . Such a phenomenon is not observed for the isobaric heat conductivity  $\Lambda_p$  of simple molecular crystals. The high-temperature  $\Lambda_v$  of molecular crystals is generally governed by the phonon interaction, the influence of rotational molecular motion, and the approach of heat conductivity to its minimum. Concerning  $\Lambda_p$ , the list of the mentioned factors should be extended to include the influence of thermal expansion of samples under investigation as well.

For a correct comparison of experimental results with theoretical ones to be done, it has to be carried out at a constant volume. However, almost the whole body of experimental data concerning the character of thermal motion in molecular crystals was obtained under isobaric experimental conditions. From experiments dealing with the heat conductivity of atomic crystals, it is known that the influence of thermal expansion gives rise to a faster reduction of heat conductivity with decrease in the temperature. In molecular crystals, thermal expansion provokes variations in the spectra of both translational and rotational vibrations. In work [1], the influence of RM on the isochoric heat conductivity of molecular crystals was studied. However, to our knowledge, no analysis has been carried out until now in the literature on how a change of the RM character affects the heat conductivity of orientationally disordered (OD) molecular crystals, if their thermal expansion is taken into account.

In this work, the influence of thermal expansion on the processes of heat transfer in OD phases of molecular crystals is studied. To separate the contributions of the processes associated with the translational and translational-rotational interactions to isobaric and isochoric heat conductivities, the modified method of reduced coordinates was applied.

## 2. Subjects of Inquiry

Solid SF<sub>6</sub>, CCl<sub>4</sub>(Ib), and C<sub>6</sub>H<sub>6</sub> crystals with different characters of molecular rotational motion were chosen to study. Solid SF<sub>6</sub> has a wide range, where a high-temperature  $\beta$ -phase exists: this substance crystallizes at  $T = 222.4$  K, whereas the phase transition that reduces a symmetry of the translational and orientational subsystems of the crystal occurs only at  $T = 94.3$  K [2, 3]. As a result of structural researches [4–6], it was found that the  $\beta$ -phase of SF<sub>6</sub> has a bcc structure with the  $I_m3m$  spatial symmetry. Noncentral interactions in SF<sub>6</sub> promote the orientational ordering in the first

coordination sphere (S–F bonds) and the orientational disordering in the second one (F–F bonds). As the temperature grows, such a character of interaction leads to an appreciable increase of libration amplitudes and facilitates molecular reorientations [4, 6]. The analysis of structural data [6] evidences for the orientational ordering of SF<sub>6</sub> molecules just above the phase transition point. The X-ray researches [7] showed that the intensities of separate reflections start to decrease and approach the values calculated in the framework of the molecular orientational disordering model only after 150 K, which testifies to an enhancement of the orientational disordering processes. The relative entropy of melting  $\Delta S_f/R$  for SF<sub>5</sub> is equal to 2.61 [8], which is close enough to the Timmermans criterion. An increase of the degree of orientational disorder with the temperature growth is not a consequence of a simple increase of the libration amplitude, but is connected with dynamic reorientations which become easier due to the frustration of the intermolecular interaction [6, 9, 10].

The plastic phase CCl<sub>4</sub>(Ib) has a rhombohedral structure with 21 molecules in a unit cell [11]. Solid CCl<sub>4</sub> melts at a temperature of 250 K [12], whereas the phase transition into a low-temperature monoclinic modification occurs at 225.3 K [13]. The plastic phase (Ib) is orientationally disordered, which follows from low values of melting entropy  $\Delta S_f/R = 1.21$  [8] and nuclear magnetic resonance data [14, 15]. Experimental results obtained in the cited works demonstrate how much the character of molecular RM in the plastic phase is close to that in a liquid.

Solid C<sub>6</sub>H<sub>6</sub> exists only in a single crystalline modification – an orthorhombic structure [16] with the spatial symmetry  $P_{bca} - D_{2h}^{15}$  [17]. The entropy of melting  $\Delta S_f/R$  for C<sub>6</sub>H<sub>6</sub> considerably exceeds the Timmermans criterion and is equal to 4.22 [8]. Structural researches of solid C<sub>6</sub>H<sub>6</sub> [16] testify that the second moment of nuclear magnetic resonance has a significant drop in the temperature interval 90–120 K, caused by molecular reorientations in the plane of a ring around the sixth-order axis. The reorientation frequency is  $10^4 \text{ s}^{-1}$  at 85 K; if the temperature grows further, it increases considerably and attains an order of  $10^{11} \text{ s}^{-1}$  near the melting point. At the same time, the frequency of benzene molecule oscillations around the sixth-order axis is  $1.05 \times 10^{12} \text{ s}^{-1}$  at 273 K. The results of neutron scattering experiments [18] testify that the frequency of C<sub>6</sub>H<sub>6</sub> molecule oscillations becomes a little lower, if the temperature decreases, while the amplitude of oscillations diminishes considerably at that.

### 3. Results and Their Discussion

The character of the temperature dependences of isobaric and isochoric heat conductivities in OD phases of molecular crystals is substantially different. At a constant pressure, the heat conductivity decreases, as a rule, but exceeds the law  $\Lambda \propto T^{-1}$ . At the same time, at a constant volume and a growing temperature, it can either decrease more weakly than the specified dependence, or depend weakly on the temperature, or grow [1]. The difference between  $\Lambda_v$  and  $\Lambda_p$  is determined by the thermal expansion of researched specimens. The thermal expansion affects all processes that govern the high-temperature heat conductivity of molecular crystals – in particular, the phonon and phonon-rotational interaction, and the approach of heat conductivity to its minimum. The analysis of works [19–21] testifies that the thermal expansion leads to a reduction of the heat conductivity minimum.

This work is devoted to the consideration of the issue how the thermal expansion influences each of two specified mechanisms of thermal motion that participate in the heat transfer processes. The separation of the contribution given by each mechanism to heat conductivity is rather a difficult problem, because – in the general case – translational and rotational vibrations propagate over the crystal volume as mixed translational-orientational vibrations rather than their two independent kinds. Therefore, in order to determine the influence of the mechanisms of molecular thermal motions considered above on the heat transfer processes, by assuming the additivity of thermal resistances provided by various mechanisms of phonon scattering, the contributions of the phonon-phonon,  $W_{pp}$ , and phonon-rotational,  $W_{pr}$ , interactions to the total thermal resistance  $W = 1/\Lambda$  of OD molecular crystals are separated in the present study. In so doing, heat was supposed to be transferred mainly by phonons, irrespective of orientational ordering, because the role of librations in heat transfer turns out insignificant owing to a low group velocity of librons.

The calculations were carried out in the framework of the modified method of reduced coordinates [22] for the isobaric and isochoric cases, which allowed the influence of the thermal expansion on heat transfer mechanisms to be determined. In the reduced coordinates, the thermal resistance of atomic crystals can be described by a unique function [23]. If one supposes that, in the reduced coordinates ( $W^* = W/W_{mol}, T^* = T/T_{mol}$ ), the thermal resistance in OD phases of molecular crystals, which

is caused by phonon-phonon scattering  $W_{pp}$ , is the same as in the crystals of inert gases, the phonon-phonon,  $W_{pp}$ , and phonon-rotational,  $W_{pr}$ , components of thermal resistance can be separated, provided that the corresponding reduced volumes  $V^* = V/V_{mol}$  are equal.

As a rule, the quantities  $T_{mol} = \varepsilon/k_B$ ,  $\Lambda_{mol} = k_B/\sigma^2\sqrt{\varepsilon/\mu}$ , and  $V_{mol} = N\sigma^3$  play the role of reduced parameters. Here,  $\sigma$  and  $\varepsilon$  are the parameters of the Lennard–Jones potential,  $\mu$  is the molar weight, and  $N$  is the Avogadro number. In this work, the temperatures  $T_{mol}$  and molar volumes  $V_{mol}$  of molecular crystals under consideration (see the Table) and the relevant parameters for the crystals of inert gases Kr and Xe at their critical points [12] were used as reduced parameters. Such a choice of the coordinates is explained by the fact that, for simple molecular substances, the critical parameters  $T_{cr}$  and  $V_{cr}$  are proportional to  $\varepsilon$  and  $\sigma^3$ , respectively. But the accuracy of critical parameter values is much higher than that of the binomial potential parameters.

The results of calculations are presented in the Figure. The required values of isobaric heat conductivity for atomic and molecular crystals were taken from works [24–27]. A recalculation to a constant density was carried out by means of the expression for the volume dependence of heat conductivity

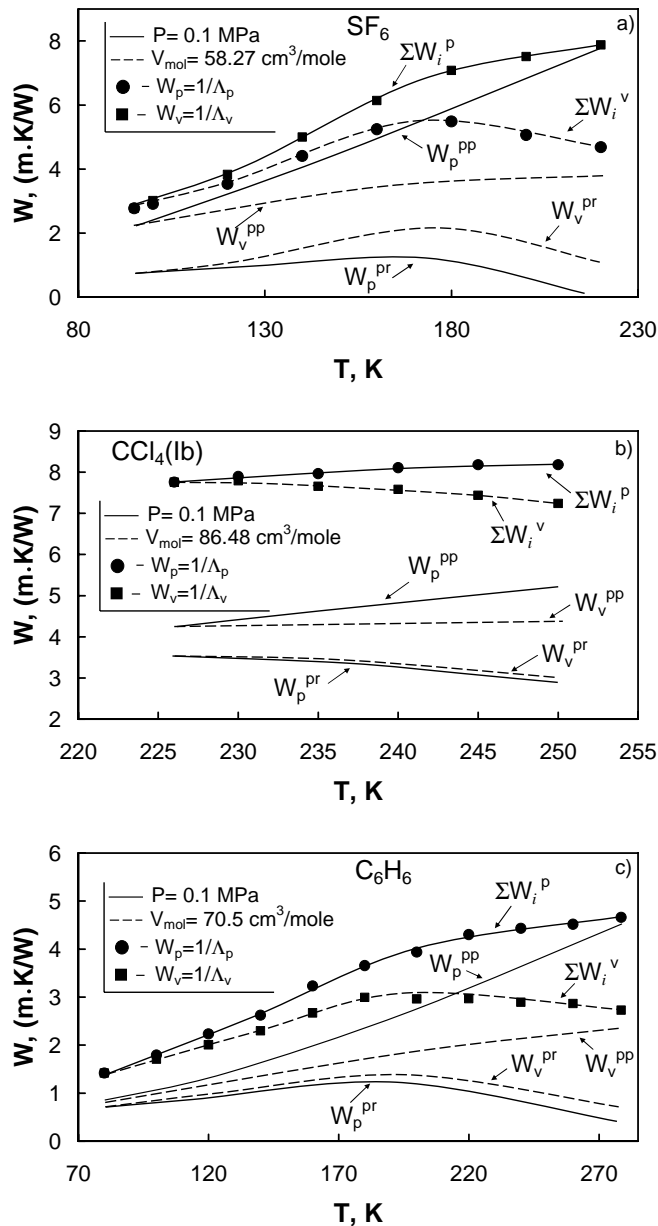
$$\Lambda_v = \Lambda_p \left( \frac{V(T)}{V_0} \right)^g, \quad (1)$$

where  $V(T)$  is the temperature-dependent molar volume of the specimen [6, 26, 28],  $V_0$  the molar volume, which the recalculation was made for, and  $g$  the Bridgman coefficient [29–31].

Thermal expansion stimulates an enhancement of the total thermal resistance  $W$  of every crystal under investigation (Figure). It should be noted that, unlike atomic crystals [29] and orientationally ordered molecular crystals [1], the characters of the temperature dependences of  $W$  for isobaric,  $W_p$ , and isochoric,  $W_v$ , cases differ considerably—in  $SF_6$  after 160 K, in  $C_6H_6$  after 190 K, and in  $CCl_4(Ib)$  within the whole

#### Reduced parameters, molar weight, and the Bridgman coefficient for crystalline Kr, Xe, $SF_6$ , $CCl_4(Ib)$ , and $C_6H_6$

Substance	$T_{mol}$ , K	$V_{mol}$ , cm <sup>3</sup> /mol	$\mu$	$W_{mol}(1/\Lambda_{mol})$ , m · K/W	$g$
Kr	204.9	92.01	83.8	8.06	9.4
Xe	289.7	119.4	131.3	10.01	9.2
$SF_6$	318.7	201.4	146.1	13.51	5.2
$CCl_4(Ib)$	556.4	257.0	153.8	13.2	6.0
$C_6H_6$	562.0	260.0	78.1	9.43	7.5



Contributions of the phonon-phonon,  $W_{pp}$ , and phonon-rotational,  $W_{pr}$ , scatterings to the total thermal resistance  $W = 1/\Lambda$  of crystalline  $SF_6$  (a),  $CCl_4(Ib)$  (b), and  $C_6H_6$  (c), calculated for the isobaric ( $W_p^{pp}$  and  $W_p^{pr}$ ) and isochoric ( $W_v^{pp}$  and  $W_v^{pr}$ ) cases. Symbols correspond to the total thermal resistance at a constant pressure,  $W_p$ , and a constant volume,  $W_v$ .  $\Sigma W_i$  is the sum of the phonon-phonon and phonon-rotational thermal resistances

temperature interval of plastic phase existence. As the temperature grows,  $W_p$  increases in the indicated temperature ranges, whereas  $W_v$  falls down. As was shown in work [1], the reduction of the total thermal

resistance of OD molecular crystals under isochoric conditions, but when the temperature goes down, is associated with decrease in the correlations between rotational motions of molecules. Therefore, the reduction of heat conductivity, which is caused by thermal expansion, exceeds the effect of heat conductivity growth caused by a diminishing of the thermal resistance, which, in turn, is connected with the phonon scattering by rotational excitations.

In the OD phase of solid SF<sub>6</sub> (Figure,*a*), the phonon-phonon component  $W_p^{PP}$  of the total thermal resistance at a constant pressure grows much more quickly than it occurs at a constant volume,  $W_v^{PP}$ . In the premelting temperature range,  $W_p^{PP}$  more than twice exceeds  $W_v^{PP}$ . Due to the phonon-rotational interaction, the temperature dependences of the thermal resistance of SF<sub>6</sub> are similar in both cases: as the temperature grows, they also grow first, then pass through a corresponding smooth maximum, and begin to decrease. Such a behavior agrees well with the data of work [6] on the enhancement of orientational disordering processes as the temperature increases; it can be explained by a reduction of the phonon scattering by collective rotational excitations of SF<sub>6</sub> molecules, when the rotational motion correlations get weaker. In this case, the thermal expansion leads to a general reduction of the thermal resistance component associated with the phonon-rotational interaction,  $W_p^{PR}$ , in comparison with the corresponding value at a constant volume,  $W_v^{PR}$ . In the premelting range, the phonon-rotational thermal resistance at a constant pressure,  $W_p^{PR}$ , is practically absent.

The temperature dependences of  $W_p^{PR}$  and  $W_v^{PR}$  in the plastic phase CCl<sub>4</sub>(Ib) differ slightly from each other and possess a similar character, decreasing weakly with the temperature growth (Figure,*b*). Such a behavior of the phonon-rotational component agrees well with the data of works [8, 14, 15]. According to them, the plastic phase of CCl<sub>4</sub> is orientationally disordered, and the character of rotational motion of CCl<sub>4</sub> molecules in it is similar to that in a liquid state. In the isobaric case, the thermal resistance associated with the phonon-phonon interaction exceeds the corresponding value at a constant volume, but this excess is not so considerable in the melting range, as it is in the case of a SF<sub>6</sub> or C<sub>6</sub>H<sub>6</sub> crystal.

In solid C<sub>6</sub>H<sub>6</sub> (Figure,*c*),  $W_p^{PR}$  is also larger than  $W_v^{PR}$ . In particular, in the premelting temperature range, the ratio  $W_p^{PR}/W_v^{PR} = 2.1$ . As the temperature grows, the thermal resistance, which is associated with phonon scattering by the orientational subsystem, first increases

(in both the isobaric and isochoric cases), passes through a maximum, and begins to decrease. In work [32], making use of crystalline C<sub>2</sub>F<sub>6</sub> as an example, it was demonstrated that the spinning up of a molecule of this substance around the C–C axis brings about the growth of the isochoric heat conductivity as the temperature increases. In accordance with the results of experimental researches [16], benzene molecules in crystalline benzene spin up in the ring plane around the sixth-order axis. Therefore, the reduction of  $W_p^{PR}$  and  $W_v^{PR}$  can be explained by the weakening of the translational-rotational interaction, when benzene molecules spin up in the ring plane. Concerning the phonon-rotational component of the total thermal resistance in C<sub>6</sub>H<sub>6</sub>, the influence of thermal expansion is realized as an insignificant reduction of  $W_p^{PR}$  in comparison with  $W_v^{PR}$ .

#### 4. Conclusions

On the basis of the results of our calculations, the following conclusions can be drawn with respect to the influence of the thermal expansion on the heat transfer processes in OD phases of molecular crystals:

1. In all studied substances, the thermal expansion brings about an increase of the thermal resistance caused by the phonon-phonon scattering and, as a consequence, a general reduction of isobaric heat conductivity in comparison with its isochoric counterpart [1].
2. The thermal resistance associated with the phonon-rotational interaction at a constant pressure decreases in comparison with the corresponding values at a constant volume. It can be explained by a lowering—due to thermal expansion—of the potential barrier, which interferes with molecular rotations. This assumption is confirmed by the results of our calculations for CCl<sub>4</sub>(Ib). According to the structural data [8, 14, 15], the character of the rotational motion of molecules in the plastic phase of CCl<sub>4</sub> is close to a decelerated rotation and weakly changes with the temperature growth. As a result, the values of  $W_p^{PR}$  and  $W_v^{PR}$  are almost identical in CCl<sub>4</sub>(Ib) (Figure,*b*), i.e. the thermal expansion practically does not affect the character of the rotational motion of molecules in this substance.
3. As follows from the comparative analysis, the general reduction of heat conductivity, which is caused by the thermal expansion, exceeds the effect of heat conductivity growth due to a reduction of the thermal resistance, which is connected with the phonon scattering by rotational excitations.

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Received 17.06.08.

Translated from Ukrainian by O.I. Voitenko

ВПЛИВ ТЕПЛОГО РОЗШИРЕННЯ  
НА ПРОЦЕСИ ПЕРЕНОСУ ТЕПЛА  
В ОРІЄНТАЦІЙНО-НЕУПОРЯДКОВАНИХ  
ФАЗАХ МОЛЕКУЛЯРНИХ КРИСТАЛІВ

O.I. Пурський

## Резюме

Проведено дослідження впливу теплового розширення на процеси переносу тепла в орієнтаційно-неупорядкованих фазах кристалічних SF<sub>6</sub>, CCl<sub>4</sub>(Ib) та C<sub>6</sub>H<sub>6</sub>. Для виділення внесків трансляційної та трансляційно-орієнтаційної взаємодії молекул у повний тепловий опір кристалів застосовано модифікований метод зведених координат.