

Role of the orientational subsystem in the expansion of pure CF_6 , CHCl_3 , C_6H_6 , CCl_4 and N_2O with Kr impurity

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The linear expansion coefficients of solid bulk samples of N_2O with Kr 5% impurity are measured by an absolute dilatometric method in comparison with pure N_2O in the temperature range 80–150 K. An additional unusual orientational effect is discussed. An analysis of the data from measurements of the linear expansion coefficients of pure solid SF_6 , CHCl_3 , C_6H_6 , CCl_4 in comparison with solid Xe in the temperature range 80–170 K is carried out in order to determine the role of molecules' orientational disordering in the thermal expansion of the given condensed systems. The results are discussed in connection with the problem of determining the contribution of orientational subsystems with different types of molecular symmetry to the total thermal expansion and its behavior in various temperature intervals of solid phase existence.

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Introduction

Unlike the hardened inert gases, the interaction between molecules in molecular crystals has a more complicated character due to the existence of angular evolutions of the orientational subsystem and also fluctuational intramolecular oscillations. In the analysis of crystal lattice dynamics the last factors can rather often be neglected [1] because of the significantly larger energy of bonding in a molecule as compared to the energy of sublimation E . It allows one to simplify the analysis and to concentrate attention on the peculiarities of the interaction between the collective translational excitations (phonons) and the orientational molecular movements.

Depending on the molecular symmetry and temperature, the orientation excitations in molecular crystals can have the collective character of waves (librons) or even almost free rotation of separate molecules. In some molecular crystals (N_2O , CO_2 , CHCl_3) the anisotropic interaction is so strong that the crystal melts before complete orientational disordering occurs. When diluted by simple atomic particles of nearly the same size, such systems often can behave in a rather unusual way. On the other hand, there still exist rather complicated problems in under-

standing of the temperature dependences of the thermal properties for many pure molecular crystals. This paper is devoted to further study of high-temperature behavior of the linear expansion of molecular crystals with different symmetry of the particles.

Main part

The studies of the thermal expansion coefficients of solid SF_6 , CHCl_3 , CCl_4 and C_6H_6 were carried out in an interval of temperatures 85–170 K on an optical laser Michelson interferometric dilatometer. We measured the linear thermal expansion factors for four samples of solid SF_6 , 6 mm in diameter and 10 cm long, each grown from the gas, and also two samples of CCl_4 , three samples of CHCl_3 , and two samples of C_6H_6 , obtained from the liquid. The total error of determination of the linear thermal expansion is 10–15 %.

The high-temperature β phase of solid SF_6 [2–9] has a cubic bcc lattice of space symmetry $Im\bar{3}m$. The existence region of the β phase is extraordinarily large: the crystallization of SF_6 occurs at 222.4 K, and the phase transition lowering the symmetry of the translational and orientational subsystems of the crystal

does not occur until 94.3 K. The interaction between the nearest neighbors in the bcc phase tends to order the molecules so that their S–F bonds lie along the {100} direction, and in the interaction with the next-nearest neighbors a repulsion between the fluorine atoms predominates. The data from recent structural studies indicate a strict orientational order in SF₆ above the phase transition temperature. This makes SF₆ different from such plastic crystals as CH₄, CCl₄, adamantane, etc., in which the destruction of the long-range order occurs immediately after the phase transition. The intensive growth of processes of orientational disordering begins in SF₆ only at temperatures above 150 K and is of a dynamic nature. The SF₆ molecule has octahedral symmetry which means a spherical rotator with three perpendicular main axes. The CCl₄ molecule is also highly symmetric (tetrahedral) and is a spherical rotator with nonperpendicular main axes. As opposed to this, the CHCl₃ and C₆H₆ molecules are less symmetrical objects. The first have an even nonzero dipole moment. They both are symmetrical rotators only (not spherical). Therefore it will cause larger barriers interfering rotation.

The contribution of rotary movement to the thermal expansion can be appraised by a comparison of the corresponding properties of molecular crystals and hardened inert gases. The properties of the latter are connected with translational movement of molecules only, without rotations. To allocate the contribution of the rotary subsystem to the thermal expansion of the molecular crystals studied, we used the already known temperature dependence of the volume thermal expansion coefficient of solid Xe [10]. The latter has a mass close to that of the molecular crystals studied. The experimental dependences for all the investigated substances in comparison with Xe are plotted in reduced coordinates in Fig. 1, where α is the coefficient of linear expansion, E is the sublimation energy and T_t is the temperature of three-phase equilibrium.

In Fig. 1 we can see the known phase transition for solid SF₆ (near 94.3 K), near which a jumplike drop is observed on the temperature growth of the thermal expansion coefficient. Such anomalies of the thermodynamic properties are caused by enhancement of the correlation of rotary movement [10]. Our dilatometric SF₆ results are in good agreement with x-ray diffraction data [11]. This allows us to check our experimental equipment. Active transitions from orientational molecular oscillations to rotations of molecules in solid SF₆ give a weak additional contribution to thermal expansion in the form a somewhat larger slope of the smoothed line in comparison with Xe. In the low-temperature phase (lower than 94.3 K), where the free rotation is absent altogether, the above-men-

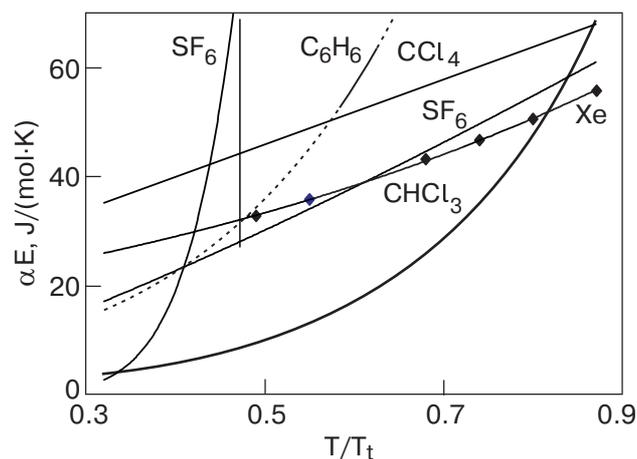


Fig. 1. Temperature dependence of the linear expansion coefficients α for solid SF₆, CHCl₃, C₆H₆, CCl₄ in reduced coordinates, where E is the sublimation energy and T_t is the triple point.

tioned effect appears significant. Thus, the weak dependence of thermal expansion coefficient for solid SF₆ at temperatures higher than the phase transition temperature in the given coordinates indicates the transition to rotational molecular movement. In other words, SF₆ molecule rotational correlations are weakened above the phase transition.

The low-temperature phase of solid CCl₄ is monoclinic ($C2/c-C_{2h}^6$) [13] and contains 32 molecules per unit cell. The molecular centers of interaction have tetrahedral symmetry and a slightly deformed cubic bcc lattice. The close values of the slopes of the reduced curves for solid CCl₄, Xe and SF₆ may also indicate the transition of the movement of some of the molecules to hindered rotation in the monoclinic phase in the temperature range 80–170 K. Similar behavior of a rotary subsystem of CCl₄ crystals is caused by the high tetrahedral symmetry of their molecules.

The high-temperature phase of solid chloroform CHCl₃ has orthorhombic structure of space symmetry $Pnma - D_{2h}^{16}$ with four molecules per unit cell, triple-point temperature $T_t = 209.5$ K [14]. The non-central forces in CHCl₃ crystals are great. The orientational order is maintained up to the melting temperature and the rotary movement constitutes librations. The reorientation frequencies do not exceed 10^4 per second [15,16].

As can be seen from Fig. 1, for the asymmetrical chloroform molecules, with a nonzero dipole moment in the low-temperature region, the additional effect is absent, as is indicated by the insignificant increase of the libration amplitude with the temperature. However, with further increase in temperature we have a stronger dependence of the thermal expansion of CHCl₃ crystals in reduced coordinates. This can be

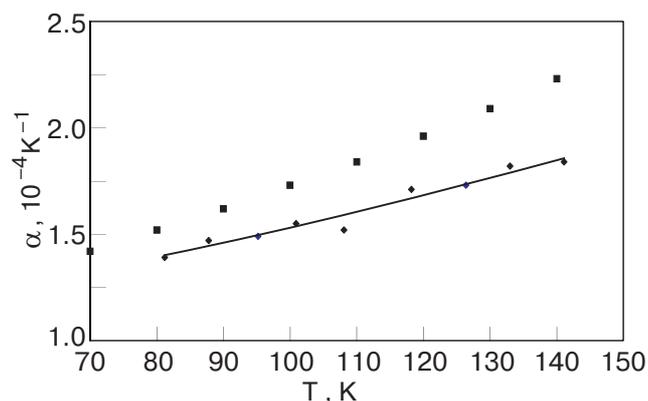


Fig. 2. Temperature dependence of the linear expansion coefficients α for solid pure N_2O (top curve) and N_2O with 5% Kr (bottom curve).

seen from a comparison with solid CCl_4 , which has a central interaction of about the same value but a lower rotary barrier. This last circumstance indicates appreciable growth of the libration amplitudes.

At pressures lower than 1.2 MPa solid benzene C_6H_6 exists in one crystalline form corresponding to space group $Pbca - D_{2h}^{15}$ with four molecules per unit cell. A weak orientation effect is present near the transition of C_6H_6 to rotation about the sixfold symmetry axis (90–120 K). At $T > 120$ K, however, the dependence of the thermal expansion in C_6H_6 in reduced coordinates is stronger even than in CHCl_3 . This may also attest to an increase of the libration amplitudes of the benzene molecules about two other twofold to the symmetry axes lying in the plane of the benzene ring.

As CHCl_3 and N_2O molecules, they are far from spherical symmetry and have a dipole moment. Studies of the thermal expansion coefficients of solid bulk samples of N_2O with 5% Kr were carried out in an interval of temperatures 85–150 K on the same equipment. We measured the linear thermal expansion factors for two samples. The experimental dependence in comparison with pure N_2O is shown in Fig. 2. As we can see, dilution with atomic Kr causes a weakening of the dependence. The difference of the thermal expansion coefficients is seen to grow with increasing temperature. This anomaly of the thermodynamic properties may be caused by easing of the free rotation due to the replacement of one-fifth of the linear by spherical atoms. It should be emphasized that there are unpublished data indicating that the solubility of Kr in N_2O is not less than 5 percent.

Conclusions

The thermal expansion orientational effect in reduced coordinates is weakly expressed for the more symmetric molecules SF_6 and CCl_4 in the high-temperature region investigated, while for the less sym-

metrical molecules CHCl_3 and C_6H_6 the effect is significant. This could be explained by the fact that for growth of the libration amplitudes the octahedral molecules SF_6 and tetrahedral CCl_4 require smaller additional volumes, and the transition to their hindered rotation is not accompanied by an appreciable volume increase. At the same time CHCl_3 and C_6H_6 molecules do not pass to the state of hindered rotation at the temperatures of experiment (except for rotation around the sixfold axis for solid benzene), and for increase of the libration amplitudes and jumps to adjacent equilibrium orientations with higher energy levels they require significant additional volumes. Substitution of the spherically symmetric impurity Kr for the N_2O molecules leads to a weaker growth of the linear expansion with the temperature then for pure solid N_2O . This may indicate that the high-temperature volume effects in solid N_2O are influenced more strongly by the rotational states than by the translational states.

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