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Effect of octupole interaction on the rotational motion of rotors in a solid Kr-CD₄ solution

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Received 18 December 2006, in final form 18 April 2007

Published 17 May 2007

Online at stacks.iop.org/JPhysCM/19/236231

Abstract

The heat capacity of solid $(\text{CD}_4)_n\text{Kr}_{1-n}$ solutions with CD_4 concentrations $n = 0.09, 0.17, 0.25, 0.35$ and solutions with $n = 0.25$ doped with 0.0005, 0.0021 and 0.0123 of O_2 impurity has been investigated at $T = 0.6\text{--}30$ K. It is found that the molecular field responsible for a qualitative change in the rotational motion of the rotators increases sharply as the number of nearest neighbours increases from one to three. Below 1.6 K the temperature dependence of the heat capacities of the rotational subsystems of the solutions can be described by a sum of the contributions made by molecules finding themselves in effective weak, moderate and strong molecular fields. The average concentration and the effective energy differences between the ground and the first excited energy levels of the CD_4 molecules in the above mentioned fields have been estimated. It is shown that the considerable changes in the experimental heat capacities of the rotational subsystem normalized to a mole of rotors are mostly due to the changes in the relative concentrations $x(n)$ of the rotors in these molecular fields. Above $T = 0.6$ K the nuclear-spin A, T and E species of the molecules reach equilibrium distribution within one measurement of the heat capacity. The O_2 impurity is found to produce great influence on the heat capacity of the rotational subsystem in the solution with $n = 0.25$ and the equilibrium composition of the nuclear-spin species of the molecules.

1. Introduction

This study was aimed at calorimetric investigation of the noncentral interaction effect upon the low temperature dynamics of an ensemble of spherical rotors (CD_4) in orientationally disordered solid $(\text{CD}_4)_n\text{Kr}_{1-n}$ solutions in a wide range of temperature (0.6–25 K) and rotor concentration (0.09–0.35). By varying the concentration of the molecules,

we can separate the contributions to the heat capacity of the solution from both the matrix-isolated molecules and the clusters of interacting molecules of different sizes and configurations.

The influence of the octupole–octupole interaction of CD₄ molecules upon their rotational motion in the (CD₄)_nKr_{1–n} system is an extraordinary phenomenon of great interest for researchers. The system essentially differs from systems with either weak (e.g. (CH₄)_nKr_{1–n}) or strong (e.g. N₂–Kr) noncentral interaction. The rotation of more quantum CH₄ molecules at liquid helium temperatures remains qualitatively the same even if over 50% of the sites in the first coordination sphere are occupied by molecules [1–3]. In contrast, in the case of strong molecular interaction (N₂, CO in Kr), even one molecule present in the first coordination sphere can cause qualitative changes in the molecule rotation and the rotational spectrum [4–6]. In the (CD₄)_nKr_{1–n} system with CD₄ concentrations $n \leq 0.05$ the rotation of most of the molecules, as in CH₄–Kr solution, is weakly hindered and their rotational spectrum is close to that of matrix-isolated molecules [7–9, 11]. However, the rotational motion becomes rather intricate in solution with $n > 0.05$ CD₄, where the noncentral interaction is essentially important [10]. The temperature dependences of the heat capacity of the rotational subsystem $C_{\text{rot}}(T)$ in concentrated (CD₄)_nKr_{1–n} solutions [2] are drastically different from $C_{\text{rot}}(T)$ in (CD₄)_nKr_{1–n} solutions with $n = 0.01, 0.05$ CD₄ [7, 8] and (CH₄)_nKr_{1–n} solutions with $n = 0.1–0.78$ CH₄ [1, 2, 11].

There are several factors responsible for the dynamics of rotors in concentrated CD₄–Kr solutions and this greatly complicates the analysis of calorimetric data. A variety of clusters of different sizes and relative CD₄ positions and orientations are possible in such solutions. The energy spectra of CD₄ molecules therefore vary widely because CD₄ molecules are exposed to different local symmetries and their non-central interactions with the surroundings are different too. It is therefore rather problematic to take into account the noncentral interaction even confining the consideration to the interaction of the CD₄ molecule with its nearest neighbours only. Because of frustration the noncentral interaction is dependent not only on the number of the nearest neighbours but on their relative positions as well.

The distinctions in the low temperature dynamics of the rotational subsystems of CH₄ and CD₄ solutions in Kr are mostly due to the short-range (decreasing as $1/R^7$) octupole–octupole interaction of the molecules in the first coordination sphere and to the quantum effects in the rotational motion of the molecules. According to calorimetric data [2], in solid solutions with equal CH₄ and CD₄ concentrations, the CD₄ molecules are subjects to a much stronger molecular field than the CH₄ molecules. This is due to the features of quantum solids: in the ground state CD₄ molecules have a higher effective octupole electric moment and a smaller amplitude of zero orientational vibrations in the solid phase.

The experimental heat capacities C_{rot} measured on solution with $n = 0.13$ [10] at temperatures below 2 K were described as a sum of contributions from molecules in effective weak, moderate and strong molecular fields. The rotors experiencing these fields are weakly hindered (WH-rotors), hindered (H-rotors) and strongly hindered (SH-rotors) respectively.

The goal of our calorimetric investigation of (CD₄)_nKr_{1–n} solution was to derive qualitative information about the configurations of rotors executing different kinds of rotational motion, as well as about the relative concentrations and the low-energy part of the rotational spectra of such rotors.

It was also planned to investigate the heat capacity of a solid solution with $n = 0.25$ CD₄ doped with O₂ impurity. The analysis of data on $C_{\text{R}}(T)$ of such a solution can furnish qualitative information about the influence of the CD₄–O₂ interaction, dilatation and O₂ induced local lattice symmetry disturbances upon the rotational motion of the CD₄ molecules. We can also obtain information about the rate of CD₄ conversion.

Table 1. The amount of substance and the concentrations of CD₄ and O₂ in the samples.

Amount of substance (mol)	CD ₄ concentration	O ₂ concentration
0.2847	0.0901	0.000 18
0.1912	0.1711	0.000 34
0.2262	0.2509	0.000 5
0.1877	0.2534	0.002 1
0.1938	0.2509	0.012 3
0.1684	0.3502	0.000 7

2. Experiment

The heat capacity at equilibrium vapour pressure was investigated on solid (CD₄)_nKr_{1-n} solutions with CD₄ concentration $n = 0.09, 0.17, 0.25$ and 0.35 , and on solutions with $n = 0.25$ doped with 0.0021 and 0.0123 O₂ in the temperature interval $T = 0.6\text{--}30$ K. The measurement was performed in pulse heating mode using an adiabatic vacuum calorimeter [12]. Gas mixtures were prepared at room temperature. The amounts of substance in the samples of the solution components were estimated from the PVT data, with the error 0.2% . The gas compositions were as follows: CD₄ of 99% isotopic and 99.20% chemical purity (N₂— 0.50% ; O₂— 0.20% , CO— 0.10% and Ar $< 0.01\%$); Kr of 99.79% purity (Xe— 0.2% , N₂— 0.01% , O₂ and Ar $< 0.01\%$); O₂ of 99.99% purity (N₂ $< 0.01\%$). The amount of substance and the concentrations of CD₄ and O₂ in the samples are given in table 1. Solid samples were prepared in a calorimeter at $T \approx 78$ K by condensing the gas mixture into the solid phase. This technique provides a homogeneous composition with a random distribution of the components. Before measurements, the calorimeter with the mechanical thermal switch in the on-condition was cooled from 1.5 to ~ 0.5 K for about 4 h and was kept at this temperature for 4–6 h. The switch was set off, and after ~ 2 h when the temperature course was $10^{-3}\text{--}10^{-4}$ K min⁻¹ the measurements of heat capacity started. The change in sample temperature ΔT_i during one measurement was $1\text{--}10\%$ of the initial temperature T_i . The heating time t_h varied from 2 to 6 min. The effective time of one measurement $t_m = t_h + t_e$ (where t_e is the time during which the calorimeter reached its temperature course close to steady-state operation since the moment of switching off the heating) changed from 40 to 10 min in the interval from 0.6 to 27 K, respectively. The results obtained at these times t_m are reproducible and independent of the temperature prehistory of the sample. The error of the heat capacity measurement was about 7% at 0.7 K, 2% at 1 K, 1% at 2 K and 0.5% above 4 K.

As with the solutions with $n = 0.13, 0.5, 0.6, 0.7$ [2, 10], the rate of temperature relaxation after heating or cooling the calorimeter suggests that the nuclear-spin conversion is rather fast in these solutions.

The heat capacity C_{rot} caused by the rotation of the CD₄ molecules in the solutions was found by subtracting the translational heat C_{tr} from experimental values of heat capacity of the solutions C_{sol} . It was assumed that C_{tr} could be presented as $C_{\text{tr}} = C_{\text{Kr}} + \Delta C_{\text{tr}}$, where C_{Kr} is the heat capacity of pure Kr and ΔC_{tr} is the change in the translational heat capacity caused by introduction of an easier impurity (CD₄) into the Kr lattice. ΔC_{tr} was calculated by the method proposed by Peresada [13, 14] without regard for a change in the force constants for the mass ratio $m_{\text{CD}_4}/m_{\text{Kr}} = 0.25$. The heat capacity C_{Kr} of pure krypton was measured beforehand in an interval of $0.6\text{--}30$ K. The results on C_{Kr} are in good agreement with the data of [15, 16]. The limiting Debye temperature at $T \rightarrow 0$ K is $\Theta_0 = 71.6$ K, and coincides with $\Theta_0 = 71.7$ K [15] and $\Theta_0 = 71.9$ K [16] within the measurement error.

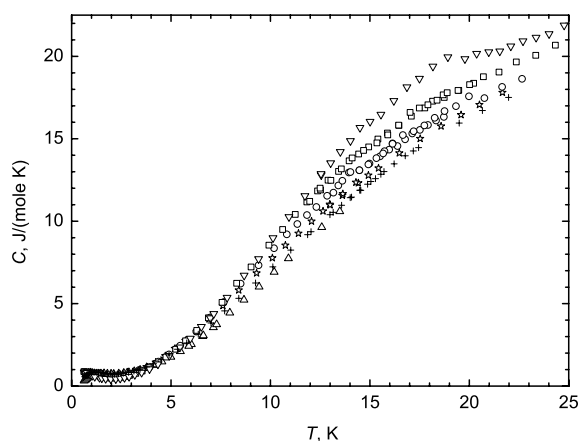


Figure 1. The experimental C_{sol} values for equilibrium vapour pressure of solid $(\text{CD}_4)_n\text{Kr}_{1-n}$ solutions with $n = 0.09$ (Δ); 0.13 ($+$) [10]; 0.17 (\star); 0.25 (\circ); 0.35 (\square); 0.50 (∇) [2].

While separating the heat capacity we subtracted the comparatively small contribution of the rotation of O_2 impurity to the heat capacity using the calorimetry results for the $\text{Kr}-\text{O}_2$ solutions [6, 17]. Our estimates based on the experimental data for the heat capacity of the rotational N_2 subsystem in $\text{Kr}-\text{N}_2$ solutions [4, 6, 18] show that the contribution made by the N_2 impurity to the heat capacity C_{rot} is negligible.

We estimated C_{rot} up to $T = 14$ K because at higher temperatures the correction $C_p - C_v$ should be taken into account. Since no complete data are available for the thermal expansion coefficients, compressibilities and molar volume of the solutions used in our investigations we were unable to separate $C_{\text{rot}}(T)$ at $T > 14$ K accurately.

3. Results and discussion

The measured heat capacities at equilibrium vapour pressure (to a high extent of accuracy $C_{\text{sol}} = C_p$) of solid $(\text{CD}_4)_n\text{Kr}_{1-n}$ solutions with CD_4 concentrations $n = 0.09, 0.17, 0.25$ and 0.35 are given in figure 1. The figure also shows the heat capacities measured earlier on $(\text{CD}_4)_n\text{Kr}_{1-n}$ solutions with $n = 0.50$ [2] and $n = 0.13$ [10]. It is seen in figure 1 that appreciable changes occur in the temperature dependences $C_{\text{sol}}(T)$ in the solutions with $n = 0.50\text{CD}_4$ [2] ($T = 18\text{--}21$ K) and the solutions with $n = 0.25$ and 0.35 [8] ($T = 13\text{--}14$ K). Earlier [17–19], anomalous behaviour of the lattice parameters and the thermal expansion coefficients of the $(\text{CD}_4)_n\text{Kr}_{1-n}$ solutions was observed in the regions of concentrations $n = 0.4\text{--}0.7$ and temperatures $T < 20$ K. The authors [2, 19–21] attributed the anomalies to the formation of the short-range orientational order.

The dependences of the heat capacity $C_{\text{sol}}(T, n)$ of the $(\text{CD}_4)_n\text{Kr}_{1-n}$ solutions exhibit certain features at liquid helium temperatures (see figure 1). They are caused by the heat capacity of the rotational subsystem $C_{\text{rot}}(T, n)$, because below 2 K the contribution of $C_{\text{rot}}(T, n)$ to $C_{\text{sol}}(T, n)$ exceeds 0.94.

Figures 2(a) and (b) show the temperature dependences of the normalized rotational heat capacity $C_{\text{R}}(T) = C_{\text{rot}}(T)/(nR)$ (n is the rotor concentration, R is the universal gas constant) for the solutions with $n = 0.05$ [8], $0.09, 0.13$ [10], $0.17, 0.25$ and 0.35 CD_4 . It is seen that behaviour of $C_{\text{R}}(T)$ is qualitatively similar for the solutions with $n > 0.05\text{CD}_4$. At low temperatures the curves $C_{\text{R}}(T)$ have a maximum (a Schottky-type anomaly). As the

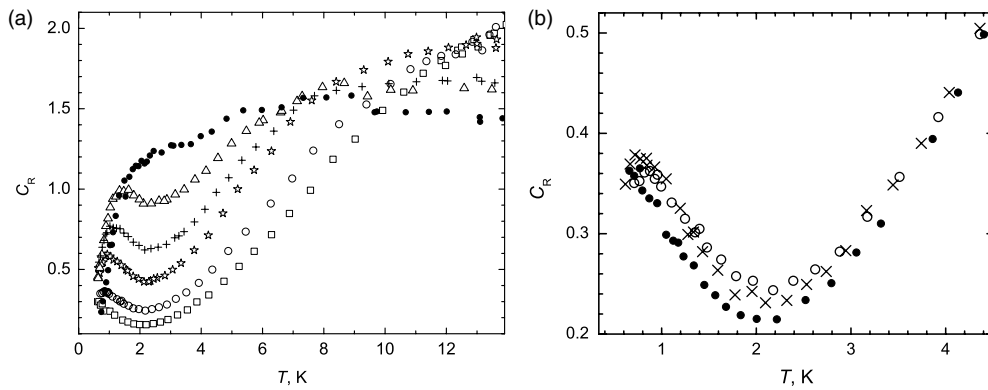


Figure 2. (a) Temperature dependence of the normalized rotational heat capacity $C_R(T) = C_{\text{rot}}(T)/(nR)$ (n is the rotor concentration, R is the universal gas constant) of $(\text{CD}_4)_n\text{Kr}_{1-n}$ solutions: $n = 0.05$ (\bullet) [8]; 0.09 (Δ); 0.13 ($+$) [10]; 0.17 (\star); 0.25 (\circ); 0.35 (\square). (b) Temperature dependence of the normalized rotational heat capacity $C_R(T)$ of the $(\text{CD}_4)_{0.25}\text{Kr}_{0.75-m}(\text{O}_2)_m$ with O_2 impurity with concentrations $m = 0.0005$ (\circ) (initial sample), 0.002 (\times); 0.012 (\bullet).

CD_4 concentration increases, the heat capacities and the temperatures at the $C_R(T)$ maximum decrease. For the sample with $n = 0.35\text{CD}_4$ the temperature of the maximum is beyond the temperature interval of our measurements (below 0.6 K).

The heat capacities of the $(\text{CD}_4)_{0.25}\text{Kr}_{0.75-m}(\text{O}_2)_m$ were investigated at different O_2 contents to reveal how the O_2 impurity influences the rotational motion of the CD_4 molecules. If the conversion does not bring the modifications to the equilibrium distribution during one measurement of the heat capacity of an O_2 -free sample, the introduction of O_2 -impurity to the solution will greatly intensify the conversion rate of the CD_4 molecules and will lead to a significant growth of the heat capacity of the solution. The normalized heat capacity of the $(\text{CD}_4)_{0.25}\text{Kr}_{0.75-m}(\text{O}_2)_m$ samples with concentrations $m = 0.0005$, 0.002 and 0.012 O_2 is shown in figure 2(b). It is seen that the O_2 impurity produces little effect on $C_R(T)$. The introduction of 0.012 O_2 causes an appreciable systematic decrease in $C_R(T)$ at $T = 0.8$ – 4 K. Above 4 K the C_R values practically coincide for all the samples. This means that at all temperatures of the experiment the distribution of nuclear spin species comes to equilibrium within the time of one heat capacity measurement t_m ($t_m \approx 0.74$ h at $T < 1$ K). On the basis of this result we estimated the upper limit to the characteristic time of conversion $\tau < 0.2$ h.

The behaviour of $C_R(T)$ in the investigated solutions shows that the measured heat capacity at $T > 0.6$ K corresponds to the equilibrium distribution of spin species.

Note that introduction of 0.01 of O_2 impurity into the solution with $n = 0.25$ significantly affects the normalized heat capacity δ : the relative change in δ is about four times larger in comparison with δ of the same solution in which the CD_4 concentration is increased by 0.01 . The effect is due to a change in the symmetry and the molecular field intensity at the lattice sites near the O_2 molecules. This leads to deformation of the energy spectrum of the molecules and changes the H- and SH-rotor concentrations.

The significant influence of N_2 and O_2 impurities on the thermal expansion of solid CH_4 with the equilibrium composition of nuclear spin species was detected in [22].

The experimental results obtained in the temperature region below 1.6 K are most interesting. In this region the rotational heat capacity is determined mainly by the transitions between lowest levels of the A-, T- and E-species with the energy difference E_{AT} and E_{AE} between these levels. The rotational heat capacity of the solutions was analysed within the

model used in [10]. It is assumed that the normalized heat capacity can be described by the following expression:

$$C_R(T, n) = x_{SH}C_{R,SH}(T, n) + x_H C_{R,H}(T, n) + x_{WH}C_{R,WH}(T, n) \quad (1)$$

for three lowest levels $i = 1, 2, 3$ of the unified effective spectra of rotors that are in weak, moderate and strong fields. In these fields the rotors execute weakly hindered, hindered and strongly hindered rotational motion, respectively. x_{SH} , x_H , and x_{WH} are used to denote the relative contents of the corresponding types of rotors ($x_{SH} + x_H + x_{WH} = 1$). The normalized heat capacity can be calculated for each type of rotors as

$$C_R(T) = T^{-2}(\langle E^2 \rangle - \langle E \rangle^2), \quad (2)$$

where $\langle E^2 \rangle = \frac{\sum_i E_i^2 g_i \exp(-E_i/kT)}{Z}$ and $\langle E \rangle = \frac{\sum_i E_i g_i \exp(-E_i/kT)}{Z}$ are mean values of rotor energy squares and energies, $Z = \sum_i g_i \exp(-E_i/kT)$ is the statistical sum, and E_i and g_i are the energy and degeneracy of level i . Energy gaps E_{AT} and E_{AE} for WH-rotors are taken from [7, 8, 23]. We also assume that in a random distribution of the solution components, the share of the WH-rotors is $x_{WH} = x_I(n) + x_{IP}(n)$, where $x_I(n)$ and $x_{IP}(n)$ are the relative concentrations of isolated molecules and the molecules in isolated pairs. The assumption is quite reasonable. According to calorimetric [7, 8, 11] and neutron spectroscopy [9, 24, 25] data for $(CD_4)_n Kr_{1-n}$ and $(CH_4)_n Kr_{1-n}$ solutions with molecule concentrations $n \leq 0.05$ the energies E_{AT} of the matrix-isolated rotors and the rotors in isolated pairs practically coincide and are in good agreement with the calculation [23, 26] for matrix-isolated rotors. This can be attributed to the spherical symmetry of the CH_4 and CD_4 rotors and the high symmetry of the FCC lattice. The molecules in isolated pairs are a potential field with relatively small local distortions of the cubic symmetry and changes in the crystal field lattice (as against the molecules in clusters of three and more molecules).

The orientationally disordered solid $(CD_4)_n Kr_{1-n}$ solutions, solid Kr and solid CH_4 in phases II have an FCC structure. We therefore assume that the SH-rotors have the structure of the tunnel level ($E_{AT}/E_{AE} = 2/3$), as in the case of orientationally ordered CH_4 molecules in phases II [27, 28]. We disregarded the changes in the rotational spectra of the SH- and H-rotors that were caused by minor local disturbances of the symmetry at the lattice sites of the solid $(CD_4)_n Kr_{1-n}$ solutions [19, 20]. The agreement between calculation and experiment can be better if we take the $E_{AT}/E_{AE} = 2/3$ for the three lowest levels (degeneracies 15 in the ground state, 54 and 36) of H-rotors in moderate fields. Therefore, we analysed $C_R(T)$ of the solution with $n = 0.13CD_4$ [10] in the region below 1.6 K on the basis of the structure assumed for the three lowest levels of H- and SH-rotors.

Table 2 gives the relative concentrations x and the effective gaps E_{AT} of the H- and SH-rotors. These data were obtained under the conditions of the optimized description of experimental $C_R(T)$ -dependences. The fitting was made assuming that the effective molecular fields averaged over the ensembles of H- and SH-rotors increase with the concentrations n of the CD_4 molecules. This assumption is supported by the fact that a long-range orientational order develops in solutions with $n \geq 0.7$ when the temperature decreases below 22 K [19, 20]. Table 2 also contains literature data for solutions with $n = 0.50, 0.60, 0.70$ CD_4 [2]. Three parameters were fitted for each solution with concentration n : x_{SH} (provided that $x_{SH} + x_H + x_{WH} = 1$), E_{AT} for H- and SH-rotors. The dependences $x(n)$ for the H- and SH-rotors taken on our solutions and the solutions with $n = 0.5, 0.6, \text{ and } 0.7$ [2] are in satisfactory agreement (see table 2 and figure 5). The experimental curves $C_R(T)$ taken below 1.6 K and the dependences calculated using the parameters of table 2 are compared in figure 3.

Table 3 shows the parameters x and E_{AT} for WH-, H- and SH-rotors. These parameters obtained by equations (1) and (2) determine the dependence $C_R(T, n)$ of the solid

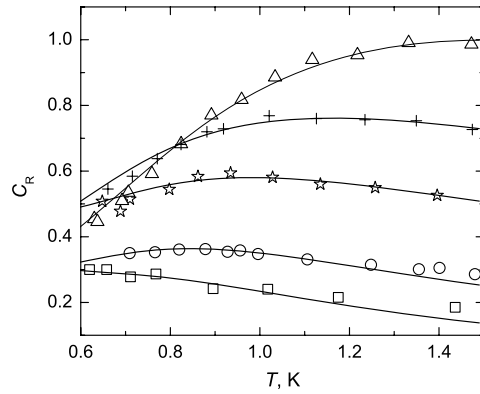


Figure 3. Normalized rotational heat capacity $C_R = C_{rot}/(nR)$ of solid $(CD_4)_n Kr_{1-n}$ solutions. Experimental values are for $n = 0.09$ (Δ), $n = 0.13$ (+) [10], $n = 0.17$ (\star), $n = 0.25$ (O), $n = 0.35$ (\square). The curves were calculated using equations (1) and (2) and the parameters of table 2 for SH-, H- and WH-rotors.

Table 2. Parameters determining $C_R(T, n)$ of the solid $(CD_4)_n Kr_{1-n}$ solutions with $n = 0.09, 0.13, 0.17, 0.25$ and 0.35 and in solutions with $n = 0.50, 0.60$ and 0.70 CD_4 [2] at $T < 1.6$ K. (Note that E_{AT} is the effective gap between the lowest energy levels of A and T nuclear-spin species of the rotational spectrum of CD_4 molecules; n is CD_4 concentration; x_{SH}, x_H and x_{WH} are relative concentrations of SH-, H- and WH-rotors in strong, moderate and weak potential fields, respectively.)

n	WH-rotors		H-rotors		SH-rotors	
	x_{WH}	E_{AT}, K	x_H	E_{AT}, K	x_{SH}	E_{AT}, K
0.09	0.52	4.8	0.31	2.70	0.17	0.88
0.13	0.31	4.8	0.34	2.52	0.35	0.66
0.17	0.18	4.8	0.27	2.54	0.55	0.64
0.25	0.05	4.8	0.19	2.46	0.76	0.42
0.35	0.01	4.8	0.13	2.32	0.86	0.44
0.50	—	—	0.10	2.4	0.90	0.36
0.60	—	—	0.085	2.4	0.915	0.34
0.70	—	—	0.075	2.4	0.925	0.33

Table 3. Parameters determining $C_R(T, n)$ of the solid $(CD_4)_{0.25} Kr_{0.75-m} (O_2)_m$ solutions with $m = 0.0005, 0.002, 0.012$ at temperatures below 1.6 K.

m	WH-rotors		H-rotors		SH-rotors	
	x_{WH}	E_{AT}, K	x_H	E_{AT}, K	x_{SH}	E_{AT}, K
0.0005	0.05	4.8	0.19	2.46	0.76	0.42
0.002	0.05	4.8	0.20	2.40	0.75	0.42
0.012	0.05	4.8	0.20	2.06	0.75	0.34

$(CD_4)_{0.25} Kr_{0.75-m} (O_2)_m$ solutions ($m = 0.0005, 0.002, 0.012$) at temperatures below 1.6 K. It is seen that the relative concentrations x and the effective gaps E_{AT} of the H- and SH-rotors are little affected when the O_2 concentration increases from 0.0005 to 0.002. A 24-fold increases in the concentration of 0.0005 O_2 also produces a very slight effect on x , but the E_{AT} decreases significantly (by 15–20%).

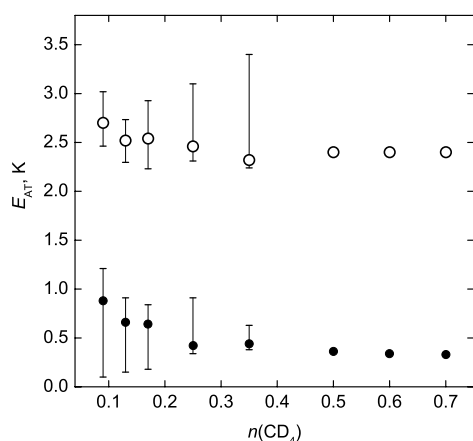


Figure 4. Concentration dependence of effective gaps $E_{\text{AT}}(n)$ of H- and SH-rotors in moderate (O) and strong (●) molecular fields in solid $(\text{CD}_4)_n \text{Kr}_{1-n}$ solutions.

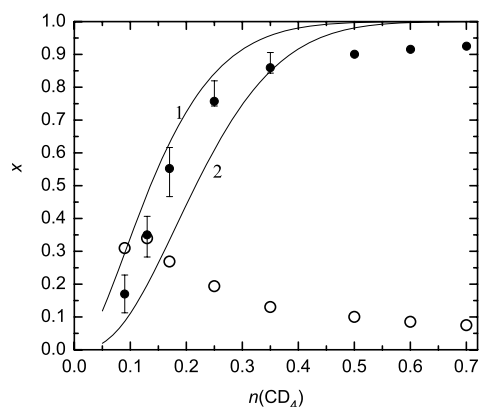


Figure 5. Experimental values of relative concentrations of the SH- and H-rotors in strong $x_{\text{SH}}(n)$ (●) and moderate $x_{\text{H}}(n)$ (O) molecular fields. Curves 1, 2—relative concentrations of rotors having no less than two $x(k > 1, n)$ or three $x(k > 2, n)$ rotors in the first coordination sphere; calculation by equation (3).

Our investigations of the $(\text{CD}_4)_{0.25}\text{Kr}_{0.75-m}(\text{O}_2)_m$ solutions have led us to conclude that small concentrations (below 0.0018) of N_2 impurity in the solutions have little effect on the parameters x and E_{AT} of the H- and SH-rotors.

The concentration dependences of the effective gaps $E_{\text{AT}}(n)$ of H- and SH-rotors experiencing moderate and strong molecular fields are shown in figure 4. The E_{AT} values marked with symbols provide the best agreement of experimental and calculated $C_{\text{R}}(T)$. The interval of possible E_{AT} values is indicated, in which the discrepancy between experiment and calculation remains within measurement error in $C_{\text{R}}(T)$.

In the model used to analyse the experimental $C_{\text{R}}(T)$, the energies E_{AT} are practically (within the measurement error) independent of CD_4 concentration for all types of rotors. It should be noted that the E_{AT} -regions are separated rather widely from each other. Since different types of rotors contribute to heat capacity at different temperatures, we can estimate quite accurately the contents of each type of rotors.

The shares of different types of rotors are shown in figure 5 and table 2 as a function of CD_4 concentration. It is seen that the share of WH-rotors $x_{\text{WH}}(n)$ decreases rapidly as the CD_4 concentration increases. The share of H-rotors $x_{\text{H}}(n)$ first increases up to a maximum near $n = 0.13$, then decreases monotonically and more smoothly than $x_{\text{WH}}(n)$, though never reducing to zero in the whole region of orientationally disordered solutions. The share of librators $x_{\text{SH}}(n)$ increases monotonically with the CD_4 concentration, first rapidly, and then at $n > 0.35$ asymptotically comes to saturation.

The obtained dependence contains important quantitative information about the effect of the noncentral interaction of CD_4 rotors upon their rotational motion. The effect on a rotor is determined by the total effective molecular field generated by the neighbouring molecules. The molecular field depends on the number of neighbours, their disposition symmetry and the character of their rotational motion. The molecules executing angular vibrations and having their orientations on average invariable for a long time excite a stronger field as compared to the molecules whose motion is hindered or weakly hindered. Since the noncentral molecular interaction is proportional to the parameter $\zeta = I_3^2/R^7$ (I_3 is the effective octupole moment, R is the distance between the centres of masses of the molecules), the contribution from the neighbours of the second coordination sphere is an order of magnitude smaller than that from the rotors of the first coordination sphere.

Although the neighbouring molecules can take on a wide variety of configurations, the experimental heat capacities $C_{\text{R}}(T, n)$ can be described adequately by the contributions of three groups of molecules (WH-, H- and SH-rotors) with distinctly different energy gaps $E_{\text{AT}}(n)$. It is probable that in different molecular configurations the distinctions of the gaps within one group are not large and the contribution of each group can be described well by one effective value of E_{AT} .

Assuming that the components of the solid solution are distributed randomly over the lattice, we can calculate the rotor share as a function of concentration $n\text{CD}_4$ for different configurations of neighbouring rotators. A comparison of these dependences with $x_{\text{SH}}(n)$ will let us find out which of the neighbouring rotor configurations can excite strong molecular fields and give rise to librators. First we consider how the concentration n influences the contents of rotors having different numbers of the nearest-neighbour rotors (the disposition symmetry is disregarded). The relative concentration of rotors $x(k, n)$ with the number k of nearest-neighbour rotors is described by a binomial distribution

$$x(k, n) = C(z, k)n^k(1-n)^{(z-k)}, \quad (3)$$

where z is the coordination number ($z = 12$ for an FCC lattice) and n is the CD_4 concentration. Calculated relative concentrations of rotors $x(k, n)$, of isolated rotors $x_{\text{I}}(n) = x(k = 0, n)$, of rotors in isolated pairs $x_{\text{IP}}(n) = 12n(1-n)^{18}$ and of WH-rotors $x_{\text{WH}}(n) = x(k = 0, n) + x_{\text{IP}}(n)$ are shown in table 4.

The calculated dependences of the relative concentrations of rotors having no less than two $x(k > 1, n)$ (curve 1) and no less than three $x(k > 2, n)$ (curve 2) rotors in the first coordination sphere are shown in figure 5 along with the experimental dependence $x_{\text{SH}}(n)$. It is seen that in the investigated solutions ($0.09 \leq n \leq 0.35$) $x_{\text{SH}}(n)$ is systematically lower than $x(k > 1, n)$ and higher than $x(k > 2, n)$, i.e. only the rotors having two or more neighbour rotors can become librators. On the other hand, the rotors having two nearest-neighbour rotors are not all librators; some of them are H-rotors. The reason is that the effective potential field acting upon a rotor is determined not only by the number of its nearest-neighbour rotors, but also by the symmetry of their disposition and the character of their rotation.

The molecules performing angular vibrations and having their orientations on average stable for a long time excite a stronger effective field as compared to the molecules whose

Table 4. Calculated relative concentrations of rotors $x(k, n)$ at FCC lattice sites with the number of rotors k in the first coordination sphere and the relative concentrations of WH-rotors $x_{\text{WH}}(n) = x(k = 0, n) + x_{\text{IP}}(n)$.

n	0.01	0.05	0.09	0.13	0.17	0.25	0.35
$x(k = 0, n)$	0.886	0.540	0.322	0.188	0.107	0.032	0.006
$x(k = 1, n)$	0.107	0.341	0.383	0.337	0.263	0.127	0.037
$x(k = 2, n)$	0.006	0.099	0.208	0.277	0.296	0.232	0.109
$x(k > 1, n)$	0.006	0.118	0.295	0.475	0.630	0.842	0.958
$x(k > 2, n)$	0.0002	0.020	0.087	0.198	0.334	0.609	0.849
$x_{\text{IP}}(n)$	0.100	0.238	0.198	0.127	0.071	0.017	0.002
x_{WH}	0.986	0.778	0.52	0.315	0.178	0.049	0.008

rotation is hindered or weakly hindered. It is reasonable to assume that if a rotor is influenced by at least two strongly hindered rotors (librators) in the first coordination sphere its rotation becomes strongly hindered too, because the neighbour librators excite a strong molecular field, which suppresses the motion of the rotor. However, the motion of these neighbours (librators) is also determined by a similar condition. As a result, a sequence of self-consistent conditions is built up, and the CD_4 molecules forming a sort of cluster should obey these conditions so that they could find themselves in strong molecular fields. Under these conditions, all the rotors become librators if they are members of a subcluster in which each rotor has no less than two nearest-neighbour rotors changed into librators. The simplest cluster of nearest-neighbour rotors–librators has the form of an equilateral triangle with the side $a/2^{0.5}$, where a is the lattice parameter.

At concentrations $n \geq 0.35 x_{\text{SH}}(n)$, $x_{\text{SH}}(n) < x(k > 2, n)$ and the experimental dependence $x_{\text{SH}}(n)$ is weaker than the calculated one $x(k > 2, n)$. This feature is due to the frustration, i.e. SH-rotors in the FCC lattice do not all have orientations such that the orientation of each pair of the nearest neighbouring SH-rotors could correspond to the minimum energy. In pure CH_4 and CD_4 , frustration leads to the formation of antiferrorotational phases II [27, 29], in which the molecular field excited by 12 orientationally ordered nearest-neighbour molecules is counterbalanced for one-quarter of the molecules. As a result, they experience only the weak crystal field and form an orientationally disordered sublattice. When molecules are randomly distributed over the Kr lattice and their concentration is below the percolation threshold $n < 0.2$, the cluster sizes and densities are not large and the vast majority of the SH-rotors take orientations corresponding to the energy minimum. However, above the percolation threshold, most of the SH-rotors belong to a common percolating cluster whose density increases with the CD_4 concentration. This leads to the frustration effects. Because of the partial neutralization of the fields generated by the surrounding SH-rotors, some molecules find themselves in moderate molecular fields. The motion of such molecules is retarded rather than librational.

The results obtained are important and unexpected. First, the wide variation of the normalized heat capacities $C_{\text{R}}(T)$ in the solutions with CD_4 concentration n (see figure 2) is caused mostly by the changes in the relative concentrations $x(n)$ of WH-, H- and SH-rotors because the changes in the energies $E_{\text{AT}}(n)$ of H- and SH-rotors are minor and insignificant (see table 2 and figure 4). Second, according to commonly accepted concepts, the short-range orientational order in cryocrystal solutions [30] occurs at molecular concentrations near the line of the phase transition to the orientationally ordered phase. As follows from x-ray diffraction structure data [19], the short-range orientational order in solutions is observed at concentrations $0.7 \geq n \geq 0.4\text{CD}_4$, when the rotors with $k < 4$ are very few in number. Our investigation

shows that in the $(\text{CD}_4)_n\text{Kr}_{1-n}$ system some of the molecules form the short-range orientational order even at concentration 0.09CD_4 .

4. Conclusions

The influence of the octupole–octupole interaction of CD_4 molecules on their rotation in the system $(\text{CD}_4)_n\text{Kr}_{1-n}$ is a nontrivial and rather intriguing phenomenon. The $(\text{CD}_4)_n\text{Kr}_{1-n}$ system is a unique object essentially different from systems with either weak (e.g. $(\text{CH}_4)_n\text{Kr}_{1-n}$) or strong (e.g. $(\text{N}_2)_n\text{Kr}_{1-n}$, $(\text{CO})_n\text{Kr}_{1-n}$) noncentral interaction. In the case of weakly interacting, more quantum, CH_4 rotors at liquid helium temperatures, their motion remains qualitatively invariable even if the molecules occupy over 50% of the sites in the first coordination sphere [1–3]. In contrast, with strongly interacting molecules (e.g. N_2 , CO), the presence of even one molecule in the first coordination sphere causes sharp changes in the rotation and the rotational spectrum [4–6].

The investigations of the heat capacities of solid $(\text{CD}_4)_n\text{Kr}_{1-n}$ solutions with CD_4 concentrations $n = 0.09, 0.17, 0.25, 0.35$ at $T = 0.6\text{--}30$ K in this study, $n = 0.50, 0.60, 0.70$ in [2] and $n = 0.13$ in [10] show that at liquid helium temperatures the ensemble of spherical rotors CD_4 exhibits more complex behaviour than CH_4 does. The presence of one molecule in the first coordination sphere caused a small deformation of the rotational spectrum of the matrix-isolated CD_4 and CH_4 molecules [7–9, 11]. However, the rotation of CD_4 molecules changes drastically in configurations with two or more nearest-neighbouring molecules. We can observe different kinds of rotation motion of CD_4 molecules depending on the number of nearest neighbours and the disposition symmetry of their arrangement. The effect is of the quantum solid-body origin. In identical configurations of the surrounding CD_4 and CH_4 molecules the total molecular field generated by the CD_4 molecules is much larger than excited by the CH_4 molecules. The reason is that the effective octupole electric moment of the CD_4 molecules in the ground state is larger and the amplitude of zero orientational vibrations in the solid phase is smaller.

The effective concentrations $x_{\text{SH}}(n)$, $x_{\text{H}}(n)$ and the energy gaps $E_{\text{AT}}(n)$, between the ground and the first excited energy levels have been estimated for molecules in strong and moderate molecular fields. The SH-rotors form a short-range orientational order and their effective energy spectrum resembles the rotational spectrum molecules in the orientationally ordered phase II of solid CH_4 . The obtained dependences $E_{\text{AT}}(n)$ and $x(n)$ together with literature data [2, 7, 8, 10] embrace the whole concentration region of existence of solid orientationally disordered $(\text{CD}_4)_n\text{Kr}_{1-n}$ solutions.

It is shown that at liquid helium temperatures the dependence of the heat capacity of the rotational subsystem on the CD_4 concentration n is mostly determined by the changes in the relative concentrations of rotors $x(n)$ performing different kinds of rotational motion.

A strong effect of the O_2 impurity on the normalized heat capacity $C_{\text{R}}(T)$ has been detected at liquid helium temperatures in the solution with $n = 0.25\text{CD}_4$ and the equilibrium composition of the nuclear-spin species of the molecules. The effect is caused by the changes in the local symmetry and the value of the molecular field at the lattice sites in the vicinity of O_2 molecules. These changes deform the energy spectrum of the CD_4 molecules.

It is shown that above 0.6 K the distribution of the molecular species comes to equilibrium within the time of one measurement.

Acknowledgment

The work was supported by the Ukraine Ministry of Education and Science (Project ‘New quantum and anharmonic effects in crystal solutions’, No 02.07/00391-2001).

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