

Heat capacity of methane-krypton solid solutions. Conversion effect

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The heat capacity of Kr- n CH₄ solid solutions with the concentrations $n = 1; 5; 10\%$ and of the solid solution Kr-1%CH₄-0.2%O₂ has been studied at 0.7–8 K. The contributions of C_{rot} to the heat capacity of the solutions caused by the rotation of the CH₄ molecules are estimated. The deviations of the measured C_{rot} from the values corresponding to the equilibrium distribution of the nuclear spin CH₄ modifications are dependent on the correlation between the characteristic times of conversion and of the calorimetric experiment. The effects of temperature, O₂ impurities, and CH₄ clusters upon the conversion rate are studied. It is shown that the hybrid mechanism of conversion proposed by Berlinsky and Nijman, which takes into account both intramolecular and intermolecular interactions of the proton spins, is predominant.

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Introduction

This work is concerned with a calorimetric investigation of the quantum behavior of CH₄ rotators in a crystal field of cubic symmetry. The degree of the quantum effect in the rotational motion can be characterized by the parameter $\lambda_{\phi} = \hbar/\sqrt{I\varepsilon_{\phi}}$, where I is the moment of inertia of the molecule, and ε_{ϕ} is the energy barrier that the molecule has to overcome when its orientation changes. The higher λ_{ϕ} is the stronger the quantum effects are in the behavior of the rotator. The moment of inertia I is quite small because the CH₄ molecule has light hydrogen atoms at its periphery. In matrices of solidified inert gases, methane molecules are surrounded by spherically symmetric atoms. Under this condition, the magnitude of ε_{ϕ} is also quite low (several tens of kelvin [1]). Solutions of methane in matrices of solid inert gases with the fcc structure are therefore most suitable for answering the questions of this study. The spectrum of a quantum rotator in a crystal field is close to that of a free rotator. As a consequence, the spectra of different nuclear spin modifications of a rotator differ considerably [2], and their mutual transformation (conversion) should be taken into account. Solid Kr has been chosen as a matrix because, of all the inert gases,

only Kr has Lennard-Jones potential parameters very close to those of CH₄. As a result, the solubility of CH₄ in solid Kr is as high as 80% at low temperatures. This offers an opportunity to investigate not only the behavior of isolated rotators but their interaction as well. Since the low concentration case more readily lends itself to interpretation, we considered it reasonable to use Kr-CH₄ solutions with CH₄ concentrations of 1–10%. The quantum behavior of rotators shows up at low temperatures. In addition, the relative contribution of the rotator subsystem to the heat capacity of Kr-CH₄ solutions decreases as the temperature rises. The temperature interval of this study was therefore bounded from above by 8 K.

We should mention some problems which are much assisted by studies of the heat capacity of solid CH₄-Kr solutions at low (helium) temperatures.

1. Mechanism of mutual transformation of nuclear spin CH₄ modifications (conversion mechanism)

It is known that CH₄ molecules can come in three modifications having different mutual proton spin orientations and rotational energy spectra.

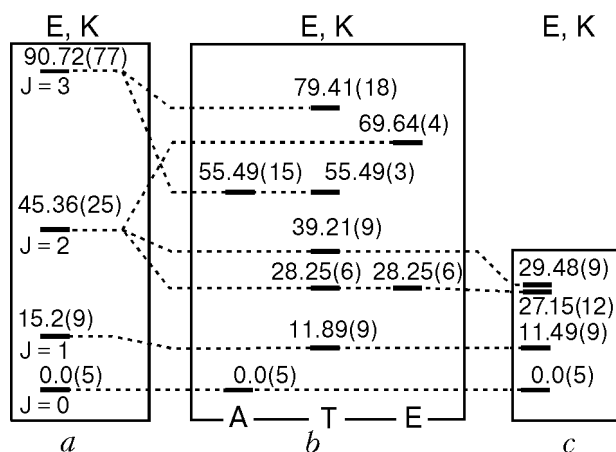


Fig. 1. Rotational energy spectra of the methane molecule: *a* – free rotator [3]; *b*, *c* – hindered CH₄ rotator in the crystal Kr field (*b* – calculation [4], *c* – experimental [5]). *J* – rotational quantum number, *R* – energy (degeneracy levels are in brackets to the right).

These CH₄ modifications, specified as *A*, *T*, *E*, have the total nuclear spins 2, 1, 0, respectively. Their rotational spectra (the low-energy region) are shown in Fig. 1 for a free rotator and a rotator in a Kr matrix.

The *A* modification has the lowest energy of the ground state. Owing to conversion, the modifications are in equilibrium at different temperatures. The temperature dependence of the equilibrium *A*, *T*, and *E* concentrations of free CH₄ rotators is shown in Fig. 2 [2]. In the high temperature limit the concentration ratio $x_A : x_T : x_E$ is 5:9:2.

Two factors are responsible for the rate of conversion – the interaction of the proton spins and the possibility for the phonons to gain energy from the transitions between different rotational states. Since the spacing of the protons is quite small within the molecule, the intramolecular spin interaction is an order of magnitude stronger than the spin interaction between the neighboring molecules. The intramolecular spin interaction is, however, only weakly connected with the translational vibrations of the lattice, and this considerably impedes conversion. According to Nijman and Berlinsky [6], a hybrid mechanism of conversion predominates in solid CH₄ at low temperatures: the intramolecular interaction mixes the nuclear spin states, and the intermolecular interaction induces transitions between the energy levels, which are accompanied by emission of phonons. CH₄-Kr solid solutions are very suitable to test the Nijman and Berlinsky model. The conversion of isolated CH₄ molecules can be studied on weak solutions. At increasing

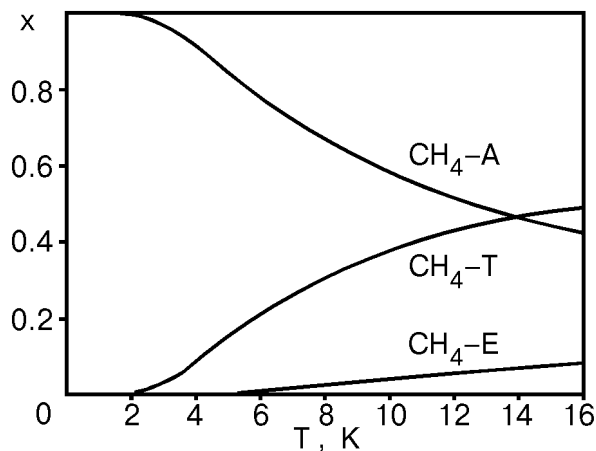


Fig. 2. The temperature dependence of the equilibrium *A*, *T*, and *E* concentrations of free CH₄ rotators [2].

concentrations, the number of clusters of CH₄ molecules increases rapidly, and they trigger the hybrid mechanism of conversion. The heat capacity of the CH₄ subsystem is very dependent on the *A*, *T*, and *E* concentrations achieved by the time of measurement and on whether their concentration ratio has a chance to change during a single measurement run. It follows from the above consideration that we can derive information about conversion from the measured heat capacity.

To avoid misunderstanding, it is appropriate to note here that our term «heat capacity» has the meaning of the derivative of the heat transferred to the system with respect to temperature, irrespective of whether the system is at equilibrium or not.

It is also interesting to investigate how small amounts of paramagnetic impurities can influence the heat capacity of diluted CH₄-Kr solid solutions. If the hybrid mechanism prevails and no paramagnetic impurity is present in the Kr-CH₄ solution, during the time of experiment the conversion will mainly occur in the clusters. The addition of a paramagnetic impurity will increase strongly the rate of conversion in the isolated CH₄ molecules and hence the heat capacity C_{rot} of the rotational subsystem. This problem can also be tackled in the context of heat capacity studies.

2. Dynamics of quantum rotators in a crystal field

The heat capacity C_V of the system is determined by its energy levels. Our heat capacities C_P ($P = 0$) estimated at a constant pressure coincide, within the experimental error, with the values C_V obtained at a constant volume. The inverse problem of obtaining the energy spectrum from heat capacity [7] can be solved uniquely only for the low-temperature heat capacity, which is determined by a small num-

ber of excited levels in the spectrum. The first excited state of the rotator subsystem estimated from the heat capacity can sometimes surpass the spectroscopic data in accuracy [8].

The high solubility of CH₄ in solid Kr [9,10] may provide more evidence about how the octupole rotator interaction influences the low-energy part of the spectrum of the rotator subsystems. The multipolar moment of quantum rotators (unlike the classical ones) is dependent on the state of the rotator. In the ground state the CH₄ molecule has the smallest [3] octupole moment. As the temperature of the Kr-CH₄ solution rises, the occupancy of the excited states of the CH₄ rotators increases, and so do the octupole moment of the CH₄ molecules and their interaction. Thus, the interaction between the CH₄ molecules changes with temperature, which should manifest itself in the behavior of the heat capacity of the rotator subsystem.

3. Octupole glasses in Kr-*n*CH₄ solutions: existence and features

At sufficiently low temperatures an orientational octupole glass can develop in a Kr-*n*CH₄ solution [14]. In our solutions with low CH₄ concentrations (*n* ≤ 10%) we can hardly expect an orientational glass to be formed due to a direct octupole interaction of CH₄ molecules. Such concentrations may, however, allow an octupole glass caused by an indirect interaction. This type of glass can develop due to an indirect interaction of impurity molecules through the strain fields induced by the impurities themselves in the host lattice. The presence and type of glass can be identified from the temperature and concentration dependences of the heat capacity [12]. Quadrupole glasses with an indirect interaction have been detected and studied by several investigators [12-14].

Experiment

The heat capacity of solid Kr-*n*CH₄ solutions with the concentrations *n* = 1; 5; 10% and the Kr-1% CH₄-0.2% O₂ solution were studied at 0.7-8 K by a pulse-heating method using an adiabatic vacuum calorimeter [15]. The temperature of the sample changed as $\Delta T_i = T_{i+1} - T_i$, where T_i and T_{i+1} are the temperatures before and after heating. The change during one measurement run was about 10% of T_i . The heat capacity corresponded to the temperature $T = (T_i + T_{i+1})/2$. The heating time t_h was usually two or three minutes. The time t_{exp} taken to measure one heat capacity value was 0.5-1.4 hour and depended mainly on the

duration (t_e) of temperature equalization over the sample after switching off the heater. The effective (characteristic) time t_m of one measurement run is taken to be $t_m = t_h + t_e$. The mass of the samples was 0.5-0.7 mole.

The purity of the gases was: CH₄ - 99.94% (0.04% N₂, < 0.01% Ar, O₂); Kr - 99.72% (0.08% N₂; 0.2% Xe); O₂ - 99.99%.

Gas mixtures with a pre-assigned composition were prepared at room temperature. The impurity concentration and the mass of the samples were found from the PVT data to within 0.2%. A solid solution was prepared in a calorimeter at $T \approx 70$ K by condensing the gas mixture into the solid phase. The error of the heat capacity measurement was 6% at 0.7 K; 2% at 1 K; 1% at 2 K and 0.5% above 4 K. To minimize the systematic measurement errors and to improve the accuracy of separation of the heat capacity component C_{rot} contributed by the CH₄ impurity rotation, the heat capacity of pure Kr was measured in the same calorimeter.

The heat capacity of Kr-CH₄ solutions was measured only once, by A. Euken and H. Veight [9] in 1936 ($T = 12-25$ K; 28-96% CH₄).

Data presentation

The heat capacity of the Kr-CH₄ solution can be presented as a sum $C_{\text{sol}} = C_{\text{tr}} + C_{\text{rot}}$, where C_{rot} is the heat capacity contributed by the rotational motion of the CH₄ molecules; C_{tr} is the heat capacity due to translational vibrations of a lattice. C_{tr} can in turn be represented as $C_{\text{tr}} = C_{\text{Kr}} + \Delta C_L$, where C_{Kr} is the heat capacity of pure krypton, and ΔC_L is the change in the translational heat capacity caused by the presence of a lighter impurity (CH₄) in the Kr lattice. ΔC_L was calculated by the Jacobi matrix method [16] for the mass ratio $m_{\text{CH}_4}/m_{\text{Kr}} = 0.2$, the force constant variation being neglected. The rotational component C_{rot} was found by subtracting C_{Kr} and ΔC_L from the experimental C_{sol} values. The C_{rot} value thus obtained was compared with calculation for three limiting cases:

1. Equilibrium distribution (ED) of the nuclear spin (*A*, *E*, *T*) modifications (fast conversion).

It is assumed that conversion is so fast that the *A*, *E*, and *T* concentrations can be thought of as equilibrium at any instant at the temperature of the experiment. This is possible if conversion occurs during the effective time t_m of a single measurement run. In this case the heat capacity is obtainable from the unified rotational energy spectrum based on all levels.

2. Frozen equilibrium distribution (FED).

The A , E , and T concentrations are equilibrium with respect to the initial temperature T_i and do not change during the effective time t_m when the sample is heated from T_i to T_{i+1} . This is possible when the characteristic conversion time is $\tau \gg t_m$. Prior to measurement, the sample must be kept at T_i during the time $t \gg \tau$. At the mid-heating temperature $T = (T_i + T_{i+1})/2$, the heat capacity is calculated as

$$C_{\text{rot}}(T) = x_A(T_i)C_A(T) + x_T(T_i)C_T(T) + x_E(T_i)C_E(T), \quad (1)$$

where x_A , x_T , x_E are the relative equilibrium A , E , and T concentrations at T_i ; C_A , C_T , and C_E are the heat capacities of the corresponding modifications at the temperature T .

3. Frozen distribution (FD) (no conversion).

The A , E , and T concentrations are constant in the whole range of temperatures and equal to the high-temperature distribution, i.e., $x_A : x_T : x_E = 5:9:2$. This occurs if at all temperatures the conversion is very slow and the A , E , and T concentrations are practically invariable during the whole experiment (several weeks). In this case the heat capacity C_{rot} can be found as

$$C_{\text{rot}}(T) = \frac{5}{16} C_A(T) + \frac{9}{16} C_T(T) + \frac{2}{16} C_E(T). \quad (2)$$

To calculate C_{rot} for the above limiting cases, we need to know the rotation spectrum of the CH_4 molecule in the crystal field of krypton. This spectrum has been calculated in [4] (see Fig. 1,*b*). The energies of four low-lying rotational levels of the CH_4 molecule in a Kr matrix were found experimentally by the method of inelastic neutron scattering [5,17]. It turns out that three of them agree well with theoretical predictions [4], the discrepancy being within 3% (see Fig. 1,*c*). The fourth level differs by about 30%. We thought it reasonable to use the spectrum of Fig. 1,*b* in the subsequent C_{rot} calculation.

Results of the measurements. Discussion

The heat capacities C_{rot} measured on the solutions with 1; 5; 10% CH_4 and normalized to the CH_4 concentration n and the universal gas constant R are shown in Fig. 3,*a* for the whole range of measurement temperatures and in Fig. 3,*b* (enlarged scale) up to 4.3 K. As seen in Fig. 3,*a*, the data scatter increases with rising temperature, and the accuracy of the C_{rot} component degrades. This

is due to the lattice contribution C_{tr} to the total heat capacity of the solution, which increases when the temperature rises: 47% at $T = 4$ K and 78% at $T = 8$ K ($n = 10\%$). The dotted line in Fig. 3,*a* corresponds to the high-temperature value, $C_{\text{rot}}/nR = 3/2$, for a mole of isolated CH_4 molecules in a Kr matrix.

Along with experimental results, Fig. 3 show the calculated heat capacities for the above three limiting cases: ED (curve 1), FED (curve 2), FD (curve 3). It is seen that in the whole temperature region, the heat capacity of the Kr-1% CH_4 solution hardly exceeds the experimental error and is much below curves 1 (ED) and 3 (FD) at $T \leq 5$ K. Curve 2 (FED) is the best description of the solution at $T \leq 5$ K. This suggests that the characteristic conversion times of this solution greatly exceed the effective times t_m of a single measurement run. This conclusion is consistent with [18,19]. According to [18] the characteristic conversion time τ of isolated CH_4 molecules in a Kr matrix is 3.5 hours at $T = 2$ K.

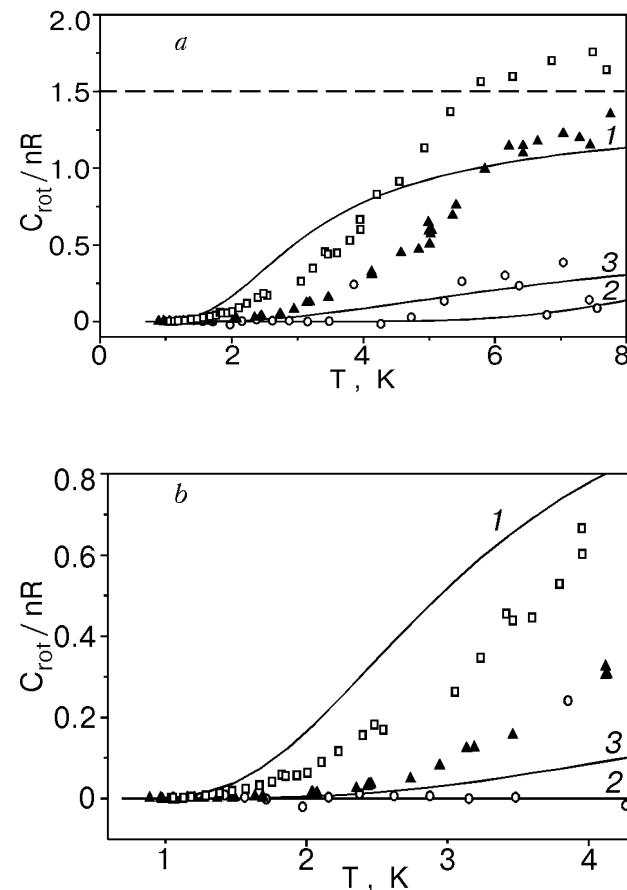


Fig. 3. Temperature dependence of reduced rotational heat capacity of Kr- CH_4 solutions containing 1% CH_4 (\circ), 5% CH_4 (\blacktriangle), 10% CH_4 (\square) for the whole temperature range (*a*) and up to 4.3 K (*b*). The solid lines are the theoretical curves for the three limiting cases mentioned (1 – ED, 2 – FED, 3 – FD).

It is seen in Fig. 3 that the reduced rotational heat capacity increases rapidly with the concentration n , and above $T \approx 4$ K ($n = 10\%$) or $T \approx 6$ K ($n = 5\%$) it exceeds the C_{rot}/nR value corresponding to the instantaneous thermodynamic equilibrium of the nuclear spin modifications of isolated CH_4 molecules. This can be explained as follows. As the concentration n grows, the number of CH_4 clusters increases, too. Clusters of two and three CH_4 molecules prevail at $n = 5; 10\%$ CH_4 . The hybrid mechanism of conversion operating in the clusters [6] enhances the conversion rate considerably. As a result, the nonequilibrium nuclear spin modifications come into equilibrium, and the entropy S of the solution increases. The higher the conversion rate is in the nonequilibrium system, the more intensively the entropy changes at the initial temperature T_i during the effective time t_m of a single measurement run. Correspondingly, the measured heat capacity $C_V = T(dS/dT)$ appears to be higher. Note that in this case the measured heat capacity can exceed that of the equilibrium system. The higher heat capacity of clustered molecules (as compared to that of isolated ones) can also contribute appreciably to the concentration dependence of the heat capacity. We should not therefore overestimate the quantitative comparison between the C_{rot} of the solutions with $n = 5; 10\%$ CH_4 and the theoretical curve describing the rotational heat capacity of the equilibrium system of isolated impurity molecules (the ED case).

Additional arguments for or against the enhanced conversion in clusters can be furnished by the consequences that follow from this assumption. Let us assume that (i) the contribution of isolated CH_4 molecules (singles) to the heat capacity is negligible, (ii) the conversion rate in a cluster is independent of its size, and (iii) the rotational energy spectrum of the molecules in clusters is also independent of the cluster sizes. If these conditions are realized, the reduced heat capacity $C_{\text{rot}}/n'R$, where n' is the molecule concentration in the clusters, will be independent of the methane concentration n . And we remember that the number of CH_4 singles in a solution containing N particles is $Nn(1-n)^{12}$; correspondingly, the number of molecules in clusters is $Nn[1-(1-n)^{12}]$, i.e., $n' = n[1-(1-n)^{12}]$.

In Fig. 4 the heat capacity of the rotational subsystem in the solutions with 5%; 10% CH_4 is shown in the reduced coordinates $C_{\text{rot}}/Rn[1-(1-n)^{12}] - T$. It is seen that the reduced heat capacities of these solutions coincide at 5–8 K within the measurement error, i.e., they

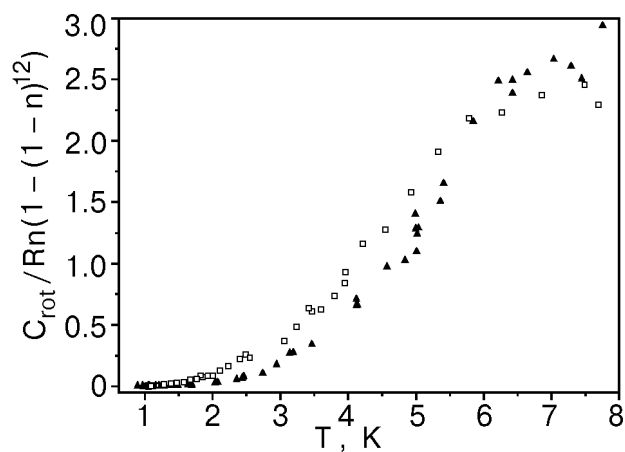


Fig. 4. Temperature dependence of rotational heat capacity of Kr- CH_4 solutions containing 5% CH_4 (\blacktriangle), 10% CH_4 (\square) in reduced coordinates.

are independent of the methane concentration. This supports the assumption of considerably enhanced conversion in clusters and suggests that the above three conditions are realized in this temperature interval.

At lower temperatures (see Fig. 4) there are some deviations from the universal dependence which exceed the experimental error. This may occur because conditions (ii) and (iii) (or one of them) are not fulfilled. According to [3], the first effective excited rotational level ($J = 1$) is somewhat lower for three-molecule clusters ($i = 3$) than for two-molecule ones ($i = 2$). Correspondingly, at rather low temperatures the heat capacity of the solution with $n = 10\%$, which contains more $i = 3$ clusters, should be appreciably higher than in the $n = 5\%$ case. Another reason may be connected with the conversion rate, which becomes dependent on the cluster size as the temperature is lowered.

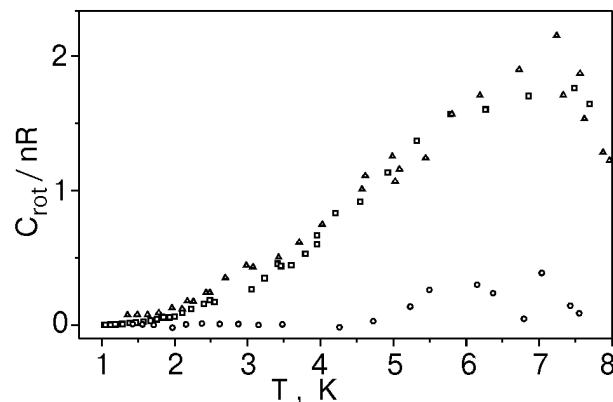


Fig. 5. Temperature dependence of reduced rotational heat capacity of binary Kr- CH_4 solutions containing 1% CH_4 (\circ), 10% CH_4 (\square) and the triple solution Kr-1% CH_4 -0.2% O_2 (\triangle).

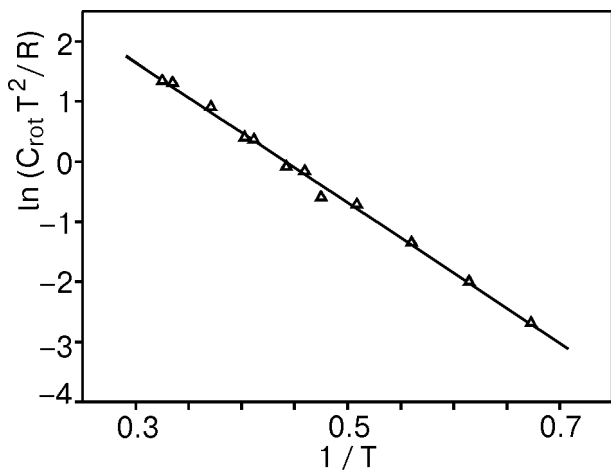


Fig. 6. Temperature dependence of C_{rot} of the Kr-1% CH_4 -0.2% O_2 solid solution in $\ln(C_{\text{rot}} T^2/R) - 1/T$ coordinates.

To estimate the effect of a paramagnetic impurity on the conversion rate and hence on the heat capacity, we investigated the heat capacity of the Kr-1% CH_4 -0.2% O_2 solution. The contributions of the impurities (CH_4 , O_2) were assumed to be additive. The contribution of O_2 to the heat capacity of the solution was estimated using the data of [20]. In the presence of O_2 the CH_4 contribution to the heat capacity is an order of magnitude higher than that in the Kr-1% CH_4 solution containing no appreciable paramagnetic impurities (see Fig. 5).

With an equilibrium distribution of the CH_4 modifications, the heat capacity at $T \leq 3$ K is determined by the position of the first excited level in the rotational spectrum of the CH_4 molecules (see Fig. 1). We assume that at $T \leq 3$ K some part of the CH_4 molecules influenced by the paramagnetic impurities convert so fast that their heat capacity corresponds to the equilibrium distribution (the ED case). Let this fraction of molecules be denoted as n'' . The value of n'' also includes a relatively small number of the fast-converting CH_4 molecules from the clusters. We then assume that the contribution of the rest of the CH_4 molecules, whose fraction is $(1 - n'')$, to C_{rot} is negligible. When the above three conditions are fulfilled, C_{rot} can be written as

$$C_{\text{rot}} = Nk_B \frac{n''}{T^2} E_1^2 \frac{g_1}{g_0} e^{-E_1/T}, \quad (3)$$

where N is the number of CH_4 molecules in the sample; E_1 is the first excited level energy; g_0 and g_1 are the degeneracies of the ground and the first excited levels, respectively; k_B is Boltzmann's constant. In Fig. 6 the measured C_{rot} of the Kr-1% CH_4 -0.2% O_2 solution is shown in the coordinates $\ln(C_{\text{rot}} T^2/R) - 1/T$.

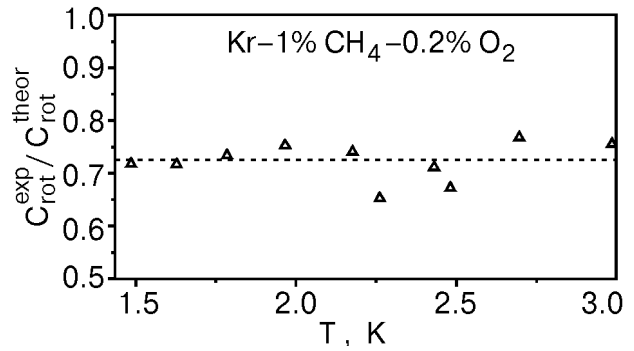


Fig. 7. Temperature dependence of the ratio of $C_{\text{rot}}^{\text{exp}}$ to $C_{\text{rot}}^{\text{theor}}$ for $E_1 = 11.7$ K.

The linear dependence $\ln(C_{\text{rot}} T^2/R) - 1/T$ is fulfilled within the experimental error, which indicates that our assumptions are realistic. The E_1 value (11.7 ± 0.4 K) was estimated from the slope of the obtained straight line and is in good agreement with the neutron-diffraction magnitude $E_1 = 11.7$ K [17].

The ratio of the experimental $C_{\text{rot}}^{\text{exp}}$ and the $C_{\text{rot}}^{\text{theor}}$ calculated for $E_1 = 11.7$ K on the assumption that all the CH_4 molecules convert during the effective time t_m of a single heat capacity measurement (the ED case) is shown in Fig. 7. It is seen that $n'' = 72\%$, which implies that only 72% of CH_4 molecules convert in the Kr-1% CH_4 -0.2% O_2 solid solution at $T \leq 3$ K during the effective time t_m of a single heat capacity measurement. This suggests that during the time t_m the conversion takes place in the CH_4 molecules which are situated in seven coordination spheres around the O_2 molecule.

Finally, we discuss the possibility of an orientational glass in our Kr- CH_4 solutions. At the CH_4 concentrations used in this study, we can only expect the orientational glass with an indirect interaction [12]. In such glasses the rotators interact through the strain fields which they form in the matrix. Our temperature and concentration dependences do not display any features typical for the heat capacity of such glasses [12]. This means that the shift of the CH_4 rotation energy levels caused by the indirect interaction of the CH_4 molecules is smaller than the distance E_1 between the ground and the first excited levels of the spectrum. It is quite possible that the glass-like behavior should be sought in the temperature and concentration dependences of CD_4 -Kr solid solutions because E_1 is smaller in that case.

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