

Thermal conductivity of solid krypton with methane admixture

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The thermal conductivity of CH_4 -Kr solid solutions is investigated at CH_4 concentrations 0.2–5.0% in the temperature range 1.8–40 K. It is found that the temperature dependence of the thermal conductivity has features typical of resonance phonon scattering. The analysis of the experimental results shows that the main contribution to the impurity-caused scattering of phonons is made by the scattering on rotational excitations of the nuclear spin T-species of CH_4 molecules. The phonon-rotation interaction parameter is estimated.

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1. Introduction

The scattering of phonons by the rotational motion of molecules in solids is much less understood than the phonon-phonon scattering is. At the same time there is experimental evidence that the phonon-rotation interaction in crystals can significantly influence both the absolute value and the temperature dependence of the thermal conductivity [1–12]. At low temperatures this effect can be predominant in systems with low-lying energy levels of the rotational motion of molecules [9]. Quantum molecular crystals (solid hydrogen and methane isotopes) and solutions of simple molecular substances in matrices of solidified rare gases belong to the above systems. To study the influence of molecular rotation upon the thermal conductivity of crystals, we chose solutions of methane in solid krypton.

Krypton and methane have close parameters of particle interaction and can therefore form a continuous solid solution over a wide range of concentrations [13].

The energy levels of CH_4 rotation in the Kr matrix are arranged so [14,15] that the phonon-rotation interaction can strongly influence the thermal conductivity at low temperatures. This is favorable for reliable separation of this interaction contribution to the thermal resistivity of the solutions.

The relative simplicity of the particles in the solution and the high symmetry of the host lattice along with information available about the rotational spectra of the CH_4 molecules in the Kr matrix make the description and interpretation of the thermal conductivity results comparatively easy.

Finally, the quantum character of the CH_4 rotation in the matrix attracts even more attention to this system. The methane molecule can exist in the form of three nuclear spin species – E, T, A, the total nuclear spins being 0, 1, and 2, respectively. Each species has its own systematics of rotational energy levels. The behavior of the impurity subsystem of the CH_4 -Kr solution is dependent on the concentrations of the above species. The characteristic time of conversion of the nuclear spin species in the solution increases with decreasing temperature and reaches several hours at helium temperatures [16]. We should remember that the experimental results correspond to the equilibrium distribution of the species concentrations only when the time of the experiment exceeds the characteristic conversion times.

2. Experiments

The thermal conductivity of solid krypton and Kr- CH_4 solutions (0.2, 0.5, 1.0 and 5.0% CH_4) were studied in the temperature range 1.8–40 K.

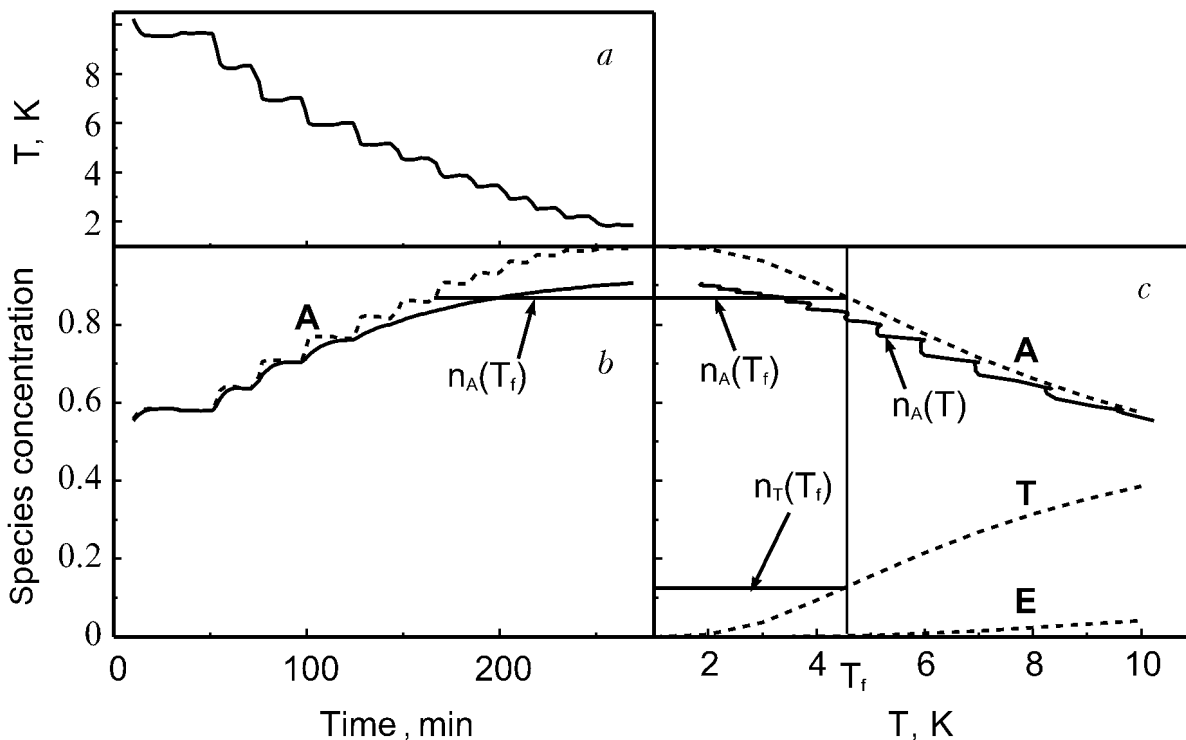


Fig. 1. Correlations between the temperature of the crystal and the CH_4 molecule distribution in nuclear spin species (illustrated for a Kr sample with 1% CH_4 admixture): dependence of the average temperature on time during measurement of thermal conductivity (a); time dependence of the equilibrium (dashed lines) and calculated (solid lines) concentrations of the species A in the impurity subsystem (b); equilibrium (dashed lines) and calculated (solid lines) concentrations of nuclear spin species as a function of temperature (c); $n_A(T_f)$ and $n_T(T_f)$ are the «frozen» concentrations of species A and T for $T = 4.6$ K.

The krypton used had the natural isotopic composition and chemical purity 99.94% (the impurities were 0.042% N_2 , 0.012% Ar, and 0.005% O_2). The chemical purity of the methane was 99.99%. The Kr- CH_4 mixture was prepared in the gas phase at room temperature.

The crystals were grown from the liquid phase in a cylindrical stainless steel container 38 mm long and 4.5 mm in inner diameter. The growth rate was 0.07 mm/min. The temperature gradient 0.18 K/mm was kept constant. The grown sample was cooled down to 30 K at a rate of 0.15 K/min, the gradient being the same.

The thermal conductivity was measured using the steady-state technique [17]. The total time taken to reach the steady state and to measure one value of the thermal conductivity varied with temperature from 2 h at 40 K to 20 min at the lowest temperature. The temperature dependence of the thermal conductivity $K(T)$ was taken at successively lower temperatures. As an example, Fig. 1,a shows the time dependence of the average temperature $T(t)$ which was obtained while measuring the ther-

mal conductivity of the sample with 1% CH_4 . The dependences $T(t)$ let us know whether the concentrations of the nuclear spin CH_4 species come to equilibrium during measurement (see below). The temperature dependence of the thermal conductivity was also taken on the 1% CH_4 sample at rising T . The K values measured at the same T points under rising and falling temperatures varied within the random experimental error (3–5%). In the sample with 0.5% CH_4 the thermal conductivity observed at 5 K remained unaltered when the crystal was warmed to 13 K and then cooled rapidly (for 5 min).

The thermal conductivity data for pure Kr and for Kr with four CH_4 concentrations are shown in Fig. 2. In the high-temperature region ($T > 20$ K) the results for pure Kr agree well with earlier data [18, 19]. In the vicinity of the thermal conductivity maximum the K value is about twice as high as in Ref. 19, which may be attributed to the better quality of our crystals. The thermal conductivity of solid Kr with CH_4 admixtures has not been studied before.

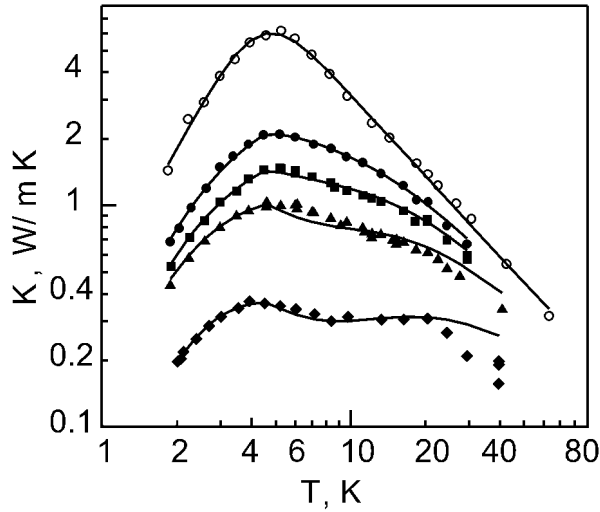


Fig. 2. Temperature dependence of the thermal conductivity of pure Kr (○) and Kr with CH₄ admixtures, %: 0.2 (●), 0.5 (■), 1.0 (▲), and 5.0 (◆); solid lines are calculated curves.

3. Results and discussion

It is seen in Fig. 2 that the CH₄ impurity strongly suppresses the thermal conductivity and alters the character of its temperature dependence. The latter feature is especially distinct in the solution with 5% CH₄. The $K(T)$ curve with a maximum at 5 K which is typically observed for pure Kr deforms into a curve with a dip near 8 K. This sort of dip is usually caused by the resonance scattering of phonons.

The thermal conductivity measured on our crystals is described within the Debye model:

$$K = \frac{k_B}{2\pi^2 s} \left(\frac{k_B}{\hbar} \right)^3 T^3 \int_0^{\Theta_D/T} \frac{\tau_{\text{tot}} x^4 e^x}{(e^x - 1)^2} dx, \quad (1)$$

where s is the sound velocity; Θ_D is the Debye temperature, $x = \hbar\omega/k_B T$; and τ_{tot} is the total phonon relaxation time for all resistive processes. The relaxation rate τ_{tot}^{-1} of the Kr-CH₄ solution is a sum of the relaxation rates of pure Kr and CH₄-induced phonon scattering:

$$\tau_{\text{tot}}^{-1} = \tau_{\text{Kr}}^{-1} + \tau_{\text{CH}_4}^{-1}.$$

The phonon relaxation rate of Kr includes the terms describing phonon-phonon scattering (U processes) τ_U^{-1} , boundary scattering τ_B^{-1} , scattering on dislocations τ_{dis}^{-1} , and Rayleigh impurity scattering τ_i^{-1} :

$$\tau_{\text{Kr}}^{-1} = \tau_U^{-1} + \tau_B^{-1} + \tau_{\text{dis}}^{-1} + \tau_i^{-1}. \quad (2)$$

The rates of the above mechanisms are described by the expressions of [20]:

$$\tau_U^{-1} = A\omega^2 T \exp(b/T), \quad (3)$$

$$\tau_B^{-1} = s/l, \quad (4)$$

$$\tau_{\text{dis}}^{-1} = D\omega, \quad (5)$$

$$\tau_{\text{imp}}^{-1} = \sum_i \frac{\Gamma_i V}{4\pi s^3} \omega^4. \quad (6)$$

Here l is the characteristic mean free path determined by the grain sizes in the sample; $\Gamma = c(\Delta M/M)^2$, where c is the concentration of point defects, M is the mass of the host particles, and ΔM is the mass difference between the host and impurity particles.

The parameters of relaxation time in pure Kr obtained by fitting to the experimental results are as follows:

U processes: (A), $c \cdot K^{-1}$	$4.41 \cdot 10^{-16}$,
(b), K	15.77,
Boundary scattering (l), m	$1.87 \cdot 10^{-5}$,
Scattering on dislocations: (D)	$2.09 \cdot 10^{-4}$,
Impurity scattering: (Γ)	$6.4 \cdot 10^{-4}$.

The isotopic scattering parameter Γ was not fitted but calculated from the concentrations and molecular weights of the impurities. The contribution of the N₂ and O₂ rotation to the thermal conductivity of pure Kr was not estimated because of a lack of information about the rotational spectra of N₂ and O₂ impurities in the Kr matrix. In fact, this contribution was effectively taken into account through selection of the other scattering parameters. The efficiency of this procedure is evident from the good agreement between the calculated curve and the experimental data for thermal conductivity of Kr (Fig. 2).

The CH₄ molecules contribute to the phonon scattering not only because their masses are different from those of the host atoms (Rayleigh scattering) but also because their rotational excitations come into interaction with phonons (phonon-rotation interaction). The expression for $\tau_{\text{CH}_4}^{-1}$ can therefore be written as a sum of the relaxation rates of these mechanisms:

$$\tau_{\text{CH}_4}^{-1} = \tau_{\text{Rayleigh}}^{-1} + \tau_{\text{rot}}^{-1} \quad (7)$$

The analysis of phonon scattering by a rotating molecule is a sophisticated theoretical problem. The mechanism of phonon scattering by an impurity with two energy levels was consistently described by Klein [3,21]. The expression in Ref. 3 was used to interpret the dips in the temperature dependence of thermal conductivity of alkali halide crystals [3,4] and of solid argon with admixtures [10]. While describing the phonon scattering on CH₄ molecules, we should take into account the occupation of the rotational levels, which is dependent on temperature. We used Klein's expression [3] to write the relaxation rate of the phonon-rotation interaction as

$$\tau^{-1} = \frac{1}{3\pi\rho(\omega)} \sum_i d_i S \frac{\gamma_i^2 (\omega/\omega_i)^4}{[1 - (\omega/\omega_i)^2]^2 + \gamma_i^2 (\omega/\omega_i)^6}, \quad (8)$$

where $\rho(\omega)$ is the phonon density normalized to unity; S is the occupation of the ground state; $\omega_i = E_i/\hbar$ is the resonance frequency, and d_i is the degeneracy of the excited state with energy E_i .

The parameter γ_i describes the relation between broadening of the rotational energy levels induced by the crystal field and the energy difference of these levels. This is the basic parameter of the phonon-rotation interaction in Klein's model. In studies [3,4] γ was used as a fitting parameter different for each level. When the phonon-rotation interaction is absent, $\gamma=0$. For a weakly hindered rotation γ must be much smaller than unity.

The experimental information about the rotational energy spectrum of CH₄ in crystalline Kr concerns only the first three excited levels (inelastic neutron scattering data [22]). These data refers to the low-energy part of the spectrum and are not sufficient to calculate $\tau_{\text{CH}_4}^{-1}$ in the whole working interval of temperatures. The energies of the rotational levels of the CH₄ molecule in the crystal field of the O_h symmetry were calculated as a function of the field strength [14,15]. We used the spectrum of [14] (Fig. 3) corresponding to the crystal field in which the energies of the low-lying excited levels are in good agreement with experimental values.

As was mentioned above, CH₄ molecules can exist in three species — E, T, A. They differ from each other by the total nuclear spin (0, 1, 2, respectively). Since the characteristic phonon scattering relaxation times are many orders of magnitude shorter than the conversion time, we can write

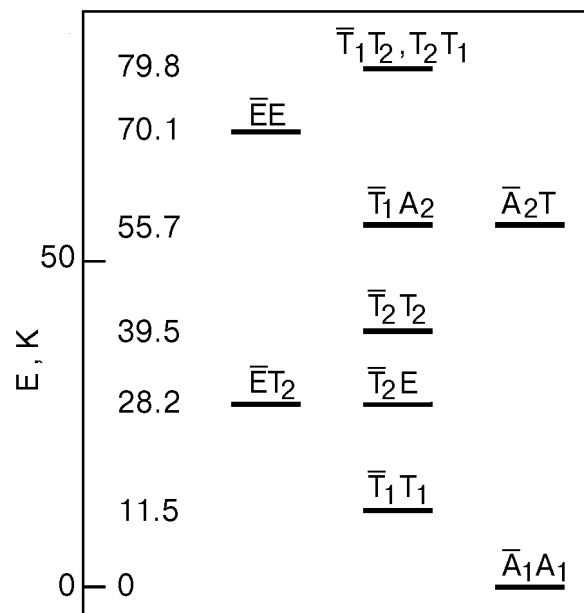


Fig. 3. Rotational spectrum of CH₄ molecule in the Kr matrix (crystal field symmetry O_h) for three nuclear spin species (according to [14]).

τ_{rot}^{-1} as a sum of expression (8) for each spin species τ_{α}^{-1} ($\alpha = E, T, A$):

$$\tau_{\text{rot}}^{-1} = c \sum_{\alpha} n_{\alpha}(T) \tau_{\alpha}^{-1}, \quad (9)$$

where c is the CH₄ concentration in the Kr matrix and n_{α} is the concentration of α species in the impurity subsystem.

The temperature dependence of the equilibrium species concentrations corresponds to the Boltzmann distribution. However, the equilibrium distribution may be disturbed significantly when the temperature changes during an experiment. According to [16], the characteristic time of CH₄ conversion in the Kr matrix increases with decreasing temperature and is 3.5 hours at 2 K.

The temperature dependences of the equilibrium E, T, A concentrations are shown in Fig. 1,c. It is seen that species A predominates at low temperatures. In Fig.1,c the equilibrium species-A concentrations $n_{A(\text{eq})}$ are compared with the corresponding $n_{A(\text{exp})}$ observed in our sample with 1% CH₄. The $n_{A(\text{exp})}$ values were calculated from the thermal prehistory of the sample using the parameters of [16] for CH₄ conversion in the Kr matrix.

In our experiment the distribution of the molecules in spin states comes to equilibrium above 6 K. At lower temperatures the concentration is considerably different from its equilibrium value. The reason is that at these temperatures the charac-

teristic conversion time is several times longer than the characteristic time of a thermal conductivity measurement (Fig. 1,b,c).

To take into account the deviations of the spin species concentrations from the equilibrium value, we calculated the thermal conductivity within the following model: A characteristic temperature T_f («freezing temperature») was introduced. It was assumed that above T_f the spin species concentrations had the equilibrium values. Below T_f the concentration of a species is assumed to be constant and corresponding to the equilibrium distribution at $T = T_f$. The feasibility of the model is evident from Fig. 1,c. The most suitable T_f is expected to be 4.3–5.0 K.

To bring the calculated and experimental temperature dependences of the thermal conductivity into agreement, we used the fitting parameters γ (phonon-rotation interaction) and l (boundary scattering). The intensity of the Rayleigh scattering by a CH_4 molecule was calculated to be $\Gamma = 0.655$ c. The parameters of the other scattering mechanisms were the same as for pure krypton. The parameters obtained by fitting at $T_f = 4.6$ K for different CH_4 concentrations are as follows:

CH_4 concentration (c), %	0.2	0.5	1	5
Boundary scattering parameter (l), 10^{-6} m	5.99	4.45	5.22	1.88
Phonon-rotation interaction parameter (γ)	0.029	0.027	0.029	0.023.

An increase in the impurity concentration usually leads to degradation of the crystal quality, which in turn is responsible for the decrease in the parameter l – the characteristic mean free path determined by the boundary scattering. We observed this on the sample with 5% CH_4 .

The calculated curves are shown in Fig. 2 (solid lines). The model proposed provides a good quantitative description of the measured thermal conductivity and reproduces the features of its temperature dependence. The model permits us to compare the contributions of two mechanisms of phonon scattering on CH_4 molecules – Rayleigh scattering and the scattering induced by the phonon-rotation interaction. For example, at $T = 8$ K the contributions of these mechanisms to the thermal resistivity are 0.2 and 2.5 m·K/W, respectively; i.e., the rotational scattering predominates.

The contribution of the T species to the resonance phonon scattering is dominant below 20 K (see Figs. 2, 3). The dip in the curve at 6–20 K is due to the resonance phonon scattering on low-energy rotational excitations of the T species. Below

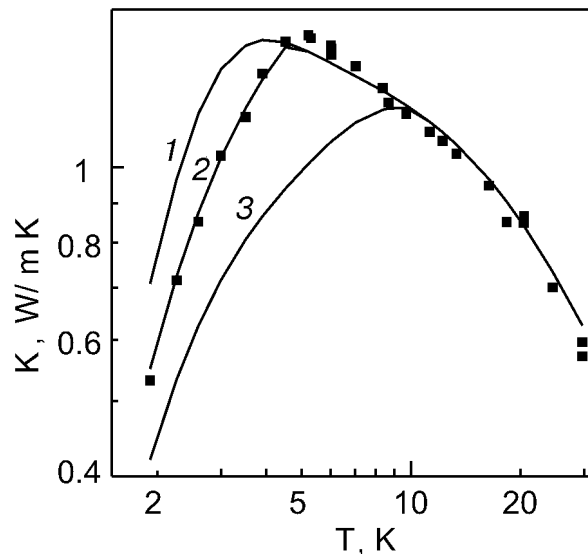


Fig. 4. Comparison of experimental data and calculated thermal conductivity curves for a Kr sample with 0.5% CH_4 . The calculation was done for various values of the «freezing temperature» T_f , K: O, equilibrium distribution in the whole region of measurements (1); 4.6 (2) and 10 (3).

6 K the behavior of the thermal conductivity is determined by the higher (nonequilibrium) concentration of the T species.

Figure 4 illustrates the agreement between the experimental and calculated temperature dependences of the thermal conductivity for the sample with 0.5% CH_4 . The calculation was made assuming (1) an equilibrium distribution of the spin species in the whole measurement region; (2) $T_f = 4.6$ K; (3) $T_f = 10$ K. The agreement is good at $T_f = 4.6$ K. The concentrations $n_A(T_f)$ and $n_T(T_f)$ of the A and T species at this temperature are shown in Fig. 1,c. It is seen that below $T = 4.6$ K the experimental curves deviate considerably from the equilibrium. Above 20 K the calculated curves run above the experimental ones. The discrepancy may be attributed to the fact that our simple calculation model does not include rotational levels whose energies exceeds 70 K.

It should be noted that the model used did not take into account the role of CH_4 clusters in phonon scattering. We actually assume identical energy spectra and conversion rates for clusters and isolated molecules. This simplification might be most conspicuous in the low-temperature part of the curve taken on the sample with 5% CH_4 . Nevertheless, the model describes the thermal conductivity of this sample quite well. In this context it would be interesting to study the low-temperature thermal conductivity of higher-concentration Kr– CH_4 solutions.

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