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Heat transfer in solid CH_4: Influence of an atomic impurity (Kr)

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The measurements of thermal conductivity of solid methane with krypton impurity (concentrations of the impurity were 0.015%, 0.338%, and 1.105%) were performed in the temperature range from 1.4 K to 20 K. The analysis of the experimental data of both pure and impurity containing crystals was performed within the framework of the time-relaxation model. The temperature dependence of thermal conductivity of solid methane was described by using the following phonon-scattering processes: boundary scattering, phonon-phonon scattering (U processes), scattering by point defects, and elastic interaction with the rotational motion of methane molecules. It was shown that the elastic interaction of phonons with almost freely rotating molecules (O_h symmetry sites) is the main phonon relaxation process that determines the thermal conductivity of methane in the low-temperature phase. The value of the phonon-rotational interaction parameter in this phase was obtained. The process of resonance phonon scattering on a heavy isotope impurity was used to describe the impurity effect of Kr. The analysis showed that the temperature dependence of thermal conductivity of doped methane can be described with the assumption that the introduction of the atomic impurity of Kr deforms the rotational spectrum of methane. [S0163-1829(98)02829-X]

I. INTRODUCTION

The results of studies of thermal conductivity of the low-temperature phase of solid methane have been published recently.[1] Thermal conductivity at maximum was found to be very low compared to atomic and simple molecular crystals. And, although it is known that the heat transport processes in this crystal are dependent on the phonon-rotation interaction, a theory of thermal conductivity in the low-temperature phase of methane is missing. Thermal conductivity of solid methane in the high-temperature phase (phase I) has been studied experimentally[2] and described with a model including the additional phonon scattering resulting from the correlation of free-rotational molecules in the crystal.[3] This paper presents results of the measurements of thermal conductivity of phase II of solid methane containing the impurity of Kr. It was assumed that the isotropic krypton impurity at concentrations below 1% would not affect the symmetry of mass centers in the crystal but would weaken the interaction of phonons with the rotational subsystem.[4–6] This, in turn, would allow the observation of quantum effects related to the transformation of the rotational motion of methane molecules upon the influence of the impurity. The results are discussed using the time-relaxation model based on the interaction of phonons with rotational excitations of molecules. This model is successfully applied to describe the experimental data of the thermal conductivity of phase-II solid methane, both pure and containing the atomic impurity.

II. EXPERIMENT

Thermal conductivity measurements of three samples of methane with krypton impurity were made in the temperature range from 1.4 to 20 K by the steady-state method, using the device described in Ref. 7. Samples were grown into a glass tube with the inner diameter of 6.4 mm and a length of 67 mm. Temperature and temperature gradient along sample were measured by germanium resistance thermometers. A relative error of the measured thermal conductivity magnitude did not exceed 10%.

Concentrations of Kr (natural isotopic contents) were 0.015%, 0.338%, and 1.105% and were determined with the mass spectrometer ''MASSTORR DX.'' CH_4 gas, which was used for the growth of samples, contained 1.76% CH_3D, 0.12% CHD_3, 0.043% N_2, and 0.007% O_2.

The crystals were grown from the gaseous phase by the desublimation method. Temperature and vapor pressure of the growth were a little below the triple point (88 K, 8.5 KPa). The sample growth rates varied in the range of 1.5 mm/h. After perfection of growth samples were cooled to 25 K with the cooling rate of about 1.2 K/h. The cooled samples were transparent without visual defects.

The time of setting of the temperature equlibrium in crystals was decreased by decreasing the temperature from 5 h at 20 K to 1 h at 5 K.

III. RESULTS AND DISCUSSION

The results of the measurements of thermal conductivity of krypton-doped methane crystals are presented in Fig. 3. It also includes the results of previous studies of phase II of solid pure methane[1] as well as the literature data for phase I.[2] For comparison, the thermal conductivity curves for crystals methane and argon[8] are also presented in the inset. The observed effect of the krypton impurity in the methane crystal is very distinct, despite the small value of thermal conductivity of the pure methane crystal. It appears to have the resonance character.

A. Phase II of pure solid CH_4

Prior to the analysis of the impurity effect, let us consider thermal conductivity of phase II of pure methane. In order to describe the temperature dependence of thermal conductivity of the high-temperature phase of solidified methane, Yasuda[3] proposed the model, according to which a phonon scattering occurs on correlated rotations of spherically symmetric molecules (O_h molecules). According to this author, the model poorly describes the results for the low-temperature part of phase I. Naturally, it is even worse for phase II, where only one from four molecules is O_h molecules. 3/4 of the molecules are orientationally ordered in D_{2d} symmetry sites (D_{2d} molecules).[9] Therefore, it was necessary to approach the heat transport in the low-temperature phase of solidified methane differently. The Callaway equation was used, with the assumption that the relaxation rate of normal phonon-phonon scattering processes is much smaller than in resistive scattering processes,[10]

$$K=\frac{k^4}{2\pi^2\hbar^3 v_s}T^3\int_0^{\Theta_D/T}\tau_{eff}(x)\frac{x^4\exp(x)}{[\exp(x)-1]^2}dx,$$

where $x=\hbar\omega/kT$, ω is a phonon frequency, $\tau_{eff}^{-1}(\omega)=\Sigma\tau_n^{-1}(\omega)$, τ_n^{-1} is a relaxation rate of a phonon-scattering process, Θ_D is the characteristic Debye temperature, v_s is the mean sound velocity.

Initially, three scattering mechanisms were included: crystal grain boundaries scattering,[11]

$$\tau_b^{-1}=\frac{v_s}{l},$$

phonon-phonon scattering[11] (U processes),

$$\tau_U^{-1}(\omega)=A\omega^2 T\exp\left(-\frac{\Theta_D}{bT}\right),$$

point defect scattering, impurity[11] (by Rayleigh),

$$\tau_p^{-1}=\frac{a_0\Gamma}{4\pi v_s^3}\omega^4,$$

where l is characteristic crystal dimension, a_0 is the lattice parameter, $\Gamma=\Sigma c_n\epsilon^2$, c_n is a impurity concentration, $\epsilon=M_i/M-1$, M and M_i are the mass of a matrix molecule and of an impurity atom, respectively.

Verified calorimetric data that might serve to calculate Debye temperature are not available. Therefore it was calculated from the sound velocity measurements. The results of sound velocity measurements[12] and lattice parameters,[13] extrapolated to 0 K ($v_l=2858$ m/sec, $v_t=1608$ m/sec, $a_0=5.858\times10^{-10}$ m, respectively) were used in calculations. Sound velocity was averaged with the following equation:

$$v_s=\left(\frac{(1/v_l^3+2/v_t^3)}{3}\right)^{-1/3}$$

and

TABLE I. Parameters of relaxation rates obtained from initial fitting.

Boundary scattering, l (m)	6.15×10^{-5}
Phonon-phonon scattering (U process)	
factor, A (1/sec K^3)	2.22×10^6
power, b	8.16
Point defect scattering (Rayleigh, impurity), Γ	9.4×10^{-4}

$$\Theta_D=2\frac{(3\pi^2)^{1/3}\hbar v_s}{ka_0}.$$

In further calculations the values of $v_s=1737$ m/sec and $\Theta_D=144.4$ K were used.

Parameters l, A, b, Γ obtained from the initial fitting of the Callaway equation to the experimental data are presented in Table I. A curve of the resulting calculation is presented in Fig. 1 (dotted line).

The value of the boundaries scattering parameter resulting from the calculations seems sensible. The value of scattering by point defects is 2.7 times higher than the one expected from the concentration of impurity that was present in the samples. According to the spectrometric analysis of the initial gas, the Γ value is calculated as 3.99×10^{-4}. However, the value of the b parameter in the exponential part of the expression for the U processes does not match the current models. It is four times higher from the expectations of the classical theory of the three-phonon scattering processes. Usually, the expression for the U processes applied by us in the analysis yields b values of 2–3. For pure crystals, this parameter limits the value of thermal conductivity at maximum.[11]

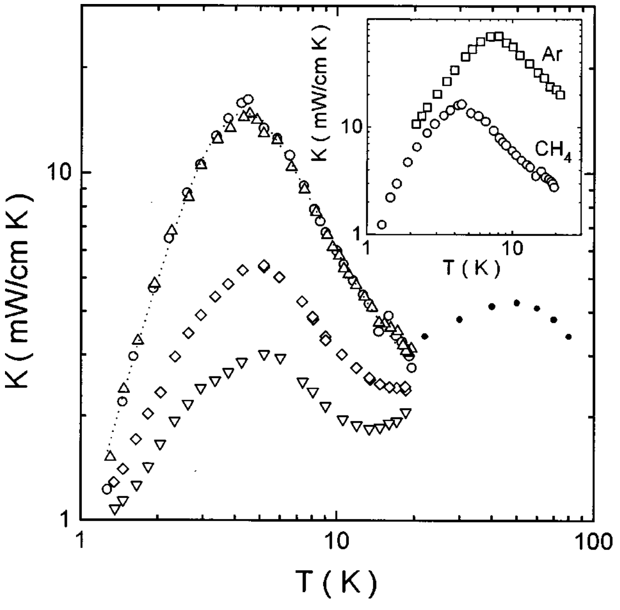

FIG. 1. Temperature dependences of thermal conductivity for solid CH_4 (○) (Ref. 1) and for CH_4 crystals with Kr impurity (experiment): △, 0.02% Kr; ◇, 0.34% Kr; and ▽, 1.1% Kr (present work); ●, data for phase I from Ref. 2. Dotted line is the dependence obtained from initial fitting of pure CH_4 data. The comparison of thermal conductivity of solid CH_4 (phase II) and Ar (Ref. 8) is presented in the inset.

TABLE II. Parameters of relaxation rates obtained from final fitting by the Callaway equation ($E_0=\hbar\omega_0$ is rotational energy level).

Boundary scattering, l (m)		6.13×10^{-5}	
Phonon-phonon scattering (U process)			
factor, A (1/sec K^3)		1.42×10^{6}	
power, b		2.27	
Point defect scattering (Rayleigh, impurity), Γ		3.98×10^{-4}	
Phonon-rotational scattering	E_0 (K)	$C(\omega_0)$	V (K)
D_{2d} molecules	1.66	63	21.7
	2.51	14	16.84
O_h molecules	12.7	9	23.87
	34.6	25	102.5

The calculations, despite the good agreement with the experiment, indicated that the chosen mechanisms of scattering did not suffice for the adequate description of heat transport in the low-temperature phase of solid methane. Additional scattering mechanisms are present in phase II of CH_4 and determine the behavior of thermal conductivity.

The small value of thermal conductivity of phase II of CH_4 indicates that there is a strong phonon scattering on rotations of methane molecules. Previous calculations showed that the biggest impact of this process is exhibited to the left of the maximum of thermal conductivity. Taking into account the fact that 1/4 of the molecules in the crystal are O_h molecules, it seems natural to assume that these molecules have the essential contribution to the additional phonon scattering. The energies of lowest rotational excitations for O_h molecules are 12.7 K (ninefold degenerated level) and 34.6 K (25-fold degeneration).[14,15] For the low-lying levels of D_{2d} molecules the corresponding values are 1.66 K (ninefold degeneration) and 2.51 K (double degeneration).[16] High-lying levels for the molecules of both types are located above 60 K.[17] Only the two lowest excitation levels were included in the further analysis of the experimental results.

It is necessary to introduce a mechanism describing scattering by rotating molecules. For this, the resonance phonon scattering by a two-level system was taken. This Raman-type process was successfully used to describe the interaction of acoustic and optical phonons in Ref. 18. In our case we have a much better basis to use this process for interaction of phonons with rotational motion of molecules of explicitly quantum character. Here, the rotational spectrum of molecules is presented as a series of two-level systems that consist of the ground and excited rotational levels.

For this case, the phonon relaxation rate is described as[18]

$$\tau_r^{-1}(\omega)=\frac{3}{2\pi\hbar^2}\sum\frac{|V|^4C(\omega_0)}{\rho^2v_s^7}\omega^4\left(\frac{2\omega_0}{\omega_0^2-\omega^2}\right)^2 \times\left(1-\tanh^2\frac{\beta\omega_0}{2}\right),$$

where ω_0 is the excited rotational level frequency (considering two lowest rotational levels of both O_h and D_{2d} molecules), $C(\omega_0)$ is the number of rotational states (by taking into account the degeneration) at the frequency ω_0 per unit volume (in this case it is the unit cell volume), V is the phonon-rotational matrix element (parameter of fitting), $\rho=539.753$ kg/m is the density, and $\beta=\hbar/kT$.

The final result of the fitting including all phonon-scattering processes with scattering on rotational modes of O_h and D_{2d} molecules is presented in Table II and in Fig. 2 (solid line). The role of the phonon-scattering processes is demonstrated in Fig. 3 that shows intensity of the relaxation rate versus the phonon energy at different temperatures. Above 4 K the scattering on O_h molecules begins to dominate over other scattering processes for phonons between 10 and 50 K that are the most important for carrying heat in the crystal in the temperature range from 3 to 20 K.

The assumption that the phonon scattering through the interaction with rotating methane molecules is the main phonon-scattering process allowed us to describe the thermal conductivity of solid methane in the low-temperature phase. The results of the calculations indicate that the scattering on spherically symmetric O_h molecules contributes the most to the phonon scattering and causes the small thermal conductivity of methane in phase II. This is the primary difference between the model proposed in this paper and the one de-

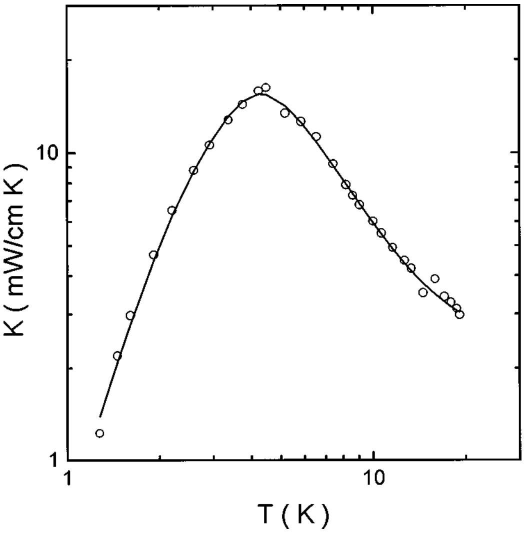

FIG. 2. The temperature dependence of thermal conductivity for solid CH_4. The points (○) are experimental data and the solid curve is the result of final fitting by Callaway model.

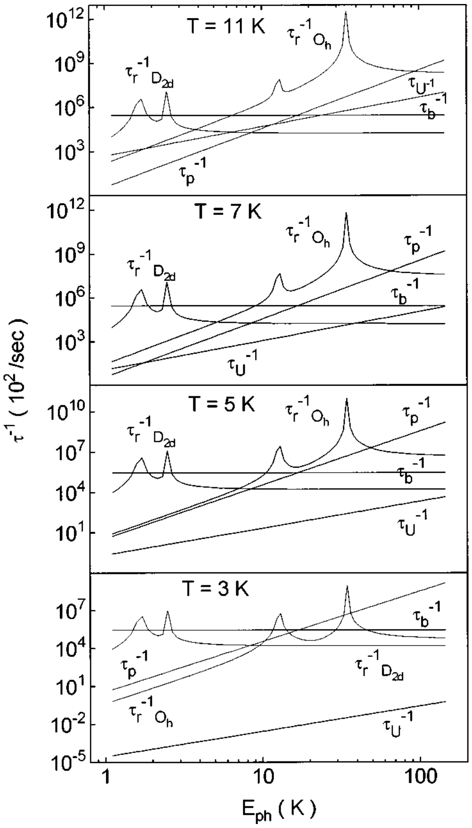

FIG. 3. Illustration of the relative magnitude of relaxation rates for different phonon-scattering processes vs phonon energy at different temperatures.

scribed in Ref. 3 for the high-temperature phase. Comparing these two models, each describing the thermal conductivity of a particular phase of solidified methane, one can say that the character of the phonon-rotation interaction changes upon the phase transition, which is related to the ordering of 75% of the molecules in the crystal. While in the high-temperature phase the noncentral interaction exhibits itself through correlated molecular rotations, in the low-temperature phase it occurs through excitations of rotational motions of individual molecules. A theoretical estimation of the phonon-rotation interaction has not been done, but the order of obtained values (100 K, see Table II) seems reasonable.

B. Kr-doped crystals CH_4

The model of heat conductivity of solid methane described above will now serve as a basis for the analysis of the effects of doped solid methane with a Kr atomic impurity obtained in our experiments.

The Lennard-Jones parameters for the krypton atom are similar to those of the methane molecule.[4] This atom has a particular property of an ''inactive'' component able to weaken molecular (noncentral) interactions in phase II of CH_4, because introduction of Kr does not affect the fcc structure of centers of mass.[5,6]

The situation of a Kr atom doped to solid CH_4 is similar to the situation of neon impurity in solid parahydrogen. The phonon scattering on heavy isotopic impurities[19] was used successfully to describe the thermal conductivity of solid parahydrogen with the neon impurity.[20] Thus, following Ref. 20 this phonon-scattering process was included in the description of Kr-doped CH_4 crystals:

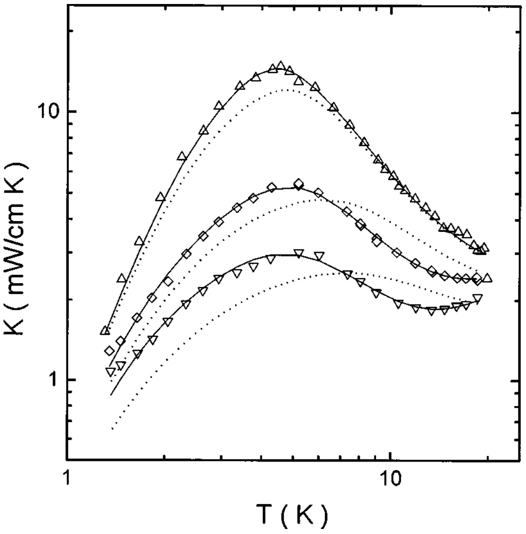

FIG. 4. The temperature dependences of thermal conductivity of methane crystals with Kr impurity. Symbols for experimental data have the same values as in Fig. 1. Dotted curves are obtained from the Callaway equation using the parameters for pure CH_4 (Table II) and the phonon scattering by heavy isotopic impurity (without fitting parameter procedure). Solid curves are the results of fitting of rotational levels energy of O_h molecules and concentration of Kr impurity.

$$\tau_i^{-1}(\omega)=\frac{3/2\pi c\epsilon^2\omega(\omega/\omega_D)^3}{(1-\omega^2/\omega_r^2)^2+9/4\pi^2\epsilon^2(\omega/\omega_D)^6},$$

where $\omega_r=\omega_D/(3\epsilon)^{1/2}$, $\omega_D=k\Theta_D/\hbar$ is the Debye frequency; in the case of Kr-doped CH_4 crystals $\epsilon=4.25$ $(M_i/M-1)$.

Calculated curves are presented together with the experimental data in Fig. 4 (dotted lines). Clearly, the experimental data could not be well described by a simple addition of the

TABLE III. Parameters of relaxation rates obtained as a result of fitting experimental data for CH_4 crystals with Kr impurity by the Callaway equation. Parameters for boundary scattering, *U* process, point defect scattering, and phonon-rotational scattering (D_{2d} molecules) are the same as with pure solid CH_4 (see Table II). $E_0=\hbar\omega_0$ and (calculated c_{Kr}), where c_{Kr} is the concentration of Kr, are the result of fitting; *M-S* test c_{Kr} is the result of mass-spectrometry analysis.

Heavy isotopic impurity scattering (c_{Kr})		Phonon-rotational scattering (O_h molecules)		
M-S test	Calc.	E_0 (K)	$C(\omega_0)$	*V* (K)
1.5×10^{-4}	2.54×10^{-5}	12.7	9	23.87
		34.6	25	102.5
3.38×10^{-3}	1.78×10^{-3}	11.8	9	23.4
		28.9	25	98.93
1.105×10^{-2}	4.68×10^{-3}	9.77	9	26.12
		24.9	25	91.81

phonon-scattering process by heavy isotopic impurity. It was necessary to variate the rotational levels of O_h molecules and concentration of impurity. The results of the fitting are presented in Fig. 4 (solid lines) and the obtained parameters in Table III.

As can be seen in Table III, doping the crystal results in the lowering of the energies of excitations of rotational levels of O_h molecules. The most probable reason is the lowering of the crystal-field symmetry in the O_h lattice sites by impurity atoms. It results in the splitting of the excited rotational levels. But the observed effect is the shift of the effective spectrum of O_h molecules towards the D_{2d} spectrum because of the perturbation of symmetry of the octopole-octopole interaction that results in retarding the rotation. Inelastic neutron-scattering studies of methane-krypton solutions at Kr concentrations higher than 2% showed that disturbance of the impurity atoms in noncentral interactions of methane molecules with the increase of their concentration drives to a characteristic shift of both tunneling levels and levels of the weakly hindered rotator.[21] For Kr concentrations of 10–20 % a differentiation between ordered and almost free-rotational molecules gradually vanishes with the impurity concentration increase.[21] Thus, at smaller impurity concentrations the influence of Kr impurity differs from that at concentrations more than 2%.

The proposed model does not describe the experimental data for doped crystals at the lowest temperatures (1.4–1.8 K) too well. This is possibly caused by a deformation of the spectrum of D_{2d} molecules, seen previously in neutronographic studies.[21] However, the temperature range of the experiments will have to be extended towards lower temperatures before one can draw conclusions.

IV. CONCLUSION

A low-temperature phase of solid methane is a unique object to study effects related to rotational excitations of molecules in a crystal. The unique position of methane in this phase is that molecules in the crystal exist in two states, i.e., oriented molecules (symmetry state D_{2d}) and almost freely rotating molecules (symmetry state O_h). We studied the effect of a small Kr impurity (concentrations smaller than 1%) on heat transfer in phase II of solid methane. A strong influence of the impurity on the thermal conductivity of the Kr-doped crystals was discovered. A time-relaxation model was obtained that described the behavior of the thermal conductivity of solid methane, both pure and with the krypton impurity, in the temperature range from 1.4 to 20 K.

We reach the following conclusions as a result of the investigation.

(1) The main phonon-scattering process in pure solid CH_4 (phase II) is the scattering by rotational excitations of almost freely rotating molecules.

(2) The magnitude of phonon-rotational interaction in phase II is of the order of 100 K.

(3) The influence of a krypton impurity on the thermal conductivity has a resonance character at a temperature of about 12 K.

(4) Deformation of the spectrum of a freely rotating molecule towards the effective decrease of energy levels, as a consequence of disturbance of octopole-octopole interaction symmetry of molecules of CH_4, is, first of all, the result of the influence of a krypton impurity at concentrations below 1%.

(5) The mass impurity effect of Kr in CH_4 turned out to be considerably weaker than the usual isotopic impurity effect. It is evidently connected with the competition of impurity scattering with phonon-rotational interaction in solid CH_4.

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