The plateau effect in thermal conductivity of solid hydrogen with neon impurity

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The thermal conductivity of solid hydrogen with 1–2 ppm Ne impurity was investigated in the temperature range 1.5–10 K on samples grown from the liquid phase at various growth rates. The result differ qualitatively from those obtained on samples grown from the gas phase: the thermal conductivity curve exhibited a dip in a broad plateau. The relaxation model is suggested to explain the effect supposedly due to linear impurity structures, arranged on dislocation lines. A comparison with the case of isolated neon atoms homogeneous distributed in the solid hydrogen is made.

Dedicated to V.A. Slyusarev's memory

Introduction

The same as helium, solid hydrogen has a very high thermal conductivity [1,2], which near the maximum is very sensitive to defects. For example, 1 ppm of the neon impurity entails a more than an order of magnitude decrease. An impurity anomaly of the resonance type was observed in gas-grown samples, in which the distribution of neon is homogeneous [3,4]. It was demonstrated that the solubility of neon in hydrogen is near 100 ppm [5]. So, it could be presumed that experiments with neon concentrations about 1 ppm would not involve the decomposition of the solution. Note that in those experiments solid parahydrogen contained an equilibrium concentration of orthospecies (0.21%). In special experiments it was proved [6] that by reducing considerably the ortho concentration (down to 0.05% o-H_2) did not result in noticeable changes of the thermal conductivity. Influence of the natural isotope impurity (deuterium) could also be neglected.

The resonance anomaly in the thermal conductivity of weak Ne in p-H_2 solid solutions is explained by the role of quasi-local vibrations (QLV) due to the presence of the heavy impurity. A specific and extremely important role in almost ideal crystals belongs to the processes of phonon–phonon scattering (N-processes), which redistribute the phonons quasi-momentum.

This paper reports results for the system of parahydrogen–neon with extremely low concentrations of the heavy neon impurity. In particular, we studied influence of the crystal growth procedure on the thermal conductivity for the case when samples were grown from the melt, which can results in a redistribution of impurities during solidification.

Experiment

Samples growth and thermal conductivity measurements of solid hydrogen with $(1-2) \cdot 10^{-4}$ ppm neon were performed in the cell described in [3]. The procedure was as follows. After the thermal conductivity of a vacuum deposited sample was measured it was melted and recrystallized at various growth rate. In Fig. 1, results of such studies are shown for the concentration of neon 1 ppm for two different growth rates in comparison with data for the vacuum deposited sample of the same concentration. As evident from the Fig. 1, the faster growth rate did not bring any differences compared with the sample growth directly from the gas phase. However, the slower rate changes the behavior. It seems that the reason is in a different impurity distribution in the sample. The slower growth led to the plateau seen in the upper part of the curve.
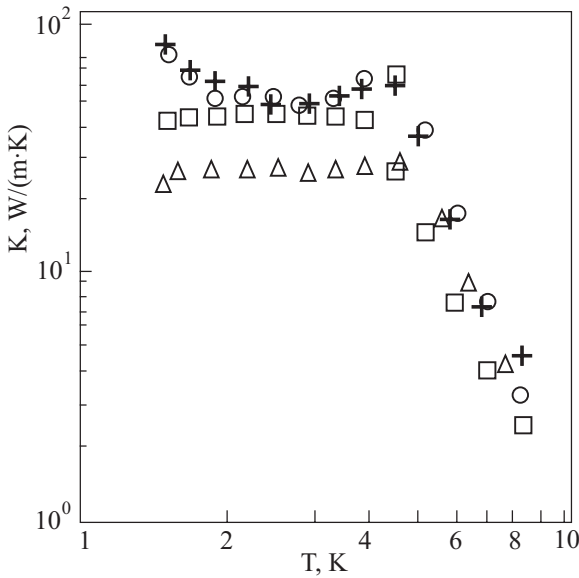
Fig. 1. Experimental temperature dependences of thermal conductivity $(p\text{-}H_2)_{1-c}Ne_c$ for various Ne concentrations and different manner of growing (received common with B.Ya. Gorodilov and A.I. Krivchikov) ($c = 1$ ppm for all samples besides triangles): sublimation from gas phase (O); from liquid after remelting under the rate of growth 8 mm/h (□); from liquid after remelting under the rate of growth 16 mm/h (+); ($c = 2$ ppm) from liquid under the rate of sample growth 8 mm/h (△).

Results and discussion

The sublimation energy of neon and its melting temperature are higher than those of hydrogen which limits neon solubility in hydrogen and provokes a decomposition of the solution when the neon concentrations exceeds a certain value. For very slow growth from the melt even with extremely small concentrations, at least a partial segregation could be expected.

On the basis of a simple gas-kinetic equation

$$K = \frac{1}{3} C v^2 \tau, \qquad (1)$$

where τ is relaxation time of the most important phonons [7]; C is the heat capacity per unit volume; v is the average phonon velocity, a qualitative estimate of the thermal conductivity as a function of temperature could be done. If the phonon scattering occurs primarily on certain defects and the relaxation rate is a power dependence: $\tau^{-1} \sim \omega^z$, where ω is the phonon frequency.

At sufficiently low temperatures the most important phonons for thermal conductivity are those with the frequencies of order the temperature. Then $x = \hbar\omega/kT$ is approximately constant [7]. Since the low-temperature heat capacity follows the law $C \sim T^3$, we get

$$K \sim \omega^{3-z}. \qquad (2)$$

Let us consider the case when dislocation scattering is the main heat resistance mechanism. If the elastic fields of dislocations scatter predominantly, $\tau^{-1} \sim \omega$ [7]. Then from Eq. (2) we have $K \sim T^2$. Such dependence is really observed, for example, after a rapid growth or a thermal shock. For the scattering on dislocation cores we have $\tau^{-1} \sim \omega^3$ [7]. In the latter case the thermal conductivity is temperature independent. However, manifestations of scattering on dislocation core was never observed in practice. Obviously it can be explained in the following way: the elastic fields of dislocations are more long range, while the core size is smaller (a few a lattice parameters). Consequently, the main dislocation contribution in the low-temperature thermal conductivity will be due to the elastic fields of dislocations. However, the situation might change, if the cores became more intensive scatters, for example, chains of with impurities present. For a fixed linear cylinder of a radius r, Relay's expression becomes $\Gamma(\omega) \sim r^4\omega^3/v^3$, that is the relaxation rate will be

$$\tau^{-1} = SN \frac{r^4\omega^3}{v^2}, \qquad (3)$$

where N is the number of rigid cylindrical objects per unit area, S is an empiric constant (we put in this work $S = 1$, see Table 1). More detailed calculations of the thermal conductivity requires taking into account the contribution of all phonon modes and of the N-processes, which are nonresistive, but actively redistribute the energy of elementary excitations.

It could be done within the framework of the relaxation model with N-processes [7,11]:

$$K = K_1 + K_2, \qquad (4)$$

$$K_1 = \frac{k}{2\pi^2 v}\left(\frac{kT}{\hbar}\right)^3 \int_0^{\theta/T} \frac{\tau_C x^4 e^x}{(e^x-1)^2} dx,$$

$$K_2 = \frac{k}{2\pi^2 v}\left(\frac{kT}{\hbar}\right)^3 \times$$

$$\times\left(\int_0^{\theta/T} \frac{\tau_C}{\tau_N} \frac{x^4 e^x}{(e^x-1)^2} dx\right)^2 \left(\int_0^{\theta/T} \frac{\tau_C}{\tau_N \tau_R} \frac{x^4 e^x}{(e^x-1)^2} dx\right)^{-1},$$

where $\hbar$ is Planck's constant, θ is the Debye temperature (for solid hydrogen, $\theta = 118.5$ K [5]), $\tau_C^{-1} = \tau_R^{-1} + \tau_N^{-1}$ is the combined relaxation rate of resistive (τ_R^{-1}) and normal (τ_N^{-1}) processes. In our work, in addition to (3), the fol-

Table 1. Parameters of phonon–phonon scattering and of other processes

Scattering mechanism	Parameter	Scattering rate	Notes
Boundaries	$L = 3$ mm	$\tau_{imp}^{-1} = v/L$	[1,2,5]
N-processes	$A_N = (1-4)\cdot 10^5$	$\tau_N^{-1} = A_N T^6 x^2$	[5,12]
U-processes	$A_U = 2\cdot 10^{-15}$, $E = 38.4$ K	$\tau_U^{-1} = A_U T^3 x^2 \mathrm{e}^{-E/T}$	[5,12]
Impurity strings	$\mathrm{const} = N r^4 \cdot 10^{-24}$	$\tau^{-1} = \mathrm{const}\cdot \dfrac{\omega^3}{v^2}$	[7]
Resonant impurity scattering	$\varepsilon = 9$, $c_1 = 10^{-6}$, $c_2 = 2\cdot 10^{-6}$, $\omega_0 = \dfrac{\omega_D}{\sqrt{3\varepsilon}} = 2.98\cdot 10^{12}$	$\tau^{-1} = \dfrac{f(\omega/\omega_D)^6}{[1-(\omega/\omega_0)^2]^2 + (2\pi\varepsilon/2)^2}$, $\quad f = \dfrac{3}{2} c\pi\varepsilon^2\omega^4/\omega_D^3$	[3,13]

lowing relaxation rates of resistive and normal processes were chosen [3,12]:

$$\tau_U^{-1} = A_U T^3 x^2 \mathrm{e}^{-E/T}, \quad \tau_N^{-1} = A_N T^6 x^2, \quad \tau_B^{-1} = \frac{v}{L}; \quad (5)$$

$$A_N \approx 991.6 \hbar N_A^{5/3}\, \frac{\gamma^2}{\mu V^{2/3}\theta^5},$$

where μ is the molar mass, γ is the Grüneisen constant, V is the molar volume, N_A is the Avogadro number. In Eq. (5) L is the dimension of the crystals, $E = \theta/\alpha$ is the constant of U-process activation. The relaxation rates of U-processes in parahydrogen with the heat flow oriented transversally and parallel to the crystallographic axis of hcp lattice, the following expressions have been obtained [12]:

$$\tau_{UT}^{-1}(\omega) = 2.4\cdot 10^{-15}\omega^2 T \exp(39.4/T),$$

$$\tau_{U\|}^{-1}(\omega) = 1.4\cdot 10^{-15}\omega^2 T \exp(31.8/T)$$

The values of the constants are placed in Table 1.

Let us assume that during slow crystallization a distribution of impurity atoms takes place in chains. For the new mechanism of phonon scattering by linear structures to be efficient the average distance between nearest impurities in a chain must be at least comparable with the wave lengths of the most important phonons at the proper temperature. For estimations we consider the left part of the plateau in Fig. 1. We assume that the start of the plateau from the low-temperature side occurs when the role of impurity scattering becomes predominant compared to boundary scattering. Then we could assume that $\tau_{bound}^{-1} \sim \tau_{imp}^{-1}$, arriving at the estimated density $N \sim 10^{13}$ m^{-2} for linear chains. A similar estimate can be obtained for the right edge of the plateau, but this time, we must compare τ_{imp}^{-1} with the inelastic phonon–phonon processes: $\tau_U^{-1} \sim \tau_{imp}^{-1}$.

It is possible to take for τ_U^{-1} the same parameters as for pure parahydrogen or the optimum for H$_2$–Ne mixtures [5]. Then we get the same order of N for impurity strings. Taking into account that the radius r of area of dislocation cores is equal to a few lattice constants, we can state that the present estimate of N is consistent with literary data [13].

To evaluate the average distance a' between impurities in a string we assume that all impurities are in linear structures. Then we get a simple formula $a' = N\mu/(\rho N_A c) = 10^{-9}$ m, where ρ is the molar density of hydrogen, c is the neon concentration. It is less than the wave lengths of the most important phonons in the temperature range of experiment. Since at lowermost temperatures the length of such waves is large, the boundary scattering is the most effective resistive mechanism. Above or near 4–5 K the wave length of such phonons decreases. Therefore impurities here are main phonon scatterers in the resonance mechanism of QLV with only one frequency (Table 1). However, as impurities aggregate in chains, such resonance «hole» evidently cannot exist. This is what we have in Figs. 1, 2,*a* for the concentration of 1 ppm: the transition on both sides of the plateau occurs with a dip without any previous growth. If the concentration of neon is twice as large (Fig. 2,*b*), there is a tendency of the thermal conductivity to increase at the right side. It might be related to some insignificant part of impurities which did not enter in chains in the process of slow growth and remained isolated and randomly distributed in the matrix of solid parahydrogen.

Calculated thermal conductivities are shown in Fig. 2. Here the relaxation model (5) was employed with the impurity mechanism (3) in comparison with the impurity mechanism of QLV with only one resonance frequency. One can see that the concentrations of 1 and 2 ppm result actually in a plateau.
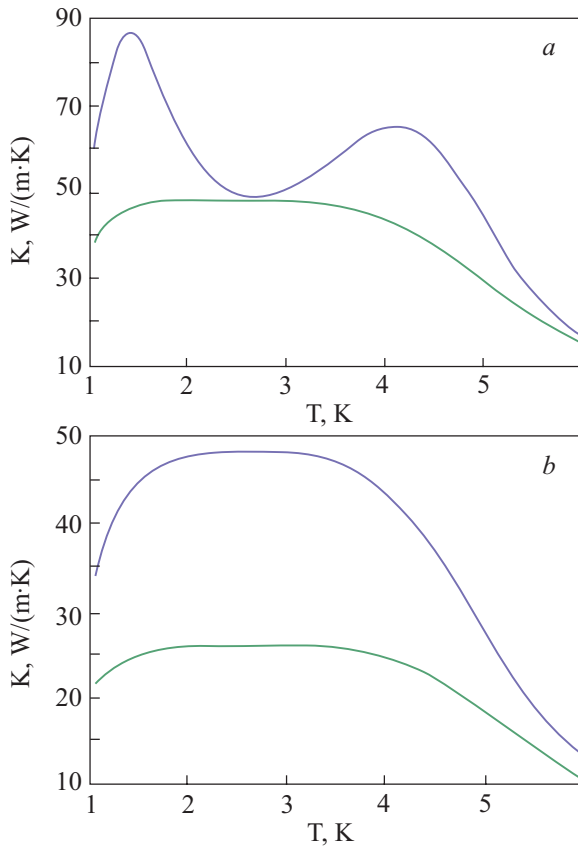
Fig. 2. Calculated temperature dependencies of the thermal conductivity $(p\text{-}H_2)_{1-c}Ne_c$. On Fig. 2,*a*: $c = 1$ ppm, up curve is for resonant case with only one impurity frequency; bottom curve — for linear impurity model. On Fig. 2,*b*: up curve — linear impurity structures with $c = 1$ ppm; bottom curve — linear impurity structures with $c = 2$ ppm.

We feel that we can formulate the following physical interpretation of the plateau. Unlike in samples grown from gas with homogeneously distributed isolated neon impurities, characterized by a unique frequency, strings form a spectrum in slowly grown samples prepared. Therefore, it is these frequencies that are solely important for heat transport, the thermal conductivity becoming a linear function temperature. In the low temperature, the thermal conductivity (proportional to T^3) due to boundary scattering can be observed. On the other hand, the high-temperature edge of the plateau will be «cut» by U-processes.

Conclusions

Our results give evidence that the effect discovered weak $(p\text{-}H_2)_{1-c}Ne_c$ solutions in the thermal conductivity (an unusual symmetric plateau) can be described and explained as being due to linear aggregates of impurities. This effect can be observed in slow grown samples. Such a transition from the spatially homogeneous distribution of isolated atomic impurities to their segregation in chains provides a new collective mechanism of phonon scattering.

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