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Thermal conductivity of solid nitrogen

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Thermal conductivity of crystalline natural nitrogen was investigated over the temperature range 1.2–38 K. The temperature dependence of thermal conductivity of α-nitrogen has been determined in temperatures below 18 K. The thermal conductivity coefficient reaches the maximum value 250 mW/cm K at 3.6 K. The results of the experiment below 14 K can be well described by integral equation obtained by the method of Callaway. Relaxation times for various mechanisms of phonon scattering have been determined. The results of our experiments are in accord with earlier literature data for temperatures above 18 K.

INTRODUCTION

Solid nitrogen belongs to the group of molecular crystals with linear molecules, which, besides rare-gas solids, are the simplest crystals with regard to crystal structure, lattice dynamics, and other physical properties.

Nitrogen, not only because of being one of the elements of greatest abundance but also because of several interesting properties, was, and still is, subjected to intense study. Its properties were investigated by, among others, Raman and infrared spectroscopy, and x-ray, electron-, and neutron-scattering methods (see, e.g., Refs. 1–10). Also propagation of sound,[11] specific heat,[12,13] and thermal expansion[14,15] have been researched.

Solid nitrogen, being in equilibrium with its vapor, exists in two crystallographic phases. The structure of low-temperature α phase ($T < 35.61$ K) is fcc with orientational ordering of N_2 molecules (space group $Pa3$).[16,17] The higher-temperature β phase ($35.61 < T < 63.15$ K) does not exhibit long-range orientational ordering; the crystal has hexagonal structure with c/a ratio close to that of close packing of spheres. The structure of the β phase belongs to the space group $P6_3/mmc$.

The thermal conductivity coefficient λ of nitrogen has been determined so far only in temperatures above 18 K.[18,19] Single points measured also at 4.2 and 14 K (Ref. 18) can be considered only as qualitative (as pointed out by the author of Ref. 18). The paper[19] presented the results of an investigation of $\lambda(T)$ over the temperature range 23–55 K. Lower thermal conductivity of the α phase of nitrogen, in comparison to solidified rare gases, has been explained by the authors of Ref. 19 as caused by scattering of phonons on librons, whereas the β phase—as caused by the interaction of phonons with fluctuations associated with correlated precession motion of molecules.

The purpose of this work was the investigation of the thermal conductivity of α-nitrogen.

The measurements have been conducted by the stationary linear-flow method in a cryostat described in Ref. 20. The samples were grown and measured in a glass ampoule with an inner diameter of 6.4 mm, a wall thickness of 1.1 mm, and a length of 67 mm. Two calibrated germanium thermometers were attached to the ampoule serving the purpose of determination of the value and the gradient of temperature. The lower thermometer was placed about 14 mm from the bottom and the upper was placed 37 mm above the lower. The nuclei of the crystal were obtained from the liquid phase, the main part being grown directly from the gaseous phase. The growth rate of the crystal, about 1 mm/h, was ensured by the drift of temperature of the ampoule base (about −0.3 K/h). After crystallization, the sample has been annealed for 12 h with the gradient of temperature amounting 0.4 K/cm, slightly below the triple point of nitrogen. Then the sample was cooled to the temperature of liquid helium, the cooling rate for both β and α phases being 1 K/h. Passing the region of phase transition—the temperature change of the ampoule bottom from 35.8 to 33.4 K—was realized in a time period of 16 h, while the gradient of temperature, about 0.3 K/cm caused the phases interface to move with a velocity of about 0.5 cm/h. The sample cooled down to liquid-helium temperatures appeared to be transparent, without notable cracks and defects. Observation of the sample in polarized light allowed us to estimate grain sizes to be about 3–4 mm. It should be emphasized that from among all the parameters influencing the sample quality, the most critical was the cooling rate in the region of the $\beta \rightarrow \alpha$ phase transition, since the change of the crystal structure was followed by a jump of the molar volume of 0.76%.[17] Too short a time of cooling the sample at the $\beta \rightarrow \alpha$ transition is, as we have found, the main cause of generating considerable amount of defects, which can be observed not only visually (opaquening of the crystal) but also in lowering the value of the thermal conductivity coefficient.

At the end of the measurements and evaporation of the crystal, the chemical and isotope composition of the sample was analyzed by a mass spectrometer. The investigated samples had natural isotope composition with impurities not exceeding 0.003% (mostly oxygen, concentration $\leq 0.002\%$).

The random error of the thermal conductivity measurement in low temperatures did not exceed 1.5%, whereas above 20 K it increased to 3%, mostly due to effects connected with spurious heat leaks. The systematic error did not exceed 3%.

RESULTS AND DISCUSSION

The results of the measurement of the thermal conductivity coefficient dependence on temperature for two samples of solidified nitrogen have been presented in Fig. 1. The behavior of $\lambda(T)$ is typical for dielectric crystals. The thermal conductivity coefficient of the investigated samples of solid N_2 at $T_{\max} \approx 3.6$ K amounts to 250 mW/cm K, which is close to the value of $\lambda_{\max}$ obtained for rare-gas solids[21-23] and for O_2.[24] It should be noted that $\lambda_{\max}$ is not a quantity essential for a substance since its value is influenced by, e.g., imperfections in the crystal structure.

At the $\alpha \leftrightarrow \beta$ transition a jump of the value of thermal conductivity connected with the change in the crystal structure is observed. The appearance of the sharp maximum of $\lambda(T)$ is evidence of good quality of the investigated samples, whereas the repeatability confirms the proper choice of the conditions to obtain them.

In Fig. 1, the results of the earlier works of Roder[18] and Koloskova *et al.*[19] were also included. A considerably lower value of λ at temperature 4.2 K (Ref. 18) was caused, probably, by a high concentration of defects introduced during growth and cooling of the samples. At temperatures above 18 K, our results agree with the data of Refs. 18 and 19.

The results of the measurement were analyzed using the method of Callaway[25] in the framework of the Debye model. The Callaway expression for the thermal conductivity of dielectric crystal is

$$\lambda = \lambda_1 + \lambda_2 \,, \tag{1}$$

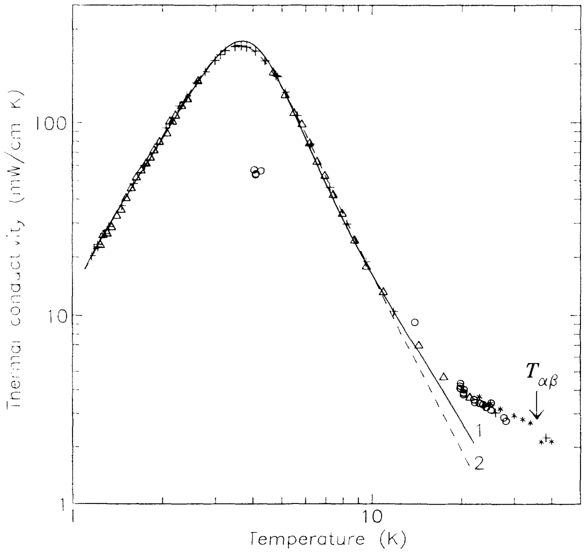

FIG. 1. Thermal conductivity of solid nitrogen. Experiment: △, + —our results; ○ —data from Ref. 18; ✱ —data from Ref. 19. Calculations: curve 1 (solid)—taking into account N processes; curve 2 (dashed)—without N processes.

where

$$\lambda_1 = GT^3 \int_0^{\theta/T} \tau_c \frac{x^4 e^x}{(e^x-1)^2} dx \tag{2}$$

would represent the conductivity if the normal process scattering were small, while

$$\lambda_2 = GT^3 \frac{\left[\int_0^{\theta/T} (\tau_c/\tau_n)[x^4 e^x/(e^x-1)^2] dx \right]^2}{\int_0^{\theta/T} (\tau_c/\tau_n \tau_r)[x^4 e^x/(e^x-1)^2] dx} \tag{3}$$

is included when normal processes are significant. $G = k^4/2\pi^2 v \hbar^3$, $x = \hbar\omega/kT$, $\theta = 83.5$ K (Ref. 13) is the Debye temperature, τ_c is the relaxation time of phonon scattering, ω is the phonon frequency, $v = [(v_l^{-3} + 2v_t^{-3})/3]^{-1/3}$ is the phonon propagation velocity averaged over longitudinal v_l and transversal v_t polarizations.[9]

Assuming additivity of the effects of scattering, the reciprocal of the total relaxation time τ_c may be written down as a sum of the reciprocals of the relaxation times for the "resistive" processes τ_r and the "normal" processes τ_n:

$$\tau_c^{-1} = \tau_r^{-1} + \tau_n^{-1} \,, \tag{4}$$

where

$$\tau_r^{-1} = \tau_b^{-1} + \tau_p^{-1} + \tau_d^{-1} + \tau_u^{-1} \,. \tag{5}$$

The following mechanisms of phonon scattering were taken into account in formulating expressions (4) and (5): scattering on grain boundaries, on dislocation stress fields, on point defects, and on phonons (three-phonon processes). The quantities

$$\begin{gathered} \tau_b^{-1} = a_b \,, \quad \tau_p^{-1} = a_p x^4 T^4 \,, \quad \tau_d^{-1} = a_d x T \,, \\ \tau_u^{-1} = a_{1u} x^2 T^5 \exp[-a_{2u}/T] \,, \quad \tau_n^{-1} = a_n x^2 T^4 \end{gathered} \tag{6}$$

are the relaxation rates of phonons scattered on grain boundaries, point defects, dislocation stress fields, respectively, and taking part in the umklapp processes and in normal processes.

The parameters a_j $(j = b, p, d, 1u, 2u, n)$ appearing in (6) were found by minimizing the functional $\sum_i [(\lambda_{ci} - \lambda_{ei})/\lambda_{ei}]^2$, where λ_{ci} and λ_{ei} are the calculated and experimental values of the thermal conductivity coefficient at ith temperature point. The following values have been obtained:

$$\begin{gathered} a_b = 2.27 \times 10^7 \text{ s}^{-1} \,, \quad a_p = 2.16 \text{ s}^{-1}\text{K}^{-4} \,, \\ a_d = 1.74 \times 10^6 \text{ s}^{-1}\text{K}^{-1} \,, \quad a_{1u} = 3.48 \times 10^4 \text{ s}^{-1}\text{K}^{-5} \,, \\ a_{2u} = 12.2 \text{ K} \,, \quad a_n = 8.26 \times 10^8 \text{ s}^{-1}\text{K}^{-4} \,. \end{gathered} \tag{7}$$

The results of the above presented analysis are depicted in Fig. 1 (curve 1). As can be seen, a good description of the experimental data was reached for $T < 14$ K. The standard deviation of the experimental points is 0.5%.

In the same figure, the result of approximation of the experimental data by Eq. (2), i.e., without taking the N processes into account (curve 2) is also depicted. It can be seen that both methods of approximation give, practically, the same result in the range 1–13 K. In the region of $\lambda_{\max}$, better approximation of the experimental data is obtained without considering the N processes. Above 13 K appears the difference between the experimental data and curve 2, increasing with temperature. Taking N processes into consideration (curve 1) slightly diminishes that difference. The divergence between the curves 1 and 2, and the experimental data for temperatures higher than 14 K is connected, most probably, with the temperature dependence of τ_u^{-1} more complicated than it was included in Eqs. (6).

In the course of the analysis of the low-temperature part of the experimental results, we took into consideration only the processes mentioned above. We considered neither the contribution of librons into heat transport nor the scattering of phonons on librons, since the excitation energy of the libron lowest energy level corresponded to 46.5 K (cf., e.g., Ref. 10).

Using Eqs. (6), the size of the crystallites, the density of dislocations, and the density of point defects have been estimated. From the expression $a_b = v/b$ the average dimension of crystallites $b = 4.4 \times 10^{-2}$ mm has been obtained. It is close to the value obtained for the crystals of noble gases.[23,26] The difference between this result and the dimensions of the crystallites obtained in visual observation can be explained by the existence of subgrain structure, observed earlier in rare-gas solids.[27] From the equation $\tau_d^{-1} \sim N_d \gamma^2 \mathbf{B}^2 \omega / 2\pi$ (Ref. 28) (N_d is the dislocation density, γ is the Grüneisen constant, $\mathbf{B}$ is the Burgers vector of the dislocation) the density of dislocations have been estimated. The obtained value, $N_d = 2.5 \times 10^9$ cm^{-2}, is three orders of magnitude higher than found for argon in x-ray investigation.[29] That difference may be caused by considering in the adopted model only the scattering on static dislocations (see, for example, Refs. 28 and 30). The obtained value of point-defect density, $N_p = 0.16\%$, is close to the concentration value of ^{15}N in the gas of natural isotope composition. To determine N_p, the equation $a_p = k^4 N_p v_a (\Delta M/M)^2 / 4\pi\hbar^4 v^3$ (Ref. 28) has been used, where v_a is the volume occupied by a molecule in the lattice, M is the molecule mass, and ΔM is the difference between masses of defect and host molecules.

CONCLUSIONS

Concluding, the thermal conductivity λ of solid nitrogen has been measured over the range of temperatures from 1.2 to 38 K, whereas the temperature dependence of λ has been determined below 18 K. The Callaway method has been applied to analysis of the obtained data. The experimental data are best described by thus adopted temperature dependences of relaxation times over the range 1.2–14 K. The temperature dependence of the umklapp-processes relaxation times has the decisive influence on the character of the obtained $\lambda(T)$ function in temperatures higher than $T_{\max}$. For the calculations, $\tau_u^{-1} = a_{1u} x^2 T^5 \exp[-a_{2u}/T]$ was used. The real dependence of $\tau_u^{-1}(T)$ exhibits a more complex character, changing from $\tau_u^{-1} \sim T \exp[-a_{2u}/T]$ to $\tau_u^{-1} \sim T^4$ with increasing temperature. The consequence of the here adopted simplification is that for temperatures about 14 K the calculated values of λ are lower than the experimental ones.

From the obtained relaxation times for the particular mechanisms of phonon scattering the average dimensions of grains of the investigated nitrogen crystals $b = 0.04$ mm were determined; also, the density of dislocations $N_d = 2.5 \times 10^9$ cm^{-2} and the density of point defects $N_p = 0.16\%$ were estimated.

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