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Excess thermal resistivity in N_2–CO solid solution at low carbon monoxide concentration

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The results of measurements of the thermal conductivity of pure and carbon-monoxide-doped nitrogen crystals, for samples containing up to 0.7% of CO molecules, in the temperature range 1.2–26 K are presented. From the preliminary analysis it results that the interaction of phonons with admixture molecule featuring the same mass, as the host molecule, is relatively weak and depends weakly on the admixture concentration within investigated range of carbon monoxide in nitrogen crystal.

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Introduction

Crystals of nitrogen and carbon monoxide belong to the same group of the simplest molecular solids. Both of them have at low temperatures a crystallographic structure featuring cubic symmetry with four molecules in an elementary cell, with molecules axes oriented along spatial diagonals of the cubic cell. A displacement of mass center relative to interaction center of CO molecule causes that the CO crystal belongs to $P2_13$ space group, while N_2 — to $Pa3$ [1].

Crystalline carbon monoxide forms homogeneous solutions with nitrogen at any concentration and the molecules mutually replace one another in the lattice sites [2]. Solid solution of N_2 with CO is a unique system for thermal conductivity investigation due to equality of masses of nitrogen and carbon monoxide molecules. In the previous thermal conductivity admixture-effect investigations the guest atom (or molecule) possessed the mass different than that of the host one, see, e.g., Refs. 3, 4. Therefore, the observed and analyzed effect was regarded as an «isotopic» phenomenon — phonons in the investigated crystals were «scattered by the mass difference». In CO:N_2 crystals the situation is different. With the absence of the mass defect one can observe phonon scattering on different force constants and related to them deformation of the lattice around the admixture molecule. In the case of nitrogen crystals doped with carbon monoxide, the deformation of the lattice is even stronger due to above-mentioned displacement of the mass and interaction centers of the admixture CO molecule.

The purpose of the experiment which preliminary results are being presented here is the investigation of phonon scattering on difference in force constants of interaction between molecules forming the crystal and related to that lattice deformation around foreign molecule embedded in the crystal.

Experimental

To investigate the same-mass-impurity effect in solidified nitrogen, the measurements of dependence of the thermal conductivity coefficient on temperature $\kappa(T)$ for several samples containing intentionally introduced carbon monoxide molecules, at different concentrations, have been carried out. The measurements have been conducted in a home-designed ^{4}He setup, described in Ref. 5. They were performed with steady-state flow method in the temperature range 1.2–26 K. The samples were grown and measured in a glass ampoule of an inner diameter 6.7 mm and a length 67 mm. Two calibrated germanium thermometers were attached (spaced 37 mm apart) to the ampoule serving the purpose of determination of the value and the gradient of temperature. The nuclei of the crystal were obtained from the liquid phase, the main part being grown directly from gaseous phase. The growth rate of the crystal, of about 1 mm/h, was assured by the drift of temperature of the ampoule base (about −0.3 K/h). When the crystal fully filled the ampoule, the sample was annealed for 12 h with the gradient of temperature amounting 0.4 K/cm,

slightly below the triple point of the mixture of gases used to obtain the sample. 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 was realized for a time period of 16 h, while the gradient of temperature, about 0.3 K/cm caused the phase interface to move with a velocity of about 0.5 cm/h. The samples cooled down to liquid-helium temperature appeared to be transparent, without notable cracks and voids.

The gases used in the experiment had natural isotope composition with impurities not exceeding 0.003%, mostly oxygen. The random error of the thermal conductivity measurements did not exceed 7%. The systematic error, which resulted mostly from inaccuracy of the geometry specification, did not exceed 5%.

Results and discussion

The results of the measurements — the thermal conductivity coefficient dependence on temperature for pure nitrogen crystal and for samples of N_2 containing 0.2, 0.25, 0.3, 0.5 and 0.7% CO — have been depicted in Fig. 1. The dependences display their behavior typical for a dielectric crystal: initially the thermal conductivity increases with increasing temperature, then after reaching a maximum value, decreases exponentially. The samples containing additional phonon scattering centers — carbon monoxide admixture molecules — show at low temperatures thermal conductivity lower than that of pure nitrogen, following the expectation. For temperatures above the maxima, where phonon-phonon scattering in U-processes begin to dominate the thermal conductivity, the data points of all samples tend to the same curve.

For preliminary analysis of the data, the reduced excess thermal resistivity ΔW^* dependence on concentration c of the admixture CO molecules has been created:

$$\Delta W^*(c) = [\kappa^{-1}_{\text{dopped}}(c) - \kappa^{-1}_{\text{pure}}]/c\big|_{T=\text{const}}.$$

In the formula, κ_{pure} and $\kappa_{\text{dopped}}(c)$ stand for thermal conductivity coefficients at a fixed temperature for the pure nitrogen crystal and the N_2:CO sample, respectively. The $\Delta W^*(c)$ obtained by smoothing the data, for the temperature 2.5 K has been shown in Fig. 2.

The dependence of reduced excess thermal conductivity on impurity concentration can be interpreted in the framework of the «most significant phonons» approximation. In this approximation one assumes that for steady state flow, at any temperature there exists such a frequency $\omega \sim T$ that a group of phonons of frequencies from the range $(\omega - \Delta\omega, \omega + \Delta\omega)$, where $\Delta\omega/\omega << 1$, carries the greatest part of the heat flux being transported in the sample. In the most significant phonons approximation, the contributions of phonons scattered in separate mechanisms to the total thermal resistivity W of a sample are additive. Therefore, the excess thermal resistivity $\Delta W^*(c)$ depicted in Fig. 2 can be regarded as the component related to the scattering of phonons on CO molecules. From the Fig. 2 one can see that the excess resistance per one molecule of the admixture hardly depends on carbon monoxide concentration. Only a slight tendency (however still within the experiment error) for an increase of $\Delta W^*(c)$ is observed. It could mean that for concentrations of carbon monoxide molecules in nitrogen crystal not exceeding 0.7% an interaction leading to weakening of the phonon scattering on the carbon monoxide molecules with increasing concentration of the admixture is observed.

It also should be noticed that in N_2:CO crystal the excess thermal resistivity per unit concentration is a small number when compared to that obtained for impurities featuring the mass different than that of host, see, e.g., Ref. 6. This confirms results of earlier theoretical investigations which have shown that the scat-

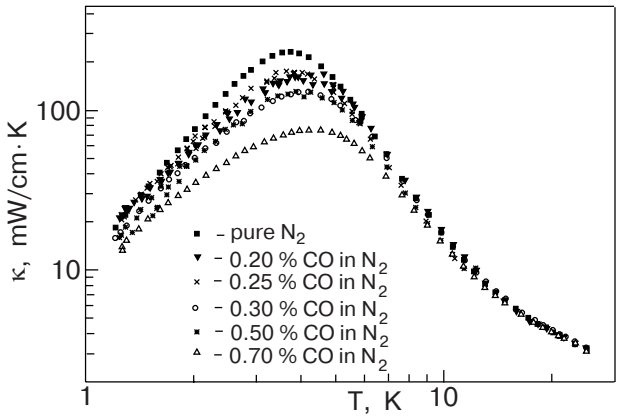

Fig. 1. Thermal conductivity of pure and carbon-monoxide-doped solid nitrogen vs temperature.

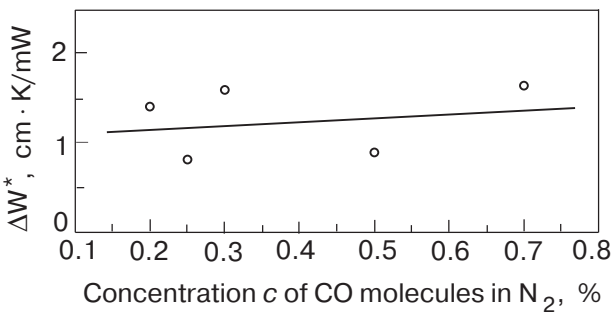

Fig. 2. Admixture effect in N_2–CO system at 2.5 K. Solid line is a plot of function $\Delta W^* = 1.07 + 0.398\ c$.

tering of phonons on point defects with different force constants and deformations of the lattice around foreign impurities is less effective then the scattering resulting from the difference between masses of host and admixture [7]. This also explains earlier success of the approach, in which foreign impurities in dielectric crystals were regarded as pure isotopic admixtures, e.g., Ref. 4.

Concluding, the thermal conductivity of pure and carbon-monoxide-doped nitrogen crystals has been measured for the samples containing 0.2, 0.25, 0.3, 0.5 and 0.7% of CO molecules, in the temperature range 1.2–26 K. The simple analysis has shown that the scattering of phonons on admixture molecules possessing the same mass as the host molecule is relatively weak when compared with the scattering on a molecule featuring different mass. It has also been found that the interaction depends rather weakly on the admixture concentration within investigated range of carbon monoxide in nitrogen crystal.

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