Lattice thermal conductivity in mixed crystals in the absence of mass mismatch: Investigation of N$_2$-CO solid solution

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Mutual solid solution of nitrogen and carbon monoxide is a unique object in terms of phonon spectroscopy investigations. The main reason for phonon interaction with foreign admixture molecule—the difference of masses of the host and the impurity molecule—is absent from that system. In the present paper the results of measurements of thermal conductivity of pure and carbon monoxide-doped nitrogen crystals, for samples containing up to 50% of CO, in the temperature range 1.2–26 K, are presented. For analysis of the experimental data the Callaway approach was applied. It has been found that the dependence of relaxation time of phonon in its interaction with varying force constants and deformation of lattice around the admixture molecule on the phonon frequency agrees with earlier theoretical considerations, however the effect is weak. It has also been found that, for concentration of the admixture molecules exceeding 1%, the mutual interaction of the impurity molecules becomes significant and lowers the thermal resistivity per unit concentration of the admixture molecule.

I. INTRODUCTION

Investigation of thermal conductivity of dielectric crystals is a good tool to study interactions of thermal excitations (phonons, librons) in solids with their crystal lattice imperfections, i.e., grain boundaries, dislocations, and impurities, both isotopic and foreign. The imperfections can be of natural origin and some of them can be introduced to the crystal intentionally. The effect of elastic scattering of phonons in samples containing controlled amounts of isotopic or foreign impurities on the thermal conductivity of rare gas, simple molecular and ionic crystals has been experimentally investigated in the past, see e.g., Ref. 1–3. However, all those observed effects were regarded as a case of "isotopic effect," i.e., the effect resulting exclusively from difference between masses of the impurity and the host atoms (molecules). In the investigations all other reasons possible for elastic phonon scattering, such as scattering on disturbances of force constants and related to them local deformations of the lattice around the admixture molecule, were neglected. In order to be able to observe these kind of interactions of phonons with impurities, not covered by the isotopic effect, the host and the admixture molecules should possess the same masses. Besides, the crystal appropriate for the investigation should have a relatively simple crystallographic structure, should feature simple intermolecular interactions and good solubility of the admixture in the host matrix. Because of the above conditions, the objects that meet requirements for such investigations are scarce. One of the few is nitrogen crystal (molecule mass $=28$ a.u.) doped with carbon monoxide (molecule mass $=28$ a.u.). Carbon monoxide dissolves in the structure of nitrogen crystal at any concentration and a CO molecule replaces N$_2$ molecule in the lattice site.[4]

The nitrogen crystal itself, with regards to its crystallographic structure and intermolecular interactions belongs to the simplest molecular crystals. The crystal at the equilibrium vapor pressure may exist, depending on the temperature, in two crystallographic phases. In its high-temperature phase β ($35.61 < T < 63.15$ K) one observes translational ordering of N$_2$ molecule centers while long-range orientational order is lacking. In this phase, the structure of the crystal belongs to the point group $P6_3/mmc$. In the low-temperature phase α ($T < 35.61$ K), the orientational ordering of the molecules appears in the nitrogen crystal. The crystal has symmetry $Pa3$. It is an fcc structure, in which molecules are oriented along space diagonals of the cubic elementary cell. High symmetry of N$_2$ molecule and weak Van der Waals interactions responsible for the crystal formation make the nitrogen crystal unusually convenient for *ab initio* theoretical investigations[5] as well as for testing new models and verifications of hypothesis in the field of solid-state physics. The aim of the presented here experiment is the investigation of influence of the difference in force constants of interactions between molecules forming the crystal and related to those, the lattice deformation around foreign molecules embedded in the crystal on phonon elastic scattering.

II. EXPERIMENT

In order to achieve the above-mentioned goal, a series of measurements of the thermal conductivity coefficient dependence on temperature [$\kappa(T)$] for solidified nitrogen containing carbon monoxide molecules in a number of concentrations have been performed. The dependence has been measured with the steady state flow method in the temperature range 1.2–26 K. The experiment was conducted in a home-designed ^{4}He setup.[6] The samples were made, thermally treated and measured in a glass ampule of an inner diameter of 6.7 mm and the length of 67 mm, placed in the measurement chamber of the setup. The crystals were grown from the N$_2$-CO gaseous mixture by the desublimation method at a temperature slightly below the triple point of the mixture. When the crystal filled the ampule completely, the sample was cooled down to the temperature of 4.2 K, at
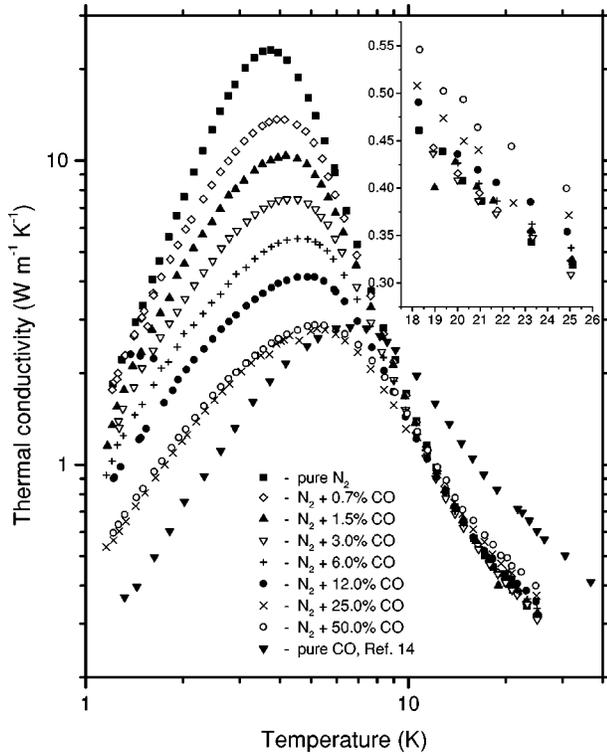
FIG. 1. Thermal conductivity of pure and carbon monoxide-doped solid nitrogen.

which the measurements began. During the process of cooling the sample, particular care was taken when passing the temperature region of the $\alpha - \beta$ phase transition. The crystal growth and the thermal treatment procedure was identical with those applied for the pure nitrogen experiment.[7]

The present series of experiments has been carried out on pure N_2 crystal and seven samples containing CO admixture, in which the concentration of carbon monoxide varied from 0.7 to 50.0%. The gases used in the experiment had a natural isotope composition with concentration of impurities not exceeding 0.003%.

III. RESULTS AND DISCUSSION

The results of the experiment, the $\kappa(T)$ dependence obtained for a pure nitrogen sample and samples containing carbon monoxide admixtures, concentration of 0.7%, 1.5%, 3.0%, 6.0%, 12.0%, 25.0%, and 50.0% have been shown in Fig. 1. The curves display the shape typical for a simple molecular crystal:[8] at low temperatures the thermal conductivity increases with temperature, then, after reaching the maximum values, thermal conductivity decreases. In terms of quality, the impurity effect agrees with expectations, i.e., crystals containing admixture exhibit of lower thermal conductivity than the pure one, and the greater the concentration of the admixture, the bigger the decrease of the thermal conductivity is observed. Also, the maximum on the $\kappa(T)$ curves shifts towards higher temperatures for higher concentrations of CO, again following expectations. For the highest investigated concentrations of carbon monoxide, the low-temperature thermal conductivity of N_2-CO alloy approaches

that obtained for pure CO crystal, which in its turn is by approximately one order lower than the thermal conductivity found for pure nitrogen crystal. As it was speculated in Ref. 9, the latest might be the manifestation of a supplementary phonon scattering in CO crystals connected with a lower symmetry of CO molecules.

For analysis of the data, the method proposed by Callaway[10] has been employed. In this approach each type of elastic scattering of phonons is represented by an appropriate relaxation time. Since the relaxation times depend, in general, on phonon frequency, they appear as functions of the phonon frequency ω in the expression called the Callaway equation:

$$\kappa = \kappa_1 + \kappa_2.$$

In the above

$$\kappa_1 = GT^3 \int_0^{\Theta/T} \frac{(\tau_c x^4 e^x)}{(e^x - 1)^2} dx$$

and

$$\kappa_2 = GT^3 \frac{\left[\int_0^{\Theta/T} (\tau_c/\tau_n)[x^4 e^x/(e^x - 1)^2] dx \right]^2}{\int_0^{\Theta/T} (\tau_c/\tau_n \tau_r)[x^4 e^x/(e^x - 1)^2] dx},$$

where $G = k_B^4/2\pi^2 v \hbar^3$, $x = \hbar \omega/k_B T$; $v = [(v_l^{-3} + 2v_t^{-3})/3]^{-1/3}$ is the phonon propagation velocity averaged over longitudinal v_l and transversal v_t polarizations,[11] $\Theta = 83.5$ K[12] is the Debye temperature of nitrogen crystal, τ_j-s stand for relaxation times of phonon scattering and T is the temperature.

With the assumption that scattering processes of different type do not influence one another, one can write

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

where

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

and where relaxation-time subscripts b, p, d, u, and n stand for relaxation times of phonons scattered on grain boundaries, point defects, dislocation strain fields, and on phonons, in Umklapp and normal processes, respectively.

The method itself consists in adjusting the relaxation time parameters to achieve the best agreement between the Callaway equation and the data obtained in an experiment.

In the fitting procedure employed here normal processes will not be taken into account. (There are two reasons that justify a neglecting of normal processes in the analysis presented below:—this analysis regards phonon scattering in nitrogen crystals by CO admixture molecules within a narrow range of concentration of carbon monoxide, in which contribution of N processes to the sum thermal conductivity would not vary significantly, but also—from estimation done in Ref. 13 results that in the thermal conductivity of crystals such as solid nitrogen, i.e., featuring relatively high molecular mass

TABLE I. Phonon relaxation rate parameters obtained by Callaway method for sample of pure N_2 and samples containing 0.7% and 1.5% of CO.

	Pure N_2	$N_2 + 0.7\%\,CO$	$N_2 + 1.5\%\,CO$
a_b	3.30×10^6 s^{-1}	2.03×10^6 s^{-1}	3.74×10^6 s^{-1}
a_p	5.24 s^{-1} K^{-4}	1.58×10^2 s^{-1} K^{-4}	3.65×10^2 s^{-1} K^{-4}
a_d	1.14×10^5 s^{-1} K^{-1}	3.32×10^5 s^{-1} K^{-1}	1.47×10^5 s^{-1} K^{-1}
a_{1u}	1.11×10^4 s^{-1} K^{-5}	1.11×10^4 s^{-1} K^{-5}	1.11×10^4 s^{-1} K^{-5}
a_{2u}	13.4 K	13.4 K	13.4 K

and Debye temperature, normal processes are of low significance.) For the remaining relaxation times the following τ_j-s expressions were used:

$$\tau_b^{-1} = a_b,$$

$$\tau_p^{-1} = a_p x^4 T^4,$$

$$\tau_d^{-1} = a_d x T,$$

$$\tau_u^{-1} = a_{1u} x^2 T^5 \exp[-a_{2u}/T]. \tag{1}$$

In these formulas a_j-s are the parameters of the relaxation rates, which were adjusted during the fitting procedure.

At the first stage of analysis of the data obtained in the reported here experiment, the Callaway equation has been fitted to the data for crystal of pure nitrogen. The best match for pure solid N_2 has been achieved for the set of parameters shown in the second column of Table I. From the relaxation times parameters obtained as a result of the fitting one can infer numerous important information regarding the sample and phonon interactions in the crystal under investigation. For example, from $a_b = 3.30 \times 10^6$ s^{-1} for the pure nitrogen crystal, using the dependence $a_b = v/b$ one can find mean grain or subgrain size[7] b of the investigated crystal equal 0.3 mm.

Also, a plot of the Callaway equation for these relaxation rate parameters has been shown in Fig. 2. As one can see, the agreement between the experimental points and the fitted curve is very good in the temperature range 1.2–12 K. For higher temperatures one should rather not expect a good match, since in the real situation, at higher temperatures, the dependence $\tau_u^{-1}(\omega)$ becomes weaker than that used during the fitting procedure and given by Eq. (1). More detailed discussion of this issue can be found in Ref. 7.

In case of a pure nitrogen sample, the point defects are the molecules containing atoms of a natural, heavier isotope of nitrogen (^{15}N) and some residual impurities (concentration of which did not exceed 0.003%, mostly oxygen) of the gas used in the experiment. For the thermal conductivity, a relevant feature of such point defects is the difference between masses of the host and the impurity molecule—a reason for phonon scattering. In CO-doped nitrogen crystals the situation is different. As it was emphasized in the Introduction, the nitrogen crystal with carbon monoxide admixture is an example of a simple system, in which the guest molecule mass is identical with the mass of the host molecule. On the
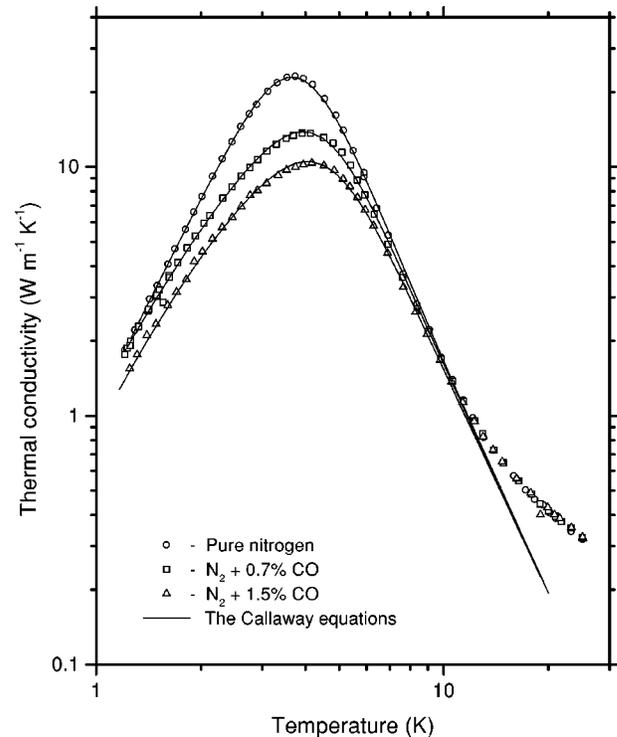
FIG. 2. The Callaway equation fitted to the data from the thermal conductivity experiment on pure and CO doped nitrogen.

other hand, the force constant of interaction between N_2 and CO molecules differs from this between N_2 molecules, which is also the reason for distortion of the lattice around the CO molecule. Additionally, a carbon monoxide molecule is nonsymmetrical with regard to its 180° reorientation, which results in a mutual displacement of its mass and interaction centers. The latter is the reason for even stronger deformation of the lattice around CO molecule embedded in N_2 crystal than that resulting merely from the difference of the force constants themselves. Similar dipolar reorientations in numerous systems containing spherical-symmetrical admixture atoms or ions have given glass-specific component in some of their physical properties, see, e.g., Ref. 14. However, no evidence being in favor of glasslike behavior has been found in heat capacity of N_2-Ar-CO and N_2-CO alloys.[15] Therefore, in our analysis we will not take into account contribution from any two-level system—in crystals such as those considered here, we will expect the thermal conductivity impurity effect to result merely from phonon scattering on disturbance of continuity of force constants and on distortion of the lattice around the admixture molecule. In this unique system the main reason for the phonon scattering on the majority of impurities—the isotopic effect—is lacking. As it is known from theoretical considerations,[8] the relaxation time dependence on phonon frequency for scattering on a small region with different force constants and on deformations of the lattice around the admixture molecule is the same as for isotopic impurities. Therefore, in the Callaway analysis one can use the same Rayleigh scattering phonon relaxation rate $\tau_p^{-1} = a_p x^4 T^4$ dependence for the system under investigation.

In the further steps of the analysis, the Callaway equation was fitted to the data for samples containing 0.7 and 1.5% CO. It was assumed that such amounts of admixture do not influence phonon-phonon interaction in N_2 crystal and therefore the a_{u1} and a_{u2} parameters were not fitted but set at values from Table I, found for pure nitrogen. Besides, the frequencies of libration of CO molecules embedded in N_2 crystal differ from these of nitrogen molecule. However, the energy of the libration is high[5] and in the analyzed temperature region there are few phonons which might interact with vibrations of the CO molecule around its mass center. Therefore, in our analysis, the scattering of phonons on libration of CO molecules has not been considered. Only parameters of the relaxation times for scattering on grain boundaries, point defects and dislocation strain fields were fitted, i.e., for different samples the difference in average grain sizes and dislocation densities, besides concentrations of intentionally introduced point defects, were allowed. The parameters of phonon relaxation rates for nitrogen samples containing 0.7 and 1.5% of carbon monoxide found by the Callaway method have been shown in Table I, in its third and fourth column, respectively. In Fig. 2 the experimental data for the samples of 0.7 and 1.5% CO have been depicted along with results of the fitting. The latter have been shown with solid lines.

From comparison of the parameters in the sets shown in Table I one can see that samples of pure nitrogen and that containing CO admixture of 1.5% had very similar grain sizes and densities of dislocation, while that with 0.7% CO featured relatively greater mean grain size and density of dislocations.

For the purpose of the current analysis, consideration of values of the parameter a_p is of the greatest interest. Being the parameter of relaxation time of phonons scattered on point defects, the a_p carries the information about concentration c_i of point defects and about strength A_i of interaction of phonons with the defect. Following Ref. 3, one can write

$$a_p = c_i A_i.$$

From comparison of the a_p-s of the sets in Table I it is seen that CO influence on thermal conductivity is by two orders of magnitude greater than the point defect scattering in pure nitrogen crystal. Therefore, the isotopic effect in the samples containing carbon monoxide admixtures can be neglected. The strength A_i (per unit concentration of CO admixture) found for sample containing 0.7% CO is $2.25 \times 10^4 \ s^{-1} \ K^{-4}$ while for the one with 1.5% CO is $2.44 \times 10^4 \ s^{-1} \ K^{-4}$. The numbers are close, which could mean that interaction of CO molecules embedded in N_2 crystal, at concentration of about 1%, is rather weak. To compare same-mass-impurity effect on the thermal conductivity against the isotopic thermal conductivity effect, the mass of a hypothetic N_2 molecule, which could cause the effect equal to that observed in the reported experiment, has been calculated. Parameter of relaxation time for phonon scattering by point defect, which results from difference between masses of the host and the impurity molecules has been expressed as $a_p = k_B^4 N_p V_a (\Delta M/M)^2 / 4\pi \hbar^4 v^3$ (adapted from Ref. 16). In

the equation, N_p stands for the ratio of number of the point defects to the number of the lattice sites in a unit volume, V_a stands for volume per molecule in the lattice, M is mass of the host molecule and ΔM is the difference between masses of the host and the admixture, $v = [(v_l^{-3} + 2v_t^{-3})/3]^{-1/3}$ is phonon propagation velocity averaged over longitudinal v_l and transversal v_t polarizations. For $a_p = 1.575 \times 10^2 \ s^{-2} \ K^{-4}$ found for the sample containing 0.7% CO one obtains $\Delta M/M \simeq 0.15$. Therefore, the strength of the impurity effect observed in our experiment corresponds to the effect, which would be caused by admixture (at the same concentration of 0.7%) of a hypothetic isotope of nitrogen of mass differing from mass of the nitrogen molecule by approximately 4 atomic units, that is, the effect is rather weak. This conclusion confirms results of theoretical investigations which have shown that the scattering of phonons on point defects with different force constants and deformations of the lattice around foreign impurities is less effective than the scattering resulting from differences between masses of host and admixture.[17] This also justifies the earlier approach, in which during the analysis of thermal conductivity experimental data, foreign impurities in dielectric crystals were regarded as pure isotopic admixtures, see e.g., Ref. 3.

As it has already been noticed, the good agreement between normalized values of relaxation time parameters for phonon scattering on point defects indicates that the interaction of CO molecules embedded in N_2 crystal at concentration of about 1% is rather weak. To estimate the effect of mutual interaction of the impurity molecules in the whole investigated range of the admixture concentration, the normalized excess thermal resistivity dependence on concentration, at fixed temperature

$$\Delta W^*(c) = [\kappa_{doped}^{-1}(c) - \kappa_{pure}^{-1}]/c$$

has been created. In the formula, κ_{pure} and $\kappa_{doped}(c)$ stand for thermal conductivity coefficients at some fixed temperature, for the pure N_2 crystal and the N_2:CO crystal at concentration c, respectively. The dependence can be interpreted in the framework of the "most significant phonons" approximation. In this exclusively qualitive approach one assumes that, for steady-state flow, at any temperature there exists a frequency $\omega \propto T$ for which a group of phonons of frequencies from the range $(\omega - \Delta\omega, \omega + \Delta\omega)$ (where $\Delta\omega/\omega \ll 1$) carries the greatest part of the heat flux. In the most significant phonons approximation, the contributions of phonons scattered in separate mechanisms to the total thermal resistivity W are additive. Since in higher, i.e., above maximum, temperature region the thermal conductivity coefficient is less sensitive to phonon scattering on grain boundaries and dislocations, the excess thermal resistivity $\Delta W^*(c)$ can be regarded as the component related to the scattering of phonons on CO molecules. A sample plot of the dependence $\Delta W^*(c)$, obtained for the temperature 5.2 K, has been shown in Fig. 3. From the figure one can see that the excess resistance per one molecule of the admixture for CO concentration higher than $\approx 1.5\%$ strongly decreases with increasing admixture concentration and follows the law $\Delta W^* \propto -\ln(c)$, while for smaller concentrations of CO the depen-
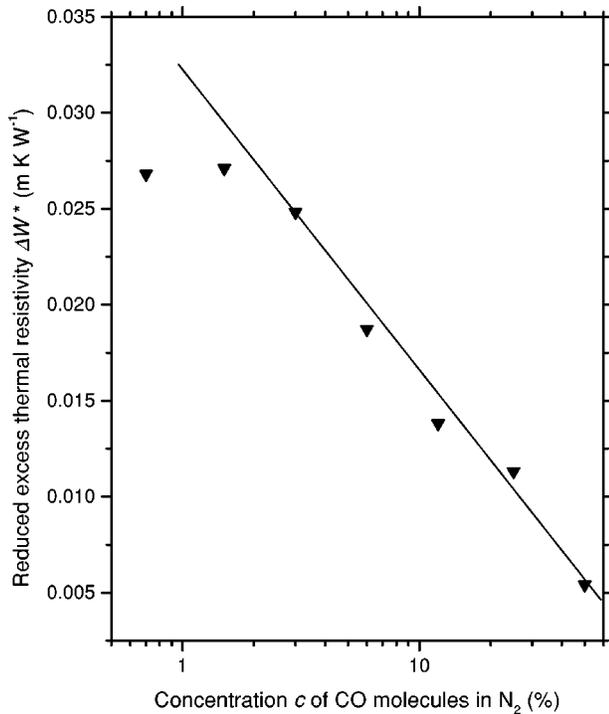
FIG. 3. Admixture effect in N_2-CO system at 5.2 K. Solid line is a plot of function $\Delta W^* = 3.3 \times 10^{-2} - 7.4 \times 10^{-3} \ln c$.

dence is noticeably weaker. It might mean that strong interaction of the CO molecules appears at relatively low concentrations, which weakens this type of scattering of phonons on point defects. On the other hand, one shall be aware that the interaction modifies the phonon spectrum of the nitrogen crystal, enriching it with modes typical for solidified carbon monoxide. The conclusion regarding relatively strong mutual interactions of CO molecules embedded in the nitrogen matrix can also be drawn by analysis of the $\kappa(T)$ dependence at

temperatures above 10 K: pure CO crystal shows the thermal conductivity significantly higher than pure N_2 crystal at temperatures above maximum of the dependence.[9] Therefore, the high-temperature increase of the thermal conductivity of N_2:CO crystal (see insert in the Fig. 1) can be explained by appearing of phonon modes typical to pure CO, resulting from mutual interaction of the admixture molecules. The effect is noticeable already at relatively low concentration— the nitrogen sample containing 6% CO shows, at the high temperature limit of ≈ 25 K, clearly higher thermal conductivity than the crystal of nitrogen which does not contain intentionally introduced impurities.

IV. CONCLUSION

Concluding, the thermal conductivity κ of solid nitrogen containing carbon monoxide admixtures of concentration up to 50% CO molecules, has been measured in the temperature range 1.2–26 K. The Callaway method has been applied to analyze the obtained data. The results confirm theoretically predicted phonon-frequency dependence of phonon relaxation time in scattering on different force constants and deformation of the lattice around the impurity. However, the effect is weaker than that caused by the mass difference itself. This fact clarifies earlier success of the approach, in which foreign impurities in dielectric crystals were regarded as pure isotopic admixtures. The successful description of the experimental data by means of the implied here model shows indirectly, that 180-degree reorientations of CO dipols do not give tunneling defect effect in thermal conductivity of N_2-CO system in the investigated temperature range. It was found, that for higher carbon monoxide concentrations the reduced excess thermal resistivity crearly decreases with increasing admixture concentration. That means a significant mutual interaction of carbon monoxide molecules embedded in the nitrogen crystal for the admixture concentration exceeding 1%.

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