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# Heat transfer in Ar and $N_2$ doped solid CO

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The measurements of thermal conductivity coefficient of a solid carbon monoxide crystal containing argon and nitrogen admixtures at different concentrations (1.5, 3, 6, 12.5, 25% for $N_2$ and 0.5, 1, 1.25, 2, 4% for Ar) were performed in the temperature range from 1.5 to 40 K by steady-state heat flow method. For analysis of the experimental data the Callaway method in the framework of the Debye model was used. The contribution of various mechanisms of phonon scattering, including scattering by disordered dipoles of the CO matrix, to the thermal conductivity of CO–$N_2$ and CO–Ar solid solutions were taken into account.

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**63.20–e** Phonons in crystal lattice;
63.20.Mt Phonon-defect interactions;
**65.40.–b** Thermal properties of crystalline solids.

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## Introduction

Solid carbon monoxide, both in terms of its crystallographic structure and intermolecular interactions, belongs to the group of the simplest molecular crystals [1,2]. This van der Waals crystal at equilibrium vapor pressure can be, depending on the temperature, in one of two crystallographic phases. In the temperature range from 68.09 to 61.57 K crystalline CO exists in the high-temperature β-phase. This phase features an hcp structure without long-range orientational ordering of the molecules. The symmetry of the phase belongs to $P6_3/mmc$ space group. Below 61.57 K the crystal undergoes a structural phase transition to the low-temperature fcc α-phase. In this phase an orientational long-range ordering of the axes of CO molecules is observed – the axes of the molecules are oriented along space diagonals of the elementary cubic cell [3,4]. At this point it should be emphasized that the molecule of CO due to its asymmetry, unlike symmetric linear molecules, has a non-zero permanent electrostatic dipole moment which amounts to $3.7356 \cdot 10^{-31}$ C·m [5]. All experiments carried out so far did not confirm existence of a new low-temperature phase with dipolar ordered molecules as predicted by theory [6–11]. On the contrary, all experiments show that CO dipoles remain disordered down to the lowest investigated temperatures, forming a disordered structure in the dipolar subsystem. This glassy state strongly influences the low-temperature physical properties of the carbon monoxide crystal and, among other things, its thermal conductivity [12].

It is well known that the thermal conductivity of a crystal can be modified by introducing foreign atoms or molecules in the crystal structure. The impurities become scattering centers for heat carriers and can modify the thermal excitation spectrum of the structure influencing the thermal conductivity of the crystal. The presence of an impurity in the crystal usually leads to additional mechanism of phonon scattering due to difference of masses of the impurities and the host atoms, resulting in the so called isotopic effect. But phonons can be scattered not only as a result of the isotopic effect. Foreign atoms (molecules) in a crystal have force constants which are different from those of the host environment. This difference causes a deformation of the structure in the vicinity of the impurity which entails an extra phonon scattering due to the admixture.

To investigate the effect of impurities on the thermal conductivity of solid carbon monoxide, we chose two types of admixtures which we introduced into the structure of the CO, namely, spherically symmetric atoms of argon and linear symmetric molecules of nitrogen. While the Ar atom differs strongly from CO molecule both in terms of its symmetry and mass (40 atomic mass units for argon vs 28

for carbon monoxide), nitrogen and carbon monoxide are considered alike molecules in many aspects. The molecular masses are the same and the parameters of the Lennard-Jones potential for both molecules are very close to each other [2]. Due to the similarity of the molecules, solid mixtures of $N_2$ and CO form homogeneous solid solutions for any mutual concentrations [13]. The solubility of argon in carbon monoxide is up to 5% in the whole temperature range [14].

## Experiment

Measurements of the thermal conductivity of solid carbon monoxide with argon and nitrogen admixtures were carried out in the temperature range from 1.5 to 40 K by the steady-state heat flow method. The concentrations of nitrogen in the samples investigated were 1.5, 3, 6, 12.5, 25% and those of argon were 0.5, 1, 1.25, 2, 4%.

The measurements have been conducted with use of a home-designed LHe cryostat [15]. The samples were grown and studied in a thin-wall stainless steel ampoule with an inner diameter of 5.5 mm and a length of 40.08 mm, the thickness of the ampoule wall was 0.5 mm. The crystals were grown directly from the gas phase, avoiding the liquid phase. The temperature and pressure of condensation were slightly below the triple-point values of the gas mixture and were maintained constant during the whole crystal growth procedure. The crystal gradually (at a constant rate of approximately 1 mm/h) filled the ampoule from bottom to top. After growth the samples were cooled down to the starting temperature of measurement at a rate of 0.2 K/h.

## Results

The results of our measurements of the thermal conductivity as a function of temperature of pure carbon monoxide and carbon monoxide containing nitrogen and argon admixtures of different concentrations are shown in Figs. 1 and 2, respectively.

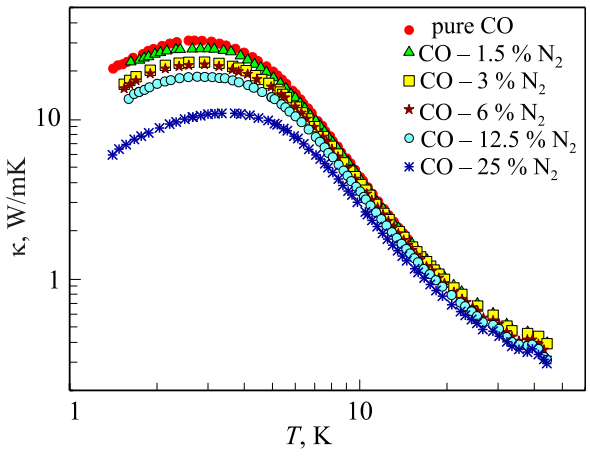


*Fig. 1*. (Color online) Thermal conductivity of pure and nitrogen doped solid carbon monoxide.

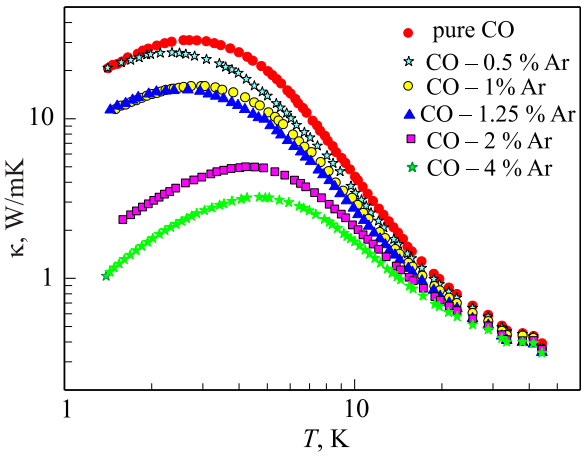


*Fig. 2*. (Color online) Thermal conductivity of pure and argon doped carbon monoxide.

The temperature dependence of the thermal conductivity is typical of a dielectric crystal [16]. The experimental curves feature a characteristic maximum. At low temperatures the thermal conductivity increases with temperature and then, after reaching the maximum value, starts to decrease. The crystals containing admixtures exhibit lower thermal conductivity than the pure one. The height of their maxima decreases with increasing concentration of the admixture for both types of dopants. In addition, the maximum shifts towards higher temperatures for higher concentrations of both doping agents.

At the lowest investigated temperatures two curves of argon-doped family (Fig. 2) show a slightly different behavior compared with the remaining ones. The thermal conductivity for the samples containing 0.5 and 1.25% of Ar as a function of $T$ below the maximum is more sloping than for other concentrations. At the same time, at the lowest temperatures the thermal conductivity of these samples is higher than one might expect and the maxima are shifted to lower temperatures compared to pure CO.

Qualitatively, the admixture of nitrogen (Fig. 1) lowers the thermal conductivity less than the argon dopant: 4% of argon reduces the low-temperature thermal conductivity by an order of magnitude while a similar admixture of nitrogen reduces the thermal conductivity by less than 40%.

For the purpose of a quantitative description of the contributions due to various mechanisms of phonon scattering to the thermal conductivity of CO–$N_2$ and CO–Ar solid solutions the Callaway method in the framework of the Debye model was utilized [17]. In this method each of the scattering mechanisms is characterized by its own relaxation time which is a measure of the average time between consecutive phonon scatterings in a particular scattering process. The relaxation time depends on phonon frequency.

The Callaway expression for the thermal conductivity $\kappa$ of a dielectric crystal can be written:

$$\kappa = \kappa_1 + \kappa_2 , \tag{1}$$

where

$$\kappa_1 = \frac{k_B}{2\pi^2 v}\left(\frac{k_B}{\hbar}\right)^3 T^3 \int_0^{\theta/T} \frac{\tau_c x^4 e^x}{(e^x - 1)^2} dx \tag{2}$$

and

$$\kappa_2 = \frac{k_B}{2\pi^2 v}\left(\frac{k_B}{\hbar}\right)^3 T^3 \frac{\left(\int_0^{\theta/T} (\tau_c/\tau_N)(x^4 e^x/(e^x-1)^2)dx\right)^2}{\int_0^{\theta/T} (\tau_c/\tau_N\tau_r)(x^4 e^x/(e^x-1)^2)dx} . \tag{3}$$

these processes are by far less important than other phonon scattering processes, which allowed us to omit them.

In our calculations the following expressions for the relaxation times were used:

$$\tau_b^{-1} = a_b, \quad \tau_p^{-1} = a_p x^4 T^4, \quad \tau_d^{-1} = a_d x T ,$$

$$\tau_D^{-1} = a_D x^{0.2} T^{2.2}, \quad \tau_U^{-1} = a_{1U} x^2 T^5 \exp[-a_{2U}/T] . \tag{6}$$

Here, $a_i$ are the parameters of the respective relaxation rates. The values of these parameters are determined within a fitting procedure to obtain the best match of Eq. (1) to the thermal conductivities obtained in the experiment.

The values of $a_i$ found for the CO–$N_2$ and CO–Ar solid solutions studied at different concentrations of nitrogen and argon admixtures are presented in Table 1 and Table 2, respectively.

Table 1. Phonon relaxation rate parameters obtained by Callaway method far sample of pure CO and the samples containing molar admixture of 1.5, 3, 6, 12.5 and 25% of $N_2$

| | CO | CO–1.5%$N_2$ | CO–3%$N_2$ | CO–6%$N_2$ | CO–12.5%$N_2$ | CO–25%$N_2$ |
|---|---|---|---|---|---|---|
| $a_b$ | $6.779\cdot10^5$ | $2.756\cdot10^5$ | $1.43\cdot10^6$ | $1.4847\cdot10^6$ | $9.275\cdot10^5$ | $1.665\cdot10^6$ |
| $a_p$ | $6.98\cdot10^2$ | $1.795\cdot10^3$ | $3.558\cdot10^3$ | $3.654\cdot10^3$ | $4.3\cdot10^3$ | $3.226\cdot10^3$ |
| $a_d$ | $9.618\cdot10^4$ | $1.991\cdot10^5$ | $1.586\cdot10^4$ | $1.087\cdot10^4$ | $2.899\cdot10^5$ | $9.566\cdot10^5$ |
| $a_{1U}$ | $1.785\cdot10^4$ | $1.820\cdot10^4$ | $1.813\cdot10^4$ | $1.95\cdot10^4$ | $2.002\cdot10^4$ | $2.531\cdot10^4$ |
| $a_{2U}$ | 8.6888 | 9.16708 | 9.1977 | 9.78 | 9.155 | 9.976 |
| $a_D$ | $6.841\cdot10^5$ | $4.413\cdot10^5$ | $3.231\cdot10^5$ | $3.615\cdot10^5$ | $3.83\cdot10^5$ | $1.348\cdot10^6$ |

Here the dimensionless variable $x = \hbar w/kT$, $v = [(v_l^{-3} + 2v_t^{-3})/3]^{-1/3}$ is the phonon velocity averaged over longitudinal $v_l$ and transversal $v_t$ polarizations [18]. For carbon monoxide $v$ = 1225.5 m/s, and $\Theta$ = 103.5 K is the Debye temperature of solid carbon monoxide [2], $k_B$ is the Boltzmann constant, $\hbar$ is the Plank constant, $\tau$ is the relaxation time of phonon scattering, $T$ is the temperature.

The combined inverse relaxation time (relaxation rate) can be written as

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

where $\tau_r^{-1}$ is the relaxation rate for resistive processes, $\tau_n^{-1}$ is the relaxation rate for normal processes.

The relaxation rate for resistive processes is a sum of relaxation rates of all resistive processes taken into account

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

This expression contains the relaxation rates for scattering by grain boundaries ($b$), by point defects ($p$), by dislocation strain fields ($d$), by the subsystem of disordered dipoles of CO molecules ($D$), and by Umklapp processes ($U$). The three-phonon normal processes have not been taken into account. For dielectric crystals such as discussed here with their structure far from that of a perfect crystal.

The relaxation time parameters obtained as a result of fitting procedure carry a lot of information regarding the structure of the investigated crystals. For example, from the value of $a_b$ one can obtain an average grain size $b$ of the crystals, which in the case of pure carbon monoxide is 1.81 mm (from the dependence $a_{\text{bound}} = d/v$, where $v$ is an the average phonon velocity [19]).

The parameter $a_p$ yields information about the concentration of point defects $c_p$ and about the strength $A_p$ of the phonon interaction with defects [20]:

$$a_p = c_p A_p .$$

For the samples containing 1.5 and 3% of $N_2$, $A_p$ are $1.19\cdot10^5$ $s^{-1}K^{-4}$ and $1.186\cdot10^5$ $s^{-1}K^{-4}$, respectively. For higher concentrations of nitrogen the parameter $a_p$ remains constant. This can be ascribed to clusterization of admixture molecules and, possibly, to some compensating mechanism which weakens the phonon-impurity interaction at higher admixture concentrations. For the argon containing samples the parameter $a_p$ increases linearly with the argon concentration. It is well understood from Fig. 2. Here the maximum concentration of Ar was 4%, so the probability of cluster formation is relatively low and the mutual interaction of the atoms is neg-

Table 2. Phonon relaxation rate parameters obtained by Callaway method far sample of pure CO and the samples containing molar admixture of 0.5, 1, 1.25, 2 and 4% of Ar

| | CO | CO–0.5%Ar | CO–1% Ar | CO–1.25%Ar | CO–2%Ar | CO–4%Ar |
|---|---|---|---|---|---|---|
| $a_b$ | $6.779\cdot10^5$ | $5.166\cdot10^5$ | $3.817\cdot10^5$ | $1.262\cdot10^5$ | $3.44\cdot10^6$ | $1.35\cdot10^7$ |
| $a_p$ | $6.98\cdot10^2$ | $9.08\cdot10^2$ | $2.639\cdot10^3$ | $4.314\cdot10^3$ | $1.805\cdot10^4$ | $2.486\cdot10^4$ |
| $a_d$ | $9.618\cdot10^4$ | $5.623\cdot10^3$ | $6.5\cdot10^5$ | $6.18\cdot10^5$ | $5.618\cdot10^6$ | $8.87\cdot10^6$ |
| $a_{1U}$ | $1.785\cdot10^4$ | $1.673\cdot10^4$ | $1.968\cdot10^4$ | $1.789\cdot10^4$ | $1.61\cdot10^4$ | $1.534\cdot10^4$ |
| $a_{2U}$ | 8.6888 | 5.75 | 6.510 | 4.565 | 3.878 | 2.043 |
| $a_D$ | $6.841\cdot10^5$ | $8.056\cdot10^5$ | $6.772\cdot10^5$ | $4.512\cdot10^5$ | $6.608\cdot10^4$ | $4.106\cdot10^4$ |

ligible. This is why we do not observe the effect of phonon-impurity interaction weakening.

For both admixtures (nitrogen and argon) the parameter $a_p$ is smaller by two or three orders of magnitude compared to other scattering mechanisms. Therefore, the scattering of phonons by point defects affects little the thermal conductivity of the samples investigated.

From the data presented in both Tables we can see that the phonon-phonon scattering parameters are almost independent of the impurity molecules in CO–$N_2$ solid solutions.

Analyzing the data for carbon monoxide crystals containing argon one can note that if we disregard the curves which differ from other ones in shape (namely, as pointed above, CO–0.5%Ar and CO–1.25%Ar), the results obtained using Callaway's method look smoother. The contribution of dislocations increases gradually with increasing argon content. The parameters of the phonon-phonon scattering processes decrease monotonically with increasing Ar concentration. It is particularly clearly seen with the $a_{2U}$ parameter, which scales the average energy of phonons involved in U-processes.

As the nitrogen content in CO is varied, the parameter $a_D$, which quantitatively describes the significance of the phonons scattering owing to the orientational disorder of CO molecules. Firstly decreases with increasing $N_2$ admixture concentration and then begins to increase. For argon doped crystals, the intensity of phonon scattering by the subsystem of disordered carbon monoxide dipoles decreases almost for all impurity concentrations.

## Conclusions

The temperature dependence of the thermal conductivity of CO–$N_2$ and CO–Ar solutions has been determined within the temperature range 1.5–40 K for the samples containing 1.5, 3.0, 6.0, 12.5 and 25% of $N_2$ molecules and 0.5, 1.0, 1.25, 2.0 and 4.0% of Ar atoms. The thermal conductivity as a function of temperature for all solutions show a behavior typical of dielectric crystals. The height of the thermal conductivity maxima decreases with increasing concentration of both admixtures.

The experimental results were analyzed within the relaxation time approximation. The phonon scattering processes due to grain boundaries, point defects, dislocation strain fields, dipoles of orientationally disordered CO molecules, and Umklapp processes have been taken into account. Phonon scattering by point defects has the least significant effect on thermal conductivity for all crystals investigated. The parameters of phonon-phonon scattering in CO–$N_2$ solutions are almost independent of the nitrogen content. The scattering of phonons by disordered CO dipoles is significant for both solutions. A correlation between this type of phonon scattering and the concentration of the admixtures was observed.

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