Extraordinary temperature dependence of isochoric thermal conductivity of crystalline CO_2 doped with inert gases

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The isochoric thermal conductivities of solid $(CO_2)_{0.905}Kr_{0.095}$ and $(CO_2)_{1-x}Xe_x (x = 0.052$ and $0.097)$ solution of different densities was investigated in the temperature interval from 150 K to the onset of melting. An unusual effect of point defects on the thermal conductivity has been detected. In pure CO_2 at $T > 150$ K the isochoric thermal conductivity decreases smoothly with increasing temperature. In contrast, the thermal conductivity of solid CO_2/Kr and CO_2/Xe solutions first decreases passing through a minimum at $200-210$ K and then starts to increase with temperature up to the onset of melting. This behavior of the isochoric thermal conductivity is attributed to the rotation of the CO_2 molecules which gains more freedom as the spherically symmetrical inert gas atoms dissolve in CO_2.

It is believed that point defects cause extra phonon scattering reducing the thermal conductivity Λ, but the sign of the dependence $\Lambda(T)$ in the high-temperature region usually remains invariant [1]. The term «point defects» is commonly used in reference to isolated impurity atoms, molecules and vacancies. Earlier, such unusual behavior of the isochoric thermal conductivity was observed in solid CO_2 doped with Xe [2]. In pure CO_2 the isochoric thermal conductivity decreases with rising temperature exhibiting a dependence weaker than $\Lambda_V \propto 1/T$ [3]. As the Xe concentration in CO_2 increases from 0.25 to 2%, the thermal conductivity magnitude decreases by $30-40\%$ and becomes temperature-independent. The explanations of this behavior can be based on the concept of the «lower limit of the thermal conductivity» [4] assuming a «diffusive» mode of site-to-site heat transfer. The thermal conductivity of the sample grown from a dense gas phase with 9.1% Xe was observed to increase with temperature but the reason for this behavior is still obscure. The isochoric thermal conductivity was usually investigated in a rather narrow interval near

the melting point $(190-230$ K$)$ and could not provide information about its behavior at lower temperatures. It was however important to know whether the decrease in the thermal conductivity with temperature lowering was continuous and thus demonstrated the behavior typical of glasses or the thermal conductivity could start increasing like in crystals.

Later on, an increase in the high-temperature thermal conductivity at rising temperature was found in orientationally disordered phases of some molecular crystals [5,6]. This occurs because the phonon scattering at collective rotational excitations grows weaker as the rotational correlations between the neighboring molecules attenuate. The same can be true for the anomalous behavior of the thermal conductivity in the solid CO_2/Xe solution. The gain a deeper insight into the effect, it was necessary to extend considerably the temperature interval of isochoric thermal conductivity measurement and to increase the pressure in the measuring cell. The investigation was made in a coaxial-geometry setup using a steady-state method [7]. The measuring beryllium bronze cell was 160 mm long,

with an inner diameter of 17.6 mm. The maximum permissible pressure in it was 800 MPa. The inner measuring cylinder was 10.2 mm in diameter. Temperature sensors (platinum resistance thermometers) were placed in special channels of the inner and outer cylinders to keep them unaffected by high pressure. A set of protecting cylinders was used to reduce the axial heat flows. During the growth process the temperature gradient along the measuring cell was about 3 K/cm. The pressure in the inflow capillary was varied in the interval 40−140 MPa to grow samples of different densities. According to electron diffraction data [8,9], the highest solubility of Kr and Xe in CO_2 in the samples evaporated from the gas phase onto a coolable substrate was no more than 30 and 5 mol.%, respectively. The solubility can be different in bulk samples grown from a dense gas phase. To keep the gas mixture in the inflow capillarity from accumulating the component that was being pushed out, several acts of short-duration depressurization by 30−40% were performed during the growth process with subsequent restoration of pressure. The pressure was produced with a thermocompressor whose working volume was an order of magnitude larger than that of the measuring cell (200 cm³ and 28.5 cm³, respectively). This excluded large variations of the component concentrations in the gas phase and inhibited a concentration gradient in the solution. When the growth was completed, the inflow capillary was blocked by freezing it with liquid nitrogen, and the samples were annealed at T = 205−210 K for 1.5−2 h to remove density gradients. The total (dominant) error of measurement was no more than 4%. The initial purity of the gases was no worse than 99.9%.

The isochoric thermal conductivities of solid $(CO_2)_{0.905}Kr_{0.095}$ and $(CO_2)_{1-x}Xe_x$ solutions (x = 0.052 and 0.097) of different densities were investigated in the temperature interval from 150 K to the onset of melting. (The concentrations are indicated for the initial gas mixture used to grow samples; they were preassigned when the components became displaced.) The isochoric thermal conductivity of the solid $(CO_2)_{0.905}Kr_{0.095}$ solution is shown in Fig. 1 for the samples grown at P = 40, 90 and 140 MPa. The temperature intervals are specified between the arrows. The lower boundary of the interval is the temperature at which the sample either separates from the walls of the cell or becomes discontinuous. In this case the «effective» thermal conductivity reaches a plateau or decreases (not seen in the figure). The region of high-temperature measurement is limited by the onset of melting. Here the thermal conductivity also decreases usually a little [7].
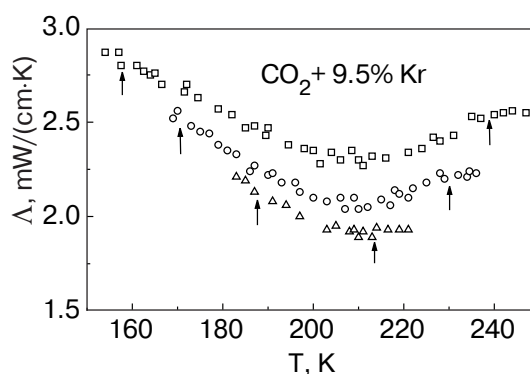

Fig. 1. Isochoric thermal conductivity of solid $(CO_2)_{0.905}Kr_{0.095}$ solution for samples grown from a dense gas phase at P, MPa: 40 (△), 90 (O) and 140 (□).

It is clearly seen that the thermal conductivity of two samples first decreases with increasing temperature, passes through a minimum at 200−210 K and then increases up to the onset of melting. This behavior is less pronounced in the CO_2/Kr solution grown under the lowest pressure (40 MPa), because it most closely approaches a free sample.

The change of the sign of the dependence $\Lambda(T)$ is rather unusual: earlier only a general decrease in the thermal conductivity of the lattice was observed after introducing an impurity [1]. The temperature of the $\Lambda_V(T)$ minimum is practically independent of the sample density, which is additional evidence that the effect has nothing to do with the premelting condition. The smoothed isobaric ($P = 0$) and isochoric (for the sample with V_m = 27.1 cm³/mol) thermal conductivities of pure CO_2 [3] and the isochoric thermal conductivity of the solid $(CO_2)_{0.905}Kr_{0.095}$ and $(CO_2)_{1-x}Xe_x$ (x = 0.052 and 0.097) grown at P = = 140 MPa are shown in Fig. 2. The temperature dependence of the isobaric thermal conductivity of pure CO_2 is close to $1/T$. The isochoric curve deviates considerably from this dependence because the thermal conductivity approaches its «lower limit» [3]. The thermal conductivity of three solutions are very close in magnitude and exhibit similar temperature dependences. The slight distinctions in the thermal conductivity of the $(CO_2)_{1-x}Xe_x$ solutions at x = 0.052 and 0.097 may be attributed to the smaller (less than 9.7%) solubility of Xe in CO_2 [9].

As mentioned above, the isochoric thermal conductivity increasing with temperature is typical of some molecular crystals with high symmetry of molecules [5,6]. (For comparison, see the isochoric thermal conductivity SF_6 of the sample with V_m = 58.25 cm³/mol at the figure bottom.) According to electron diffraction data [8,9], Kr or Xe dissolved in CO_2 loosen the crystal lattice and reduce the contribution of the anisotropic component to the binding energy of the
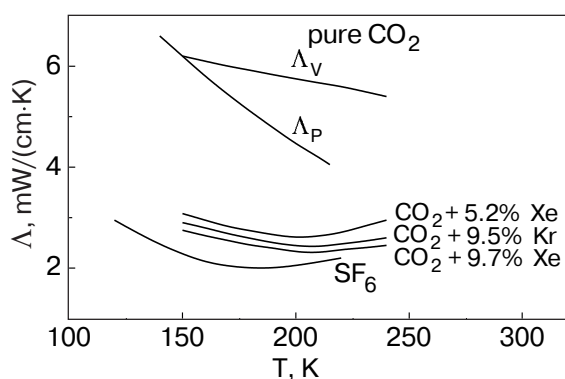
Fig. 2. Smoothed isobaric ($P = 0$) and isochoric ($V_m = 27.1$ cm^3/mol) thermal conductivities of pure CO_2 and the isochoric thermal conductivity of solid CO_2/Kr and CO_2/Xe solutions grown at $P = 140$ MPa. For comparison the isochoric thermal conductivity SF_6 of the sample with $V_m = 58.25$ cm^3/mol is shown at the bottom.

molecular crystal. Unfortunately, the structure of condensed films was investigated only up to 46 K in CO_2/Kr and 60 K in CO_2/Xe. The results of our study suggest that the rotational motion of the CO_2 molecules in these solutions is to a great extent free at premelting temperatures.

As was shown in our previous studies, the considerable freedom of the rotational motion of the molecules in molecular crystals leads to an increase in the isochoric thermal conductivity [5,6]. This occurs because the phonon scattering at collective rotational excitations becomes weaker as the rotational correla-

tions of the neighboring molecules attenuate. The extraordinary behavior of the isochoric thermal conductivity of solid CO_2 doped with inert gases prompts the conclusions about intensive reorientational motion of the molecules in these solid solutions at premelting temperatures.

1. R. Berman, *Thermal Conduction in Solids*, Oxford, Clarendon Press (1976).
2. V.A. Konstantinov, V.G. Manzhelii, and S.A. Smirnov, *Fiz. Nizk. Temp.* **14**, 749 (1988) [*Sov. J. Low Temp. Phys.* **14**, 412 (1988)].
3. V.A. Konstantinov, V.G. Manzhelii, S.A. Smirnov, and A.M. Tolkachev, *Fiz. Nizk. Temp.* **14**, 189 (1988) [*Sov. J. Low Temp. Phys.* **14**, 104 (1988)].
4. D.G. Cahill, S.K. Watson, and R.O. Pohl, *Phys. Rev.* **B46**, 6131 (1992).
5. V.A. Konstantinov and V.G. Manzhelii, in: *Die Kunst of Phonons,* T. Paskiewizc, and T. Rapsewizc (eds.), New York, London: Plenum Press (1994), p. 321.
6. O.I. Purskii, N.N. Zholonko, and V.A. Konstantinov, *Fiz. Nizk. Temp.* **29**, 1021 (2003) [*Low Temp. Phys.* **29**, 749 (2003)].
7. V.A. Konstantinov, S.A. Smirnov, and V.P. Revyakin, *Instr. Exp. Tech.* **42**, 133 (1999).
8. S.J. Kovalenko and A.A. Solodovnik, *Fiz. Nizk. Temp.* **18**, 749 (1992) [*Low Temp. Phys.* **18**, 626 (1992)].
9. S.J. Kovalenko and A.A. Solodovnik, *Fiz. Nizk. Temp.* **19**, 336 (1993) [*Low Temp. Phys.* **19**, 238 (1993)].