Thermal conductivity of solid argon with oxygen admixtures

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(Received 6 October 1997)

Thermal conductivity investigations of pure and oxygen doped argon crystals have been carried out over the temperature range 1.3–26 K. Samples with oxygen concentration of 0.008, 0.024, 0.063, 0.225, and 0.390 mol % were measured. The result is that the interaction of phonons with the spin-rotational motion of oxygen molecules in an argon matrix is the most significant among possible mechanisms of phonon scattering by the impurities. In the thermal conductivity of the samples, no mutual interaction of the oxygen impurities has been observed over the investigated impurity concentration range. [S0163-1829(98)01129-1]

I. INTRODUCTION

Argon crystal is the best experimentally known noble gas. As with other rare gas solids, it is bound by van der Waals forces and has a fcc structure in the whole range of temperatures and pressures.

The first measurements of its thermal conductivity were made in the 1950's by White and Woods.¹ Up to now, a number of measurements have been made by other experimentators, both at constant volume and at equilibrium vapor pressure, in various temperature intervals (e.g., Refs. 2–4).

Investigations of the influence of impurities on the thermal conductivity of such a simple solid can be a source of information on lattice dynamics and dissipation processes. Because of the abundance of data on the effect of isotopic impurities on the thermal conductivity of rare gas solids, studies in which the impurity possesses additional degrees of freedom (besides different mass and force constants) compared to the matrix atoms are particulary interesting. Results of such investigations are presented in Ref. 5, where the crystal of argon was doped with nitrogen molecules. The argon-oxygen system seems particularly interesting for such investigation since molecular parameters of argon and oxygen are similar and, moreover, oxygen molecules possess spin and rotational degrees of freedom.

From structural investigations (see Ref. 6, and references therein) it is known that argon crystals doped with oxygen at a concentration below 1% form homogenous solutions with the same fcc structure, where matrix atoms are substituted with O_2 molecules. The spatial distribution of the molecules is statistical. The latter was confirmed by results of heat capacity⁷ and thermal expansion⁸ investigations.

II. EXPERIMENT

To determine the influence of oxygen impurities on the temperature dependence of the thermal conductivity of argon crystal we made a series of measurements in which we examined pure argon crystal as well as solidified argon samples doped with oxygen of 0.008, 0.024, 0.063, 0.225, and 0.390 mol % in the temperature interval of 1.3–26 K. The samples were obtained and their conductivity was examined in a glass ampoule installed in the cryostat described in our earlier paper.⁹ The ampoule was made from a glass pipe of a circu-

lar crosssection. The ampoule was 67 mm in length, its inner diameter was 6.4 mm, and the thickness of the wall about 1 mm. The measurements of the thermal conductivity were made by means of the steady state method.¹⁰

We used argon of a natural isotopic composition and purity 99.997% for sample preparation. The gas was contaminated mainly with oxygen; its concentration was about 30 ppm. The oxygen for dopping was obtained by the thermal decomposition of KMnO₄. The latter gas was of a natural isotopic composition with 0.01% of CO₂. The crystals of argon, both pure and doped, were grown by the desublimation method at pressures and temperatures of condensation which are a little below the triple point of argon, at conditions assuring the crystal growth in fcc phase (see Ref. 11, Ar-O₂ phase diagram). The rate of the sample growth was about 1 mm/h with a temperature gradient along the sample of about 0.3 K/cm. To lower the amount of defects the sample was annealed for 12 h at a temperature close to that of the triple point.

III. RESULTS AND DISCUSSION

The temperature dependence of the thermal conductivity $\kappa(T)$ for the examined samples is shown in Fig. 1. The results are typical for dielectric crystals. Each curve determined by experimental points has the characteristic maximum. The magnitude of this maximum decreases and its temperature increases with the increase of the oxygen concentration.

In order to determine the mechanisms of the phonon scattering in the argon-oxygen system we introduce the function

$$\Delta W(c,T) = W(c,T) - W(T)$$

which describes the additional thermal resistivity to that of the matrix of pure argon W(T). The thermal resistivity of the crystal doped with oxygen is denoted by W(c,T), where *c* stands for oxygen concentration. We define the inverse of the thermal conductivity as the thermal resistivity. Figure 2 illustrates the temperature dependence of the normalized additional thermal resistivity $\Delta W(c,T)/c$, which can be interpreted as the resistivity per impurity (oxygen) molecule. The values of $\Delta W(c,T)/c$ lie, in the first approximation, on a single curve (const $\times T^{-2}$). This means that at sufficiently

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FIG. 1. The thermal conductivity of pure and oxygen doped argon crystals. \bullet : pure Ar, \Box : Ar, 0.00008 mol O₂; \triangle : Ar, 0.00024 mol O₂; \bigcirc : Ar, 0.00063 mol O₂; +: Ar, 0.00225 mol O₂; \bigtriangledown : Ar, 0.00390 mol O₂.

low concentrations (less than 0.0039 mol) the impurity molecules do not interact mutually with each other.

Let us consider now what phonon scattering mechanisms can be expected after introducing an oxygen molecule to a pure argon crystal. One can presume in general that there is Rayleigh scattering, resonance scattering, following from the difference of the masses between the matrix atom and impurity molecule, scattering by impurity rotations, and scattering related to spin degrees of freedom of the impurity.

The thermal resistivity resulting from Rayleigh scattering should be a linear function of the temperature.¹⁰ The resonance scattering should also be excluded, since the mass ratio (of the impurity to matrix atom) in our case is less than the threshold value of 1.2 (Refs. 12,13). This means that the resonance peak of the phonon spectrum of the crystal will be present in the vicinity of the Debye frequency of the argon



FIG. 2. The normalized additional thermal resistivity per unit oxygen concentration in argon matrix. Result for samples \Box : Ar, 0.00008 mol O₂; \triangle : Ar, 0.00024 mol O₂; \bigcirc : Ar, 0.00063 mol O₂; +: Ar, 0.00225 mol O₂; ∇ : Ar, 0.00390 mol O₂.



FIG. 3. The thermal conductivity of solid argon containing 30 ppm of O_2 . \bigcirc : experimental data. The lines denote result obtained from the Callaway equation: dashed lines are for the approximation without the resonant scattering and solid lines for the approximation taking the resonant scattering into account.

crystal. Therefore, the resonance scattering should also have no impact in the temperature interval examined by us, and only impurity rotations and spin degrees of freedom contribute to the thermal conductivity in the case of the investigated system.

A linear molecule in the noble gas crystal matrix is an example of the rotator hindered in the crystal field, and its behavior can be described by the DMM model.¹⁴ Interaction of rotating admixture molecules with environment is effectively taken into account by renormalization of their moments of inertia. The spin-rotational energy spectrum of the oxygen molecule in the argon crystalline field was given in Ref. 7. (In the spectrum one can distinguish two groups of molecule energy levels by mean energies of 2 and 12 K). Thus, numerous transitions between the energy levels are possible. Each transition is accompanied with an energy exchange between the molecule and the phonon field.

Further argument for the essential contribution of the phonon scattering on the rotation of the oxygen molecule is supplied by the following fitting procedure. Consider first whether the thermal conductivity $\kappa(T)$ of the matrix (doped with oxygen at 30 ppm, see above) can be described by the Callaway equation¹⁵ which accounts for the phonon scattering on grain boundaries, isotopic impurities, dislocation strain fields, and U processes. The Callaway equation describes the thermal conductivity temperature dependence using phonon relaxation times for different scattering mechanisms; parameters of the relaxation times can be varied to obtain the best fitting of the equation to the experimental points. The result of such a fitting (in the equation, the normal processes were not taken into account; the relaxation time frequency dependencies for the phonon scaterring processes were the same as used in Ref. 16) is marked by the dashed line in Fig. 3. The inflection point in the vicinity of 3 K is not reproduced and, moreover, the magnitude at the maximum is wrong. A good fitting is obtained when a term describing the phonon scattering by the impurity rotations¹⁷ is additionally taken into account. This is shown by the solid



FIG. 4. The normalized additional thermal resistivity vs reduced temperature. Data for samples. \blacktriangle : Ar, 0.00390 mol O₂; \bigoplus : N₂, 0.0020 mol O₂.

line in Fig. 3 and is clearly better at the temperatures above 2.5 K than that represented by the dashed line. The single resonant frequency resulting from the fitting is $\omega = 1.217 \times 10^{12} \text{ s}^{-1}$, which corresponds to 9.3 K. When relating this value to the energy spectrum (Ref. 7), it can be assigned to the difference of the two distinct groups of levels in the spin-rotational spectrum of O₂. An improvement of the fitting at the temperatures lower than 2.5 K can be obtained by introducing further resonant scatterings of lower energies into the Callaway equation. They should describe other allowed transitions between the energy levels in molecular spectra.

Finally, it is worth comparing the additional thermal resistivity $\Delta W/c$ in the systems of argon-oxygen and nitrogen-

oxygen. In Fig. 4 such a comparison is made for the values of $\Delta W/c$ vs T/Θ , where Θ is the Debye temperature, for the samples containing 0.0039 mol of oxygen in argon and 0.0020 mol of oxygen in nitrogen.¹⁸

The characters of the dependencies are different, and at low temperatures the values corresponding to the nitrogenoxygen system are three orders of magnitude lower than those of the argon-oxygen one. Such a big difference can be a consequence of a strong coupling between phonons and rotations of the linear impurity, occurring in noble gas crystals doped with molecules of the linear symmetry¹⁹ on the one hand and merely a slight modification of the nitrogen vibrational spectrum by molecules of O₂ introduced into the N₂ matrix, on the other.

IV. CONCLUSION

One can say that the introduction of oxygen impurities into argon crystal causes a significantly stronger effect on its low-temperature thermal conductivity than the introduction of oxygen impurity into nitrogen matrix. From among possible phonon scattering mechanisms by oxygen impurities in argon crystal the most efficient one is the elastic phonon spin-rotational impurity molecule motion interaction. The effect has a distinct resonant character and allows us to describe singularities of the $\kappa(T)$ curve for argon crystal doped with oxygen. In the samples over the investigated oxygen concentration range (0.008, 0.024, 0.063, 0.225, 0.390 mol %) no mutual interactions of impurity molecules were observed.

ACKNOWLEDGMENTS

We gratefully thank Dr. Krzysztof Durczewski and Dr. Boris Ya. Gorodilov for their valuable discussions.

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