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## LETTER TO THE EDITOR

# Thermal conductivity of solid oxygen doped with nonmagnetic impurities

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**Abstract.** Measurements of the thermal conductivity ( $\kappa$ ) of solid oxygen doped with nonmagnetic impurities of N<sub>2</sub> (0.34 and 0.94%) and Ar (1%) were made in the temperature range 1–35 K. It was shown that in the antiferromagnetic  $\alpha$  phase doping with nonmagnetic impurities has a drastic effect on low-temperature thermal conductivity which supposedly is a result of suppression of the magnon contribution to the heat transport by the impurities. At the same time, the jump in the thermal conductivity at the  $\alpha$ – $\beta$  transition and the thermal conductivity in the  $\beta$  phase are practically insensitive to the doping effect which we attribute to strong magnetostriction effects characteristic of the  $\beta$  phase.

Solid oxygen reveals anomalies in most of its thermodynamic, magnetic and optical properties (see e.g. [1] and references therein). Recently it was found [1] that the thermal conductivity of solid oxygen also displays an anomalous character. Solid oxygen combines properties of a molecular crystal and a magnet. The temperature dependence of its thermal conductivity differs, however, pronouncedly both from typical simple molecular crystals, such as N<sub>2</sub> [2], and from antiferromagnets [3].

In particular, there is a considerable jump in the thermal conductivity at the phase transition from low-temperature antiferromagnetic  $\alpha$  phase to intermediate  $\beta$  phase that possesses a strong short-range magnetic order ( $T_{\alpha\beta} = 23.9$  K). The jump amounts to two-thirds of the total thermal conductivity below the transition point. In the  $\beta$  phase the thermal conductivity does not practically depend on temperature. In the magnetically and orientationally disordered  $\gamma$  phase ( $T_{\beta\gamma} = 43.8$  K) the thermal conductivity increases with temperature.

As stated in [1], the anomalous character of the thermal conductivity of solid oxygen is supposedly of magnetic origin. More specifically, the lower magnon mode has a relatively small gap ( $6.4$  cm<sup>-1</sup> [4]) and the large dispersion i.e. large group velocity of magnons contributes considerably to the heat transport. Thus, in the low-temperature region the total thermal conductivity is the sum of the phonon thermal conductivity and the magnon contribution from a lower magnon mode, whereas librations and the upper magnon mode, due to large gaps in their energy spectrum, contribute mostly to scattering processes.

As none of the measured thermodynamic characteristics, or the molar volume, show a jump at the  $\alpha$ – $\beta$  transition point [5], the observed jump of the thermal conductivity at the  $\alpha$ – $\beta$  transition was associated in [1] with the magnon component of the heat transport.

After the transition into the magnetically disordered  $\beta$  phase this contribution disappears. This gives rise to the jump.

Measurements of thermal conductivity in high magnetic fields, shifting positions of the magnon modes and at the same time not disturbing the phonon modes, could shed light on the nature of the jump.

There exists another possibility to verify the hypothesis of the magnon origin of the anomalies in the thermal conductivity. It involves doping solid oxygen with nonmagnetic impurities. Such impurities damp and change the frequencies of the magnon modes. This influences the magnon contribution to thermal conductivity.

We took  $N_2$  and Ar as nonmagnetic impurities which have parameters  $\epsilon$  and  $\sigma$  of the Lennard-Jones intermolecular potential close to those of oxygen. Inspection of phase diagrams of solid solutions of  $O_2$ - $N_2$  [7] and  $O_2$ -Ar [8] revealed that the solubility of  $N_2$  does not exceed 1% in  $\alpha$ - $O_2$  and 2% in  $\beta$ - $O_2$ . The solubility of Ar in  $\alpha$ - $O_2$  does not exceed 2%; in the  $\beta$  phase near the point of  $\alpha$ - $\beta$  transition the solubility increases to 5%, falling to 2% with increasing temperature.

Far-infrared absorption spectra of the solid solutions studied allow us to gain information about the effect of the impurities on the position, half-width and intensity of magnon modes. Such investigations are described in [9] for the  $O_2$ - $N_2$  system and in [10] for the  $O_2$ -Ar system. Unfortunately, information presented in these works seems to be incomplete, and, besides, refers only to the upper magnon mode. In particular, it was shown [10] that the increase of Ar concentration in the sample up to 1% had no tangible effect on the frequency of the magnon mode. However, the intensity of the mode decreased 2.5-fold, and its half-width increased more than twofold when compared to the respective values for pure oxygen. The intensity of the magnon mode in doped samples declined with increasing temperature more rapidly than it did in undoped ones, and above 20 K the mode became unobservable.

Thus, it should be expected that doping solid oxygen with impurities will influence the thermal conductivity considerably more strongly than in the case of nonmagnetic molecular crystals.

In the present work the thermal conductivity of solid solutions  $O_2$ - $N_2$  (0.34% and 0.94%  $N_2$ ) and  $O_2$ -1% Ar in the temperature range 1-35 K was investigated.

The measurements of the thermal conductivity were carried out by the stationary heat flow method in a glass ampoule 20 mm long and 3.95 mm in diameter, of 0.50 mm wall thickness. The temperature of the sample and the temperature gradient were determined with two germanium resistance thermometers attached to the ampoule 8.10 mm apart. The lower thermometer was placed approximately 7 mm from the ampoule bottom.

The purity of the investigated substances was as follows:  $O_2$ , 99.99% (main impurity, 0.01%  $CO_2$ );  $N_2$ , 99.9995% (main impurity,  $O_2$ ); and Ar, 99.995% (main impurities,  $O_2$  and  $N_2$ ).

Gaseous mixtures for the samples were prepared by the *PVT* method. Composition analysis of the sample was performed before and after the measurements with a mass spectrometer. The error of the composition determination did not exceed 0.01%.

The samples were grown from the liquid phase. The conditions of crystal growth and the sample cooling rate were the same as in [1]. The random error of the thermal conductivity measurements did not exceed 3%.

The experimental data obtained are shown in figures 1-3. Figure 1(a) shows the temperature dependence of thermal conductivity for solid oxygen [1] and solid solutions of  $O_2$ -0.34%  $N_2$ ,  $O_2$ -0.94%  $N_2$  and  $O_2$ -1% Ar. Figure 1(b) shows, for comparison, the thermal conductivity for pure solid  $N_2$  [2] and the solid solution  $N_2$ -1.12%  $O_2$  [11].

The data for the  $O_2$ -0.94%  $N_2$  and  $O_2$ -1% Ar solid solutions are shown in figure 2 as

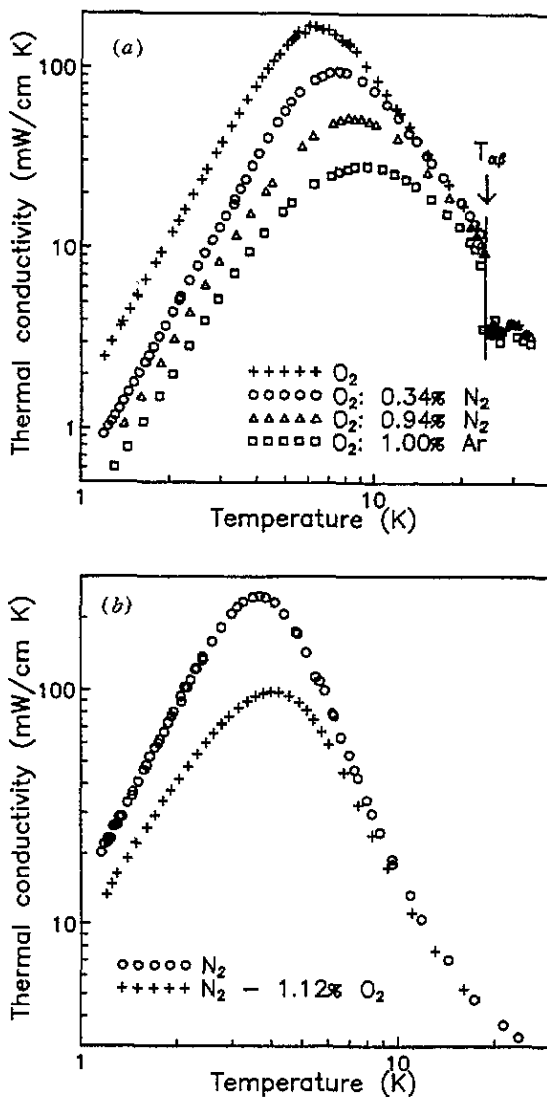


Figure 1. The temperature dependences of thermal conductivity of (a) pure solid oxygen [1] and the solid solutions O<sub>2</sub>-N<sub>2</sub> and O<sub>2</sub>-Ar and (b) pure solid nitrogen [2] and the solid solution N<sub>2</sub>-O<sub>2</sub> [11].

plots of  $\Delta W$  against  $T$  where  $\Delta W$  is the excessive thermal resistivity obtained by subtracting the thermal resistivity of pure oxygen from the values for solid solutions.

Figure 3 shows the temperature dependence of  $\Delta W/W(\text{O}_2)$  (the relative value of the excessive thermal resistivity) for the solid solutions studied. For comparison, the analogous quantity  $\Delta W/W(\text{N}_2)$  for the system N<sub>2</sub>-1.12% O<sub>2</sub> [11] is shown. To compare data relating to different concentrations ( $c$ ), the curves were normalized to 1% of impurities, i.e. to the value  $c^* = 100c$ .

The curves of thermal conductivity versus  $T$  for all the solid solutions studied, as well as for pure oxygen, exhibit well defined maxima (figure 1(a)). Doping with impurities leads to considerable lowering and widening of the maxima, and shifting of the maximum

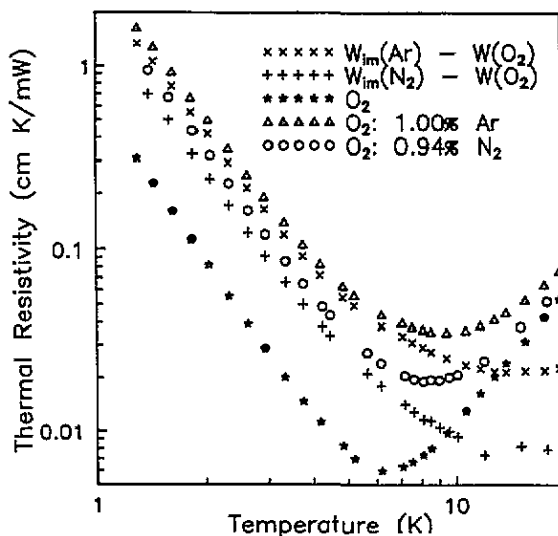


Figure 2. A comparison of excess (relative to the matrix) thermal resistivity of the solid solutions  $O_2$ -Ar and  $O_2$ - $N_2$  with the total resistivity of pure solid oxygen and  $O_2$ -Ar and  $O_2$ - $N_2$  solutions.

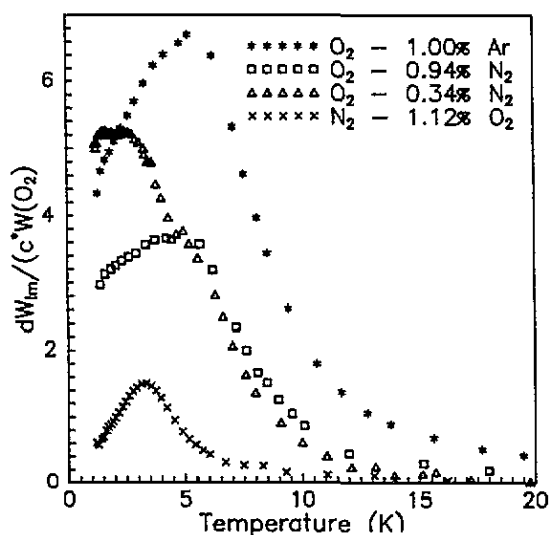


Figure 3. A comparison of the temperature dependences of the relative (to the matrix) thermal resistivity of the solid solutions  $O_2$ -Ar,  $O_2$ - $N_2$  and  $N_2$ - $O_2$ , normalized to 1% of admixture.

positions towards higher temperatures. All the effects are notably stronger in the case of impurity-doped solid oxygen than in the case of impurity-doped solid nitrogen (figure 1(b)) [11]. Doping  $O_2$  with 1% Ar results in a shift of the thermal conductivity maximum relative to its position for pure oxygen amounting to more than 3 K; in the case of  $O_2$ -0.94%  $N_2$  it amounts to 2.5 K. On the other hand, in the case of  $N_2$ -1.12%  $O_2$  the shift does not exceed 0.4 K [11].

Examination of figures 2 and 3 reveals that, in the low-temperature region, the excessive

thermal resistivity of solid solutions exceeds the thermal resistivity of the matrix, i.e. scattering of the thermal flow on impurities turns out to be the main cause of the thermal resistance. The maximum value of  $\Delta W/c^*W(O_2)$  for nitrogen-doped solid oxygen is more than twice (in the case of  $O_2$ -1% Ar over four times) that for solid  $N_2$  doped with oxygen.

The data on the low-temperature thermal conductivity ( $T < 3.4$  K) can be described as a power law of the form  $\kappa \propto T^\delta$ . The exponent  $\delta$  which, in general, is a function of the impurity concentration, turned out to be the same for pure oxygen and for the solid solutions containing 0.34% and 0.94%  $N_2$ . As a result, the curves  $\Delta W/W(O_2)$  (figure 3) contain near-horizontal sections in the low-temperature range. This is the region where according to [1] the magnon contribution for pure oxygen to the heat transport is considerable. This contribution can be roughly estimated from the data in figure 3. The total thermal conductivity is the sum of a phonon thermal conductivity  $\kappa_{ph}$  and a magnon contribution  $\kappa_m$ . The relative value of the excessive thermal resistivity can be expressed in terms of  $\kappa_{ph}$  and  $\kappa_m$ :

$$\Delta W/W = (\kappa_{ph}^0 + \kappa_m^0) / (\kappa_{ph} + \kappa_m) - 1$$

where  $\kappa_{ph}^0$  and  $\kappa_m^0$  are the values for pure solid oxygen.

Assuming that in the solid solution with a considerable content of impurities the magnon contribution is suppressed,  $\kappa_{ph} \gg \kappa_m$ , we obtain the expression

$$\Delta W/W = \kappa_{ph}^0/\kappa_{ph} + (\kappa_m^0/\kappa_{ph}^0)\kappa_{ph}^0/\kappa_{ph} - 1.$$

Taking the value for the solid solution  $N_2$ -1.12%  $O_2$  from figure 3, for an estimation of  $\kappa_{ph}^0/\kappa_{ph}$  we arrive at the estimation of the relative contribution  $\kappa_m^0/\kappa_{ph}^0 \sim 2$  which is in agreement with the estimation obtained in [1].

In the low-temperature range the effects of doping is essentially nonlinear with respect to concentration. However, at  $T \gtrsim 5$  K the effect is approximately linear with respect to concentration of  $N_2$ . When temperature increases, the relative value of the impurity effect decreases. For the  $O_2$ -0.34%  $N_2$  solid solution above 18 K the effect becomes insignificantly small, but for the solutions  $O_2$ -0.94%  $N_2$  and  $O_2$ -1% Ar the influence of impurities is distinctly observable up to the point of the  $\alpha$ - $\beta$  transition.

The two most unexpected effects are found to be (i) preservation of the jump in the thermal conductivity at the  $\alpha$ - $\beta$  transition in the presence of impurities and (ii) the fact that the thermal conductivity in the  $\beta$  phase is essentially insensitive to the presence of impurities (figure 1).

Although the value of the jump depends on the kind and concentration of the impurities (for pure  $O_2$  and solid solutions containing 0.34%  $N_2$  the jump amounts to  $\sim \frac{2}{3}$  of the total thermal conductivity; for  $O_2$ -0.94%  $N_2$ ,  $\sim \frac{2}{5}$ ; for  $O_2$ -1% Ar,  $\sim \frac{1}{3}$ ), the jump in the thermal conductivity appears to be an intrinsic property of the  $\alpha$ - $\beta$  transition.

There is a reason to believe that the jump in thermal conductivity at the  $\alpha$ - $\beta$  transition point and the insensitivity of the thermal conductivity of the  $\beta$  phase to the presence of impurities have a common origin, namely, peculiar features of the  $\beta$  phase. As recently demonstrated in an x-ray investigation [12], strong spontaneous magnetostriction is characteristic of the  $\beta$  phase. It leads to a considerable inhomogeneous lattice distortion. This distortion contributes to the thermal resistivity so significantly that scattering on impurities turns out to be just a small additional contribution.

Therefore, the data obtained suggest that the statement presented by us in [1] that the jump in the thermal conductivity at the  $\alpha$ - $\beta$  transition is connected entirely with the magnon

contribution to the heat flow should be revised. The quantity that undergoes the jump at the transition point is rather the phonon mean free path. It may be suggested that the drop in the phonon mean free path is a result of the appearance of a new scattering factor—the existence of the regions of inhomogeneous lattice distortion caused by strong magnetostriction effects, peculiar to the  $\beta$  phase of solid oxygen—but only measurements of thermal conductivity in a strong magnetic field will make it possible to separate unambiguously the contributions of the two effects in the jump.

To conclude, we have presented results of the measurements of thermal conductivity of solid oxygen doped with impurities of  $N_2$  and Ar. It was shown that in the antiferromagnetic  $\alpha$  phase at temperatures  $T < 10$  K doping with nonmagnetic impurities has a pronounced effect on thermal conductivity. We suggest that in the low-temperature range the nonmagnetic impurities strongly suppress the magnon contribution to heat transport. The jump in the thermal conductivity at the  $\alpha$ - $\beta$  transition, revealed earlier in pure oxygen, is preserved in solid solutions. The thermal conductivity of the  $\beta$  phase turned out to be practically insensitive to the presence of impurities. Contrary to a supposition presented earlier, that the jump in thermal conductivity at the  $\alpha$ - $\beta$  transition is connected entirely with the magnon contribution to heat flow, the present work suggests that it is the phonon mean free path that undergoes the jump at the transition to the  $\beta$  phase. This fact, as well as the insensitivity of the thermal conductivity of the  $\beta$  phase to the content of impurities, are results of strong magnetostriction effects, characteristic of the  $\beta$  phase.

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