Thermal Conductivity of Solid Oxygen

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This paper reports the results of the first measurements of the thermal conductivity of the α, β, and γ phases of solid oxygen over the temperature range of 1-52 K. A simple qualitative analysis was performed to explain the observed anomalies in thermal conductivity, which manifested themselves by a jump at the α-β transition, the anomalously weak temperature dependence in the β phase, and an increase of the conductivity with temperature in the γ phase.

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Solid oxygen, a unique crystal combining properties of a molecular crystal and a magnet, has been a subject of intensive experimental and theoretical studies during the last two decades (see, for example [1-17], and references therein). The following picture has emerged as a result of those studies. Oxygen exists under the equilibrium vapor pressure in three crystalline modifications. The orientationally ordered monoclinic low temperature α phase ($C2/m$) is a collinear two-sublattice quasi-2D antiferromagnet. The phase transition ($T_{\alpha\beta}=23.9$ K) into the intermediate rhombohedral β phase ($R\bar{3}m$) is associated with the transformation of the magnetic structure. The nature of this transformation is still a subject for discussion [13].

Though none of the measured thermodynamic characteristics as well as the molar volume [5] show any jump at the α-β transition point and, moreover, the heat of transition has not been detected in precise calorimetric study [3], the α-β transformation is beyond all doubts a first order phase transition. This conclusion follows, for instance, from the observation of hysteresis of the magnetization curves at the transition [11].

The long-range magnetic order in β-oxygen is most probably absent; however the short-range order with the correlation length of 5 Å in three-sublattice or incommensurate helicoidal structures persists over the whole range of the existence of the phase [11,14,15].

Both the low temperature phases have the same orientational structure in which the molecular axes are collinear and perpendicular to the close packed layers. The spectrum of elementary excitations in the α phase consists of (besides acoustic modes) two libron modes at 43 and 78 cm^{-1} [2] and two magnon ones at 6.4 and 27 cm^{-1} [1,4]. No magnon excitations were found in the β phase and there is one twofold degenerated libron mode at 50 cm^{-1} [2].

The β-γ transition ($T_{\beta\gamma}=43.8$ K) is accompanied by a radical rearrangement of the lattice, a considerable jump (5.4%) of volume [5], and high value of the latent heat of the transition [3]. The γ phase has an eight-molecule cubic cell with an orientationally disordered structure with $Pm3n$ symmetry. It exhibits paramagnetic properties with a quasi-1D magnetic short-range order [9,10].

In this paper we report results of the first measurements of the thermal conductivity of the α, β, and γ phases of solid oxygen.

The measurements of the thermal conductivity were carried out by the stationary heat flux method over a temperature range of 1-52 K. The design of the measurement cell was described in [18]. A glass ampoule of 19.9 mm height, inner diameter of 3.93 mm, and wall thickness 0.52 mm was used. The temperature gradient was measured with two calibrated (by Lake Shore Cryotonics) germanium resistance thermometers attached to the ampoule wall, separated 8.5 mm from each other. The lower thermometer was placed 5 mm from the ampoule bottom.

The oxygen used for sample preparation was of 99.99% purity, obtained by thermal decomposition of $KMnO_4$. The composition analysis was performed before and after the measurements by means of a mass spectrometer. Before the experiments there was 0.01 mol% of CO_2 impurity in the gaseous phase. The method of growing of the crystalline samples prevented any ingress of that impurity into the measuring cell. The relative uncertainty in the measured thermal conductivity was not higher than 10% in the whole temperature range. More experimental details are given in [18].

The high jump of the volume during the β-γ transformation and the anomalously low equilibrium vapor pressure made the growing of large single crystals of α- and β-O_2 unfeasible. That is why the studies of the thermal conductivity, which impose high demands upon the sample quality, were never performed for the two low temperature phases of solid oxygen. The sole measurement of the thermal conductivity was done for a single point at 48 K in the γ phase [19].

The most comprehensive study on the influence of

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growth conditions upon sample quality was performed by Prikhotko, Pikus, and Shanskii [20]. It was shown there that the number of nucleation centers of the β phase could be significantly reduced by slowing down the velocity of passing through the γ-β transition point and annealing the samples just below the transition point. The latter gives rise to amalgamation of the closely oriented grains and growth of some of them at the expense of others. The authors reported that they had managed to grow single crystals of the β phase of sizes up to 0.2–0.4 mm and the crystals did not crack during subsequent cooling.

In the present study the samples of solid oxygen were grown from the melt with the velocity of movement of the solidification front of ca. 1 mm/h. The samples were annealed slightly beneath the triple point for about 6 h.

As a result we obtained transparent single crystals of γ-oxygen. The rate of cooling from T_{tr} to the point of the γ-β transformation was 1 K/h. The total time of the γ-β transition passage was about 100 h. During this time the temperature of the sample bottom was decreased from 43.9 to 42.5 K, while the temperature gradient along the vertical axis of the sample was kept constant (0.6 K). The same gradient was maintained during the cooling cycle down to liquid helium temperature. The cooling rate of β-oxygen was 1.5 K/h. The region of the β-α transition was traversed during 5 h. The samples of α- and β-oxygen were transparent without visible defects, although slightly cloudy.

Results of the thermal conductivity coefficient κ measurements of the α, β, and γ phases for three separated samples of solid oxygen performed during cooling are given in Fig. 1. Also, the data obtained for one of the samples taken during heating through the region of phase transitions are presented in this figure. As one can see, the temperature dependence of the thermal conductivity in the α phase is typical for a dielectrics curve with a maximum around 6 K. The magnitude of the thermal conductivity at the maximum (approximately 0.17 W/cm K) is nearly the same as the maximum thermal conductivity of the classical rare gas solids like Ar or Kr [21]. It is also close to the sole measured simple molecular crystal, solid nitrogen [22]. However, it is distinctly smaller as compared to the maximum thermal conductivity of quantum solids like He [21] or H_2 [23].

The most intriguing feature is a jump in the thermal conductivity of the solid oxygen at the α-β transition point. The decrease of the κ value at the transition temperature amounts to 70%. It should be stressed that the data are not only reversible for both directions of temperature change but also reproducible for different runs and samples.

In the β phase thermal conductivity only slightly decreases with rising temperature. The temperature dependence can be represented by the equation $\kappa=(3.92-0.0117T)\times10^{-3}$ W/cm K. The total change of the thermal conductivity over the temperature range of existence of the β phase equals ca. 10%. At the β-γ transition point the thermal conductivity drops by 60%. In the γ phase the thermal conductivity increases nearly linearly with increasing temperature.

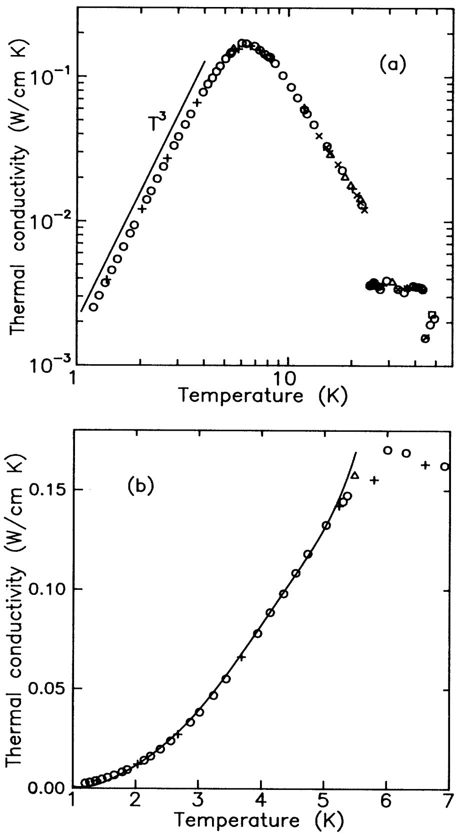

FIG. 1. Thermal conductivity of solid oxygen as a function of temperature. (a) Present experiment: ○, +, △, cooling; ×, heating; □, point from [19]. (b) ○, +, △, experiment; solid line, theoretical calculation [sum of coefficients κ_{ph} and κ_m, Eqs. (1) and (2)].

Summarizing, we can say that the character of temperature dependence of the thermal conductivity of solid oxygen is anomalous and differs pronouncedly from both typical antiferromagnet [24] as well as molecular crystal [22].

Considering that the dynamics of solid oxygen includes the coupling between phonons, librons, and magnons, one might expect that the quantitative analysis of the thermal conductivity of solid O_2 is rather complex. This will be the subject of further work. Below we will discuss qualitatively the anomalies found in the thermal conductivity of solid oxygen: the jump in the thermal conductivity at the α-β transition and the temperature dependences of thermal conductivity in the β and γ phases.

In the magnetically ordered α phase the total thermal conductivity is the sum of a phonon thermal conductivity κ_{ph} and a magnon contribution κ_m, whereas librons, due to a large gap in their energy spectrum, contribute mostly to the scattering mechanisms. The main contribution to the magnon thermal conductivity comes from the lower magnon mode with the quasi-2D energy spectrum [25]: $E(\mathbf{k})=E_1+(\hbar^2/2ma^2)(k_x^2+k_y^2)$, where E_1 is the lower antiferromagnetic resonance frequency [4], and $m^{-1}=(a^2/2\hbar^2)(I/E_1)^2E_1$. Here m denotes the magnon effective mass, $I=\eta zJ$ is the effective exchange field, η is the magnetic order parameter, z is the number of magnetic nearest neighbors, J is the exchange constant, and a is the lattice constant. At temperatures below the maximum, the heat transport is limited by phonon and magnon scattering against grain boundaries. The low temperature asymptotes for the phonon and magnon thermal conductivities read

$$\kappa_{\mathrm{ph}}=\frac{12}{\pi^2}\frac{R}{V}vl\left(\frac{T}{\Theta_D}\right)^3, \tag{1}$$

$$\kappa_m=\frac{1}{3\sqrt{\pi}}\frac{R}{V}E_1a\frac{l}{\hbar}\frac{E_1}{I}\left(\frac{E_1}{T}\right)^{1/2}\exp\left(-\frac{E_1}{T}\right), \tag{2}$$

where R is the gas constant, V the molar volume, Θ_D the Debye temperature, l a mean free path, and v an average sound velocity which was computed on the basis of experimental data of the longitudinal and transverse sound velocities v_l and v_t [19,26], $v=[(v_l^{-3}+2v_t^{-3})/3]^{-1/3}$.

The total thermal conductivity calculated as the sum of Eqs. (1) and (2) in the temperature range $T<5$ K follows fairly well the experimental data [see Fig. 1(b)]. The mean free path l obtained from the comparison of the observed and the calculated thermal conductivities is 10^{-2} cm. This value is in a good agreement with the grain size of α-O_2 samples grown by Prikhotko, Pikus, and Shanskii [20] under similar conditions.

The relative contribution $\kappa_m/\kappa_{\mathrm{ph}}=(\pi^{3/2}/36)(\Theta_D^2/E_1I)\times(E_1/T)^{7/2}\exp[-E_1/T]$ passes through maximum at $T=2/7E_1$. Using the measured values for $E_1=6.4\ \mathrm{cm}^{-1}$ [4], $\Theta_D=104$ K [3,27], and $I=200$ K [25] we obtain that the ratio reaches the maximum of 2.2 at $T=2.6$ K.

This estimation shows that the magnon heat transport may be a considerable part of the total heat transport. With increasing temperature magnons gradually start to contribute also to scattering processes and upon approaching the α-β transition the upper magnon mode 27 cm^{-1} will take part both in the scattering and the heat transport.

We associate the observed jump of the thermal conductivity at the α-β transition with the magnon component of the heat transport, which then amounts to $\frac{2}{3}$ of the total heat flow. This contribution naturally disappears after the transition into the magnetically disordered β phase, which gives rise to the jump. The phonon mean free path calculated with this assumption is continuous at the α-β transition (Fig. 2), as in the case of typical antiferromagnets like CoF_2 and MnF_2 [24], where the heat transport near the magnetic transition is mostly due to phonons. If, on the contrary, we supposed that in α-oxygen the heat is carried only by phonons it would mean that the phonon mean free path drops above the transition to $\frac{1}{4}$ of its value below the transition. Taking into account that all the parameters of the β phase, namely, the molar volume, the lattice parameters, the sound velocities, and the lattice heat capacity are continuous at the transition, the latter assumption seems to be highly improbable.

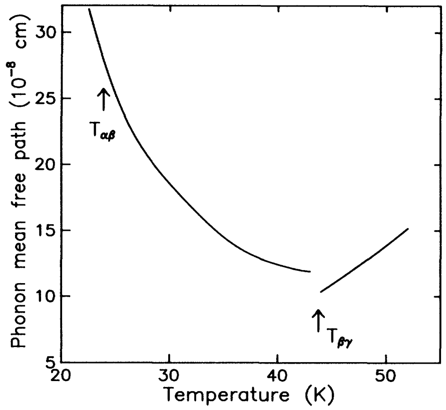

FIG. 2. Temperature dependence of the phonon mean free path. The arrows indicate the temperature of transitions.

An anomalous character of $\kappa(T)$ in the β phase [Fig. 1(a)] is a consequence of the anomaly in temperature dependences of the sound velocities [19,26], which in turn is a result of unusually high magnetoelastic coupling in solid oxygen. According to [26], the sound velocities increase with temperature throughout nearly all the range of existence of β-oxygen with the increase reaching 30% in the case of the transverse sound. The phonon mean free path, calculated taking into account the sound velocities data [26], the molar volume [5], and the lattice heat capacity [5], reveals the "normal" (for this temperature range) temperature dependence (Fig. 2).

As for the increase of the thermal conductivity with temperature in γ-oxygen [Fig. 1(a)], it can be understood if we take into account that the molecular rotation is becoming progressively less hindered with rising temperature and the magnetic correlation length is decreasing. As a result, phonon scattering decreases and the phonon mean free path is rising with temperature (Fig. 2). A similar effect for so-called plastic phases was observed in molecular crystals [28].

In summary, we present the results of the measurements of thermal conductivity of the α, β, and γ phases of solid oxygen. A simple qualitative analysis is given to explain the anomalies observed. We tie a jump in the thermal conductivity at the α-β transition with the magnon contribution to the heat transport. We attribute the anomalously weak temperature dependence of thermal conductivity in the β phase to the anomaly in temperature dependence of sound velocities, and the increase in thermal conductivity in the γ phase to a weakening of the phonon scattering by the hindered rotation and by the decrease of short-range magnetic order with rising temperature.

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