

# Extended infrared absorption spectroscopy study of the magnetic properties of solid oxygen at high-pressure and low-temperature

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The antiferromagnetic  $\alpha$  and  $\delta$  phases of solid oxygen have been investigated by means of infrared absorption spectroscopy along several isotherms, decreasing pressure at several temperatures, in the pressure range from 0.6 to 9.1 GPa between 30 and 298 K. The path followed in the  $P$ - $T$  plane also crosses the recently proposed hypothetical phase boundary between the antiferromagnetic  $\delta$ -I phase and the nonmagnetic  $\delta$ -II phases. No evidence of this phase transition has been observed in the spectra and, more importantly, strong evidence of antiferromagnetic ordering of the molecular spins has been observed in the region assigned to the nonmagnetic  $\delta$ -II phase.

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Among simple molecular systems, solid oxygen has always attracted special interest due to the interplay between its structural and magnetic properties.<sup>1</sup> In the past ten years, knowledge of the physics of its solid phases has largely increased due to structural, vibrational, and magnetic studies at high pressure. Structural studies have recently clarified the phase diagram below 8 GPa and at low temperatures by determining the boundary between the  $\alpha$  and  $\delta$  phases<sup>2</sup> and ruling out the distinction between the  $\alpha'$  and  $\delta'$  phases and the  $\alpha$  phase. Vibrational spectroscopy studies are in agreement with this result.<sup>3</sup> Furthermore, a neutron diffraction experiment<sup>4</sup> has confirmed the antiferromagnetism of  $\alpha$  and  $\delta$ -O<sub>2</sub>, which was previously suggested on the basis of vibrational spectroscopy studies.<sup>5</sup> The vibrational spectrum of the  $\varepsilon$  phase, which was discovered in the 1980s by Nicol *et al.*,<sup>6</sup> has been initially interpreted with the hypothesis of clustering of oxygen molecules into O<sub>4</sub> molecular units.<sup>7</sup> More recently, refinements of x-ray diffraction (XRD) data<sup>8,9</sup> have shown that the molecular units are, indeed, O<sub>8</sub>. The results of these experimental studies all agree on the point that the  $\varepsilon$  phase is diamagnetic and that, consequently, a magnetic collapse should take place at the  $\delta$ - $\varepsilon$  transition. Similarly, computer simulations, even if not yet able to reproduce the experimental structure of  $\varepsilon$ -oxygen, suggest a molecular association with the formation of O<sub>2</sub> chains<sup>10,11</sup> and indicate that the  $\varepsilon$  phase should be diamagnetic. This expected magnetic collapse was, indeed, indirectly suggested by the dramatic change of the spectrum of the low energy electronic transitions<sup>12</sup> and also predicted in a computer simulation.<sup>13</sup> The magnetic collapse was finally experimentally observed in a neutron scattering experiment.<sup>14</sup> At about 96 GPa, solid oxygen transforms into the  $\zeta$  phase, becoming metallic and even a superconductor.<sup>15</sup> The crystal structure of this phase has not been assessed with unanimous consensus.<sup>11,16-18</sup> At high temperatures, in a region of the phase diagram bounded by the  $\beta$ ,  $\varepsilon$ , and fluid phases, a new crystal phase (named  $\eta$ ) has recently been discovered by means of Raman spectroscopy.<sup>19</sup>

Despite the great amount of research and the major ad-

vances discussed above, the physical properties of solid oxygen in the region in the  $P$ - $T$  plane that extends between the  $\beta$  and  $\varepsilon$  phases, at temperatures below the  $\beta$ - $\delta$ - $\varepsilon$  triple point and above 6 GPa, still remain unclear (see Fig. 1). In particular, although there is a general consensus on the crystal structure (i.e., orthorhombic with the  $Fm\bar{3}m$  space group), an open question regarding the magnetism of solid oxygen at these temperatures and pressures still persists. In a recent work, Goncharenko<sup>14</sup> proposed the existence of two phases having the same crystalline structure of the orthorhombic  $Fm\bar{3}m$   $\delta$  phase but different magnetic states: the low-temperature antiferromagnetic  $\delta$ -I and the high-temperature nonmagnetic  $\delta$ -II. This hypothesis sounds quite exotic since for solid oxygen, structural and magnetic properties are

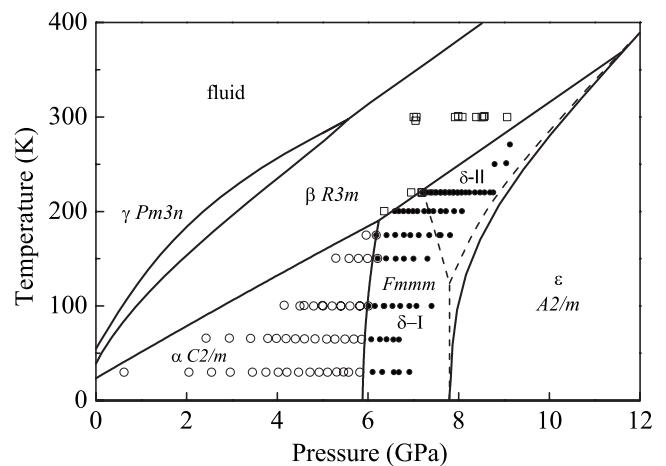


FIG. 1. Phase diagram of oxygen. Dashed lines are those reported by Goncharenko (Ref. 14). The almost vertical phase boundary at about 6 GPa between the  $\alpha$  and  $\delta$  phases is the result of a fitting procedure of the diffraction data reported in Ref. 2. The symbols represent the pressure and temperature conditions of the infrared absorption measurements. Empty squares, full circles, and empty circles represent the points where the infrared absorption spectrum has been assigned to the  $\beta$ ,  $\delta$ , and  $\alpha$  phases, respectively.

strongly correlated in all known solid phases. The only appeal of this hypothesis is that it could remove the possibility of a “temperature induced” magnetism, which would take place upon an increase in the temperature along an isobar from the nonmagnetic  $\epsilon$  phase to the high-temperature antiferromagnetic  $\delta$  phase.

A powerful tool to investigate magnetic ordering in solid oxygen is provided by infrared absorption spectroscopy. The presence, in the  $\alpha$  and  $\delta$  phases, of an IR absorption peak at the frequency of the intramolecular vibration is, indeed, related to the long range antiferromagnetic order of the molecular spins, which doubles the crystallographic unit cell. Without this doubling, the molecular vibron could not give rise to IR absorption but would be active only for Raman scattering.

That the IR vibron absorption is caused by the magnetic ordering is strongly supported by the fact that its intensity is proportional to the square of the order parameter, decreasing to zero when temperature increases and approaches the  $\delta$ - $\beta$  phase transition temperature. The structural and magnetic transitions coincide at least up to 7 GPa.<sup>5</sup> Moreover, from the difference of the frequencies of the Raman and IR vibron modes, it has been possible to derive the vibrational coupling parameter and demonstrate that this is related to the magnetic exchange interaction, which, in turn, is responsible for the antiferromagnetic ordering. As a result, the IR vibron absorption is an indirect but sensitive probe of the antiferromagnetic order in the  $\alpha$  and  $\delta$  phases. In this Brief Report, we use this method to verify whether or not the  $\delta$ -II phase is antiferromagnetic.

We have used a diamond anvil cell (DAC) of the membrane type, which is loaded by immersion into high purity (99.99%) liquid oxygen that is condensed in a sealed vessel. The cell is fixed to the cold finger of a He flux cryostat. The temperature is determined by a silicon diode, which is placed very close to one of the diamonds, with good accuracy ( $\pm 1$  K). The pressure is measured by observing the shift of the ruby fluorescence wavelength,<sup>20</sup> which is corrected for measurements at low temperature.<sup>21</sup>

IR absorption spectra have been measured by using a Fourier transform Michelson interferometer (Bruker IFS 120), which was custom modified in order to allow measurements on samples in the DAC at low temperature.<sup>22</sup> Type IIa diamonds were used in order to remove the diamond one phonon IR absorption band. The samples were typically 150  $\mu\text{m}$  wide and 50  $\mu\text{m}$  thick. The instrumental resolution used was better than 0.5  $\text{cm}^{-1}$  in all the measurements.

The  $\alpha$ - $\delta$  transition is difficult to observe especially during a pressure increase at low temperature, since a mixture of  $\alpha$  and  $\delta$  phases generally appears at the transition. In order to unambiguously locate the phase transition pressure, we have performed several isothermal decompressions, starting from an annealed sample in the  $\delta$  phase, which has a good crystalline quality. This was the procedure also followed during our previous XRD study.<sup>2</sup> We think that the annealing of the crystal in the  $\delta$  phase, at a relatively high temperature, is an important requisite, and that the different results obtained in other experiments, which were performed following different  $P$ - $T$  paths but which did not observe the transition, are due to the difficulty in producing a pure orthorhombic  $\delta$  phase.<sup>23,24</sup>

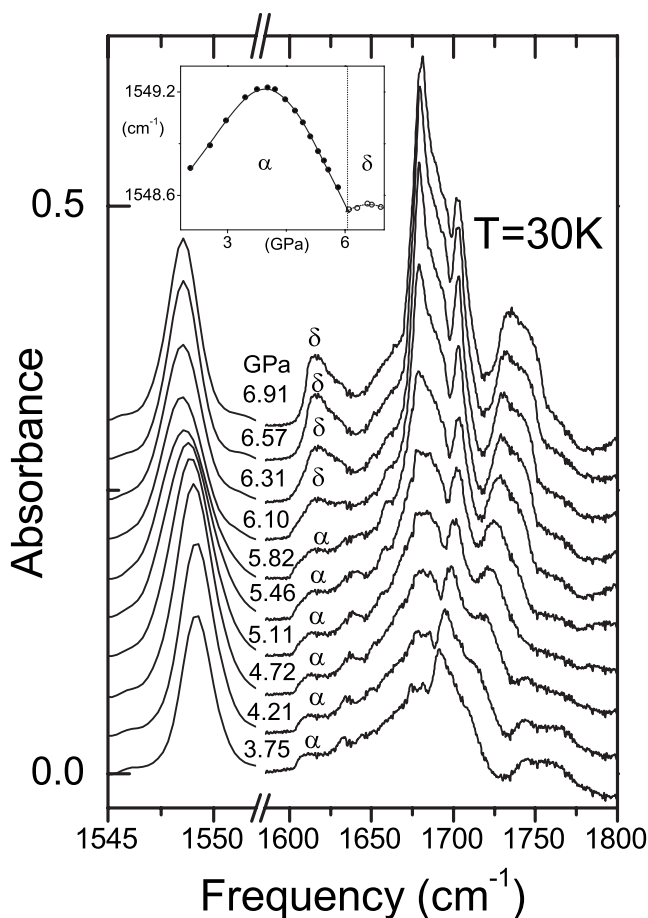


FIG. 2. Selected IR absorption spectra obtained during the isothermal pressure decrease at the lowest temperature of this work, i.e., 30 K. The inset shows the pressure evolution of the vibron peak frequency, with an evident cusp at the  $\alpha$ - $\delta$  transition pressure.

The aim of this work is to clarify the physics of solid oxygen in the whole  $P$ - $T$  region of the  $\delta$  phase, which has recently been discussed in literature,<sup>14</sup> and also to monitor the  $\alpha$ - $\delta$  transition using the IR absorption technique.

Figure 1 shows the  $P$ - $T$  phase diagram of oxygen. Solid lines have been drawn as in Ref. 2 and dashed lines delineate the new  $\delta$ -II phase proposed by Goncharenko.<sup>14</sup> In Fig. 1, the symbols mark the  $P$ - $T$  values relative to the present study. We observed the evolution of the IR spectrum along several isotherms in the region enclosed by the  $\beta$  and  $\epsilon$  phases, following a procedure which tries to verify the presence of the  $\delta$ -II phase and add experimental points to the  $\alpha$ - $\delta$  phase boundary. Full and empty circles and open squares represent the experimental points that have been assigned to the  $\delta$ ,  $\alpha$ , and  $\beta$  phases, respectively, based on the IR absorption spectrum as discussed in the following. Figure 2 shows some IR absorption spectra relative to the isotherm at 30 K, which is the lowest temperature of this work. The spectrum is constituted by the vibron absorption peak around 1550  $\text{cm}^{-1}$  and the phonon Stokes sideband, which extends from about 1600 to 1800  $\text{cm}^{-1}$ . The anti-Stokes phonon combination band is not detectable at this temperature. As already discussed in Ref. 5, the IR sharp vibron absorption is the signature of a long range antiferromagnetic order among

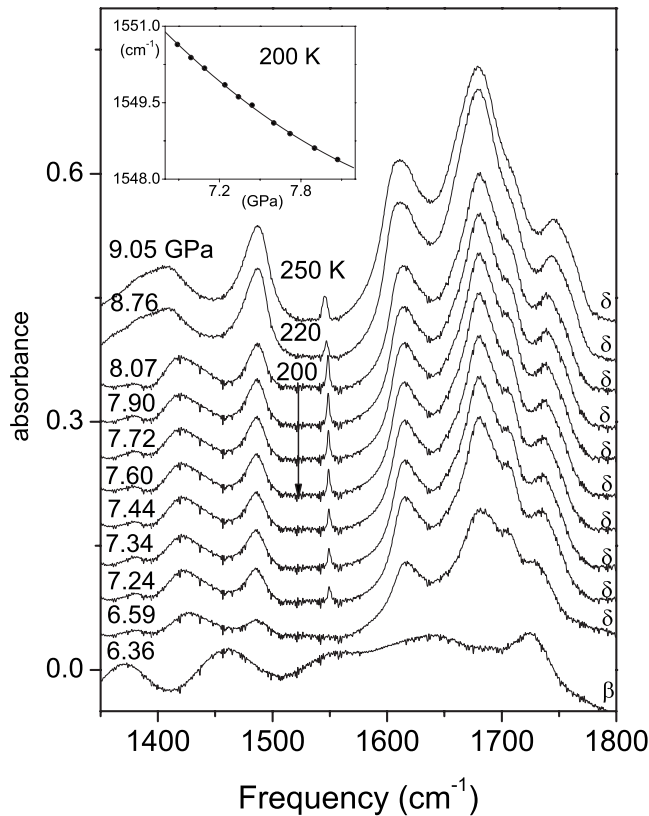


FIG. 3. Selected IR absorption spectra relative to the isotherm performed at 200 K upon decreasing pressure and two spectra that do not belong to the same isotherm: 8.76 GPa at 220 K and 9.05 GPa at 250 K. The inset shows the pressure evolution of the vibron peak frequency along the 200 K isotherm.

the oxygen molecular spins, both in the  $\alpha$  and in the  $\delta$  phases. The phonon sideband, whose shape mostly reflects the one phonon density of states, is very strong in comparison with other molecular crystals, such as nitrogen,<sup>25</sup> where it is, indeed, absent. This anomalous intensity has been explained in terms of magnetoelastic coupling.<sup>1</sup>

The evolution of the IR absorption spectrum with pressure, as reported in Fig. 2, shows that the vibron peak is, in a first approximation, hardly affected by pressure changes, while the phonon sideband exhibits a continuous intensity increase with increasing pressure. At a closer look, the frequency of the vibron peak exhibits a clear cusp at the  $\alpha$ - $\delta$  transition, as reported in the inset of Fig. 2, while the intensity profile of the phonon sideband shows the sudden appearance of a characteristic feature around 1610 and 1680  $\text{cm}^{-1}$  at the transition pressure. These effects at the  $\alpha$ - $\delta$  transition were not observed in previous IR absorption studies,<sup>23</sup> which is probably due to a metastability of the  $\alpha$  phase, which remains present within the stability domain of the  $\delta$  phase.

Figure 3 shows some IR absorption spectra relative to the isotherm performed at 200 K and two spectra that do not belong to the same isotherm: 8.76 GPa at 220 K and 9.05 GPa at 250 K. The spectrum exhibits the vibron absorption peak at around 1550  $\text{cm}^{-1}$  and the phonon sideband, which extends from about 1600 to 1800  $\text{cm}^{-1}$ . The anti-Stokes side of the phonon sideband is also visible at this temperature.

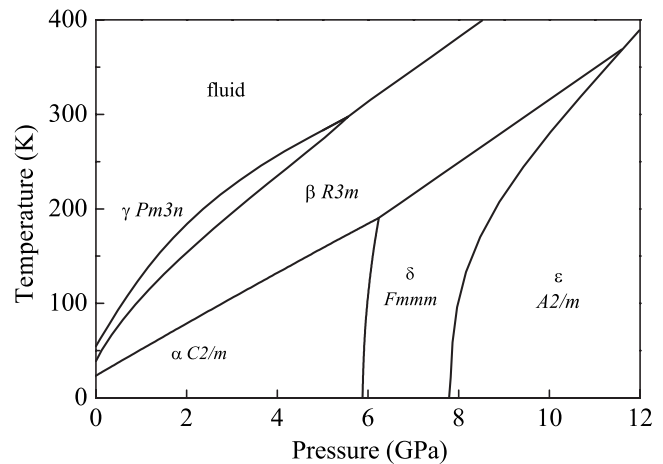


FIG. 4. Final oxygen phase diagram based on this work.

The vibron peak is clearly detected along the entire isotherm at 200 K. Its intensity decreases upon decreasing pressure and approaching the  $\delta$ - $\beta$  transition (about 6.57 GPa at 200 K). The IR absorption spectrum relative to the  $\beta$  phase is also reported at the bottom of Fig. 3. This is definitely different from those of the  $\delta$  phase and shows only a weak feature in the Stokes phonon sideband region, around 1725  $\text{cm}^{-1}$ , superimposed to a damped sinusoidal background, due to the interference of light passing through the sample enclosed by the diamond windows. The interference pattern changes dramatically at the  $\delta$ - $\beta$  transition due to the recrystallization of the sample, which enhances the contrast of the interference fringes. Interestingly, this isotherm ( $T = 200$  K) crosses the hypothetical  $\delta$ -I- $\delta$ -II phase boundary at about 7.3 GPa, where no spectral changes of any kind are detected, either in the sideband or in the vibron peak. This is also quantitatively shown by the continuous evolution with pressure of the vibron frequency, which is reported in the inset of Fig. 3. Moreover, the presence of the IR vibron peak is a strong proof of the presence of a long range antiferromagnetic order in the  $\delta$ -II phase region, which, in contrast, was proposed to be nonmagnetic.<sup>14</sup> The two spectra at 220 and 250 K show the presence of the IR vibron peak deeply inside the hypothetical  $\delta$ -II phase at pressures higher than the  $\delta$ - $\varepsilon$  transition pressure at low temperatures. This observation demonstrates that oxygen appears to be the only known material that shows a magnetic ordering with increasing temperature: from the nonmagnetic  $\varepsilon$  phase at low temperatures to the magnetic  $\delta$  phase at high temperatures. This apparently exotic behavior is not forbidden by first principles, as the  $\varepsilon$  phase is not paramagnetic and we are not dealing with a disorder-order magnetic transition. This apparent anomalous temperature induced magnetic ordering is, indeed, related to the peculiar molecular transformation that takes place at the  $\delta$ - $\varepsilon$  phase transition: diamagnetic  $\text{O}_8$  molecules at low temperatures in the  $\varepsilon$  phase and  $\text{O}_2$  molecules, which possess a molecular spin ( $S=1$ ) at higher temperatures in the antiferromagnetic  $\delta$  phase.

In order to try to address the reason for the disagreement discussed above, we can use one argument to speculate against the magnetic transition suggested by Goncharenko.<sup>14</sup>

The existence of a nonmagnetic  $\delta$  phase has been claimed on the basis of only one isobaric measurement at only five different temperatures. The nominal pressure is 7.6 GPa and, as stated by the author, the accuracy of the pressure along the isobar, which is given by the sum of the accuracy of the pressure determination and by the pressure stability along the isobar itself, is 0.4 GPa. This isobar lies at a pressure very close to the  $\delta$ - $\varepsilon$  phase transition and the poor pressure accuracy poses serious doubts on the fact that the isobar was really performed on a pure delta phase sample. A mixture of  $\delta$  and  $\varepsilon$  phases, with the latter phase being nonmagnetic, could make the study of the evolution of the magnetic dif-

fraction peak along the isobar not significant.

In conclusion, these measurements locate the  $\alpha$ - $\delta$  transition in agreement with what was experimentally observed by using the XRD technique and do not show any evidence of a nonmagnetic  $\delta$ -II phase. In Fig. 4, we show the final phase diagram of oxygen, which is derived from the results of this work.

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