Low-energy magnetic neutron scattering from α-oxygen

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A high-resolution inelastic neutron scattering experiment has been carried out in the α and β low-temperature phases of solid oxygen. Direct comparison between the spectra of both phases as well as with previous experiments and lattice dynamics calculations, allow one to identify a feature appearing at $\approx$ 4.3 meV in the low Q region of the spectra as arising from the antiferromagnetic excitations, the existence of which had been postulated from optical work. [S0163-1829(97)05717-2]

Condensed molecular oxygen constitutes an interesting localized-spin system where magnetism comes from a direct overlap of molecular orbitals.[1] Despite its simplicity, its magnetic behavior remains a subject of controversy mainly due to the extreme difficulty of obtaining single crystals for the lowest temperature phases (due to a large volumic contraction during the γ-β transition that cracks the crystals) as well as to the interaction of the magnetic and structure-related vibrations. Oxygen has, in its solid form and at ambient pressure, three different phases, from which only the two lower temperature ones, α and β, are considered in this work. The crystal structure of $\alpha-$oxygen ($T \leqslant 23.9$ K at $P=0$), is monoclinic ($C2/m$) and its magnetic order corresponds to a collinear antiferromagnet as evidenced by neutron diffraction,[2] muon spin relaxation (μSR),[3] susceptibility,[4] and antiferromagnetic (AFMR) resonance experiments.[5] The β phase ($23.9 \leqslant T \leqslant 43.8$ K) shows a rhombohedral ($R3m$) structure and the nature and extent of its magnetic order is still under discussion. From a crystallographic stand, the structures of α-O_2 and β-O_2 are closely related by a small displacive transition[2] and most of our current knowledge of the α-β transition portrays it as a magnetoelastic phenomenon.[6] Several attempts to clarify the spin dynamics of α-O_2 have been reported in the past. Estimations of the lowest frequency AF-magnon dispersion curves have been reported some time ago by Wachtel and Wheeler[7] which result in two AF-magnon branches showing dispersions bounded by $\approx 0.8 \leqslant \hbar\omega \leqslant \approx 4.5$. Subsequent spin-wave treatments such as that due to Meier[8] provide estimates for the two $\vec{\mathbf{Q}}=0$ frequencies not far from those previously quoted of 0.85 meV and 4.8 meV, respectively, and an additional treatment couched in terms of a ''quasi-two-dimensional'' model to account for the heat capacity and AFMR resonance frequencies[9] resulted in two dispersion curves showing the same $\vec{Q}=0$ gaps but reaching frequencies of about 9.3 meV at the π/a and π/b zone boundaries. A recent calculation,[10] while confirming the presence of a magnetic excitation in α-O_2 at 9.6 meV, did not find any lower frequency ones within such a phase, whereas a series of finite-frequency features appearing at 0.8, 6.3, and 6.9 meV are predicted to occur within the β phase.

On the experimental side, most of what is now known has come from pioneer optical (IR and Raman) investigations[11,12] reported quite a while ago. Those experiments revealed the presence of two features: one appearing at $\approx$ 3.5 meV and another at $\approx$ 0.75 meV. Their dependence with the magnetic field[8] as well as with temperature[12] led those authors to identify these features as low energy antiferromagnetic excitations. However, the experimental procedure consisted of the subtraction of the β-oxygen spectra from that of the α phase, something which might result in some uncertainties, especially if, as postulated in Ref. 10, well-defined finite-frequency spin waves were still present in β-O_2.

An attempt to identify such an excitation using polarized inelastic neutron scattering (INS) was carried out by Stephens and Majkrzak.[5] The spin-flip channel in the polarized INS experiment showed a broad inelastic feature centered at about 10 meV which was identified as a $b^*/2$ zone boundary antiferromagnetic excitation.[5] Unfortunately, the reported experiment was severely limited by resolution in energy transfers (2.5 meV) as well as counting statistics which hindered the exploration of the region examined by optical means. Our purpose here is then to verify the magnetic nature of those features reported by optical studies by means of high-resolution INS. Although the experiments reported here did not make use of neutron polarization analysis, previous experience in separating the structural and magnetic responses in the plastic crystal (γ- oxygen), liquid,[13] and β phases,[14] indicates that such a separation may be achieved at least on semiquantitative grounds. Moreover, the close relationship of the lattice structure and excitations of the β and α phases will enable the identification of a feature as arising from atomic vibrations if the coupling of lattice modes to magnons can be quantified. Fortunately, it has been shown that such couplings are small for low-energy magnons,[8] although they are expected to become

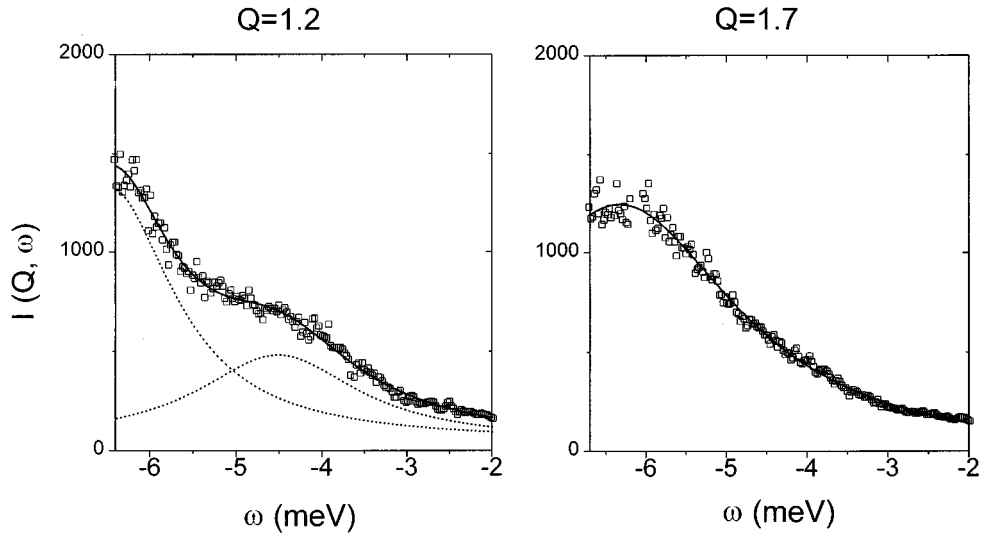

FIG. 1. Two different spectra of α-oxygen taken at $T=5$ K and two different momentum transfers: $Q=1.2$ and $Q=1.7$ Å^{-1}. The fitting functions are Lorentzians, as described in the text. For $Q=1.2$ Å^{-1} two Lorentzians have been used to fit, while at $Q=1.8$ Å^{-1} only one is necessary.

substantial for higher energy spin waves, such as the one detected in the previous INS experiment.[5]

Finally, the interest in the study of the low energy spectrum of spin waves arises from the need to understand the anomalies exhibited by some transport properties such as the thermal conductivity, and especially the origin of the abrupt changes appearing after crossing the α-β transition,[15] since, for such purpose, a better knowledge of the low energy spin-wave frequencies is required.

The measurements were carried out at Laboratoire Léon Brillouin (LLB, Saclay, France) using the Mi Bemol chopper spectrometer. Runs were performed at two different temperatures: at 5 K to study the α phase, and as close to the phase transition as possible but within the β phase, at 27 K. The energy of the unpolarized incident beam was kept constant at $E_i=9.1$ meV, achieving a resolution in energy transfers of 0.7 meV (FWHM). The data were corrected for the detector efficiency and self-attenuation as well as converted into constant momentum transfers.

The measurements were done on oxygen powders following a procedure developed to obtain virtually free-texture samples used in previous diffraction experiments.[16]

In the angle-averaged spectrum obtained by INS on α oxygen at $T=5$ K, two finite-frequency features, centered at some 4.5 meV and 6.5 meV, have been detected. Owing to the lack of polarization analysis a careful study based on direct comparison with the β phase needs to be carried out. Such a comparison is based upon two physical facts: first, the close similitude of the α and β crystal structures is expected to result in a homology of their structure-related excitations [as evidenced from calculations of the vibrational density of states, $Z(\omega)$, within the harmonic approximation[14]]; second, the nonexistence of magnetic long-range order (MLRO) within the β phase points towards a lack of finite-frequency magnetic excitations (as experiments, including the present, have proved so far). However the broad and strong paramagnetic background present in β oxygen makes it impossible to determine by direct inspection the contribution of the antiferromagnons to the scattering. To proceed, the measured intensities have been decomposed into different (nuclear and magnetic) components. The model used to represent the experimental data considers the magnetic response in purely hydrodynamic terms:

$$I_{\mathrm{tot}}(Q,\omega)=A[S_{\mathrm{nuc}}(Q,\omega)+S_{\mathrm{mag}}(Q,\omega)]\otimes R(\omega), \quad (1)$$

$$S_m(Q,\omega)=[f(Q)]^2\frac{\chi_m\omega}{1-\exp(-\hbar\omega/k_BT)} \times\left[\frac{\Gamma_m}{(\omega-\omega_m)^2+\Gamma_m^2}+\frac{\Gamma_m}{(\omega+\omega_m)^2+\Gamma_m^2}\right], \quad (2)$$

where A stands for a global scaling constant, $\otimes$ defines a convolution with experimental window function, a simplified (Lorentzian) representation was found to be adequate to account for $S_{\mathrm{nuc}}(Q,\omega)$, $f(Q)$ stands for the magnetic form factor of the oxygen molecule and the frequency dependence of the magnetic response is characterized in terms of an average frequency ω_m, the static value of the susceptibility χ_m and a damping constant Γ_m. Figure 1 shows two different spectra at $Q=1.2$ Å^{-1} and at $Q=1.7$ Å^{-1} with their fitted functions. For data at $Q=1.2$ Å^{-1} two Lorentzians are needed to provide a reasonable fit, whereas at the higher Q only one is necessary. The feature appearing at 4.5 meV will be referred to as L, while that at 6.5 meV will be called H. The most significant parameters derived from the fits are shown in Fig. 2. There a comparison is shown between the Q dependence of the fitted frequencies and those $\omega_{\max}(Q)$ corresponding to maxima of peaks appearing in $\langle S(Q,\omega)\rangle$, that is a polycrystalline average of the dynamic structure factor arising from the lattice dynamics calculations.[14] Notice that such frequencies for low wave vectors approach the hydrodynamic dispersions for longitudinal and transverse sound. The remarkable result arising from such comparison is the resemblance of the shape of our H branch with that of the two other phonon branches (not only the shape but the magnitude of the values too, taking into account the polycrystalline character of our samples), as well as the appearance of the L branch below the minimum corresponding to the transverse acoustic phonons. It also seems worth pointing out the fact that the measured points for the L branch are compatible with some estimates of the antiferromagnon frequencies near the zone boundary.[5,7] Additional evidence for such an as-

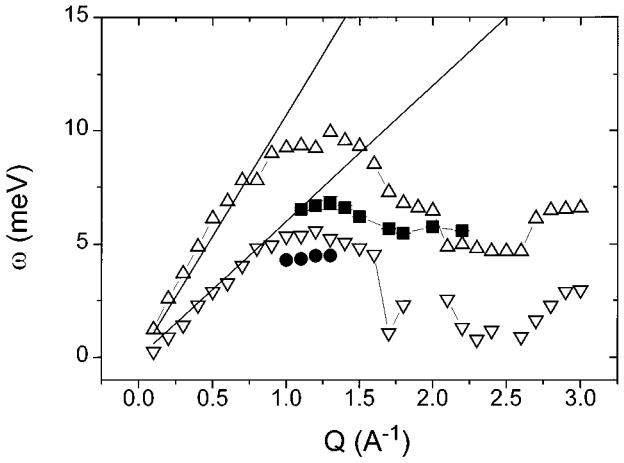

FIG. 2. Comparison of the dependence with momentum transfers of the fitted frequencies of features L (filled circles) and H (filled squares) with those $\omega_{\max}(Q)$ corresponding to maxima of the lower frequency peaks in $\langle S(Q,\omega)\rangle$ as arising from the lattice dynamics simulations (Ref. 14). The straight lines correspond to the dispersion of hydrodynamic longitudinal (through the open triangles) and transverse (through the open inverted triangles) sound.

signment comes from the Q dependence of the intensity of both H and L contributions. It is interesting to see how feature L has a very smooth dependence with Q and around 1.4 Å^{-1} its intensity drops sharply, which is in agreement with the usual sharp decay of the magnetic structure factor of solid oxygen. The decay in the intensity due to magnetic excitations is counterbalanced by the strong increase in the response arising from the phonons, something which severely limits the range of momentum transfers where such a decomposition becomes practicable.

At this point it seems worth commenting that the frequency of the feature appearing at $\approx$ 4.5 meV comes just 0.3 meV below the value derived for the spin wave from a calculation,[8] whereas is about 1.2 meV above the zero-field value observed in IR measurements. The discrepancy between the calculated value and the experimental one from optical studies has been attributed to some magnetoelastic coupling which results in some substantial softening of the $\vec{\mathbf{Q}}=0$ AF-magnon frequencies. There is a point worth considering regarding such an explanation which concerns the plausible coupling mechanisms between the phonons and spin waves. Two low frequency excitations assigned as librational modes appearing at $\approx$ 6 meV and $\approx$ 10 meV were reported from Raman experiments.[17] The lower frequency mode was, because of its low energy, a plausible candidate for the coupling to the AF magnon, whereas the higher frequency one occurs at the very same frequency as the spin-flip excitation reported in Ref. 5, and therefore should have a substantial component of magnetic origin. The similitude of the phonon spectra in both α and β phases, also evidenced in this work, seems to rule out any strong coupling between structure-related excitations of frequencies about 6 meV and the spin waves since a more dramatic difference between the shape of the experimental spectra would otherwise appear once the coupling disappears upon transformation into the β phase. On the other hand, the arguments elaborated in the appendix of Ref. 5 establishing the relative importance of magnetovibrational effects should also apply in our case.

Finally, the present results also seem to be of relevance for the understanding of the surprising behavior exhibited by the thermal conductivity.[15] At low temperature, the behavior of $\kappa(T)$ conforms to what could be expected for a crystalline dielectric, showing a $\kappa(T)\propto T^3$ up to some 5 K and a maximum of 0.17 $\text{W cm}^{-1}\,\text{K}^{-1}$ at about 6 K, which becomes comparable to that exhibited by other insulators (rare gas solids, crystalline nitrogen[18]). What appears as a rather distinctive feature is a strong decrease of $\kappa(T)$, which amounts to some 70% of its value, once the transition to the β phase is crossed,[15] as well as the fact that within such a phase the thermal conductivity *increases* with temperature some 10% along the range of existence of such crystalline modification, executing an additional drop of about 60% after crossing into the γ phase. Such facts became rather surprising, especially the difference in conductivities between α and β-O_2 since having the α and β phases such a similar vibrational frequency distribution one would expect that the jump in $\kappa(T)$ would have to be far more moderate. Taken at its face value, such a fact may indicate, as proposed in Ref. 15 that a substantial portion of heat transport mechanisms is due to AF excitations, since only overdamped (paramagnetic) spin-wave motions are expected to occur within the β phase. However, this seems to contradict the estimates of the magnetic contribution to the specific heat.[1] In fact, an upper bound for this magnitude can be derived by subtraction of a lattice contribution $C_{\text{lat}}(T)=12\pi^4R/5\Theta_D^3T^3$ where R stands for the gas constant and $\Theta_D=$ 104.5 K is the Debye temperature, to the experimentally observed values.[19] This would result in an estimate of the magnetic specific heat $C_{\text{mag}}(T)$ which increases with temperature up to some 4.8 $\text{J K}^{-1}\,\text{mol}^{-1}$ at 22 K (just below the $T_{\alpha\beta}$ transition which represents some 27% of the total measured value for $C_p(T)$ at such a temperature. Alternatively, one can estimate the contribution $C_{\text{lat}}(T)$ using the frequency distribution calculated by LD which seems more realistic than the Debye approach at least for temperatures above some 8 K.[1] Such an exercise would yield a maximum contribution of $C_{\text{mag}}(T)$ at 22 K of some 2.23 $\text{J K}^{-1}\,\text{mol}^{-1}$, which now accounts for about 12% of the total value of C_p. A decrease as high as 70% in $\kappa(T)$ at $T_{\alpha\beta}$ would then necessarily have to be accompanied by a major decrease in l, the excitation mean free paths. Since both $\vec{\mathbf{Q}}\rightarrow 0$ AF-magnon branches are needed to account for $C_{\text{mag}}(T)$ (see Fig. 10 of Ref. 1), it should be obvious that the drop in $\kappa(T)$ has to be produced by strong scattering of phonon and spin excitations by the thermally induced disorder present in the β phase. As it became clear after INS and μSR studies on the dynamics of such a phase, a strong paramagnetic background which relaxes on frequency scales rather close to those characteristic of the AF-excitation reported here [see Fig. 5 of Bermejo *et al.* (Ref. 3)] provides a very effective mechanism of scattering able to decrease l associated with phonon or spin waves down to the characteristic scale of $10\leqslant l\leqslant 15$ Å needed to account for the experimental data.[15]

As a concluding remark, the AF magnon, whose existence had been conjectured by several optical studies, has been

detected using INS. This assessment is supported by direct comparison between spectra of α and β phases (based on the similarity between their crystalline structure and the truncated antiferromagnetic long range order of β oxygen) as well as with previous experiments and lattice dynamics calculations.

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