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LETTER TO THE EDITOR

Evidence for magnetic excitations in liquid oxygen

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Abstract. We briefly describe the results of a neutron scattering study on the dynamics of liquid oxygen ($T = 55.0$ K, $p = 2$ bar), performed at a temperature just above the melting point. The wavevector dependence of the inelastic intensities shows a pronounced feature of magnetic origin centred at $Q = 1.2$ Å^{-1} ('zone boundary') reminiscent of those found in the solid β-phase. These indicate a dynamical antiferromagnetic (AF) interaction in liquid oxygen at a temperature of approximately $2T_N$ ($T_N \simeq 30$ K for solid α-phase). The AF coupling extends over only a very short range ($\simeq$5.2 Å) and an energy scale of between 0.7 and 3 THz.

The study of the magnetic properties of the condensed phases of oxygen has attracted considerable effort during the last decade [1, 2]. The interest in this material stems from the fact that it is perhaps the only magnetic insulator where the exchange interactions arise from direct overlap coupling, thus leading to a strong interplay between structural, magnetic and orientational degrees of freedom. Between 4 K and the melting temperature ($T_M = 54.4$ K, at normal pressure), three crystalline phases have been described for oxygen (α, β and γ). The higher-temperature ones (β and γ) show magnetic short-range order [1], not very different from that revealed in a polarized neutron diffraction experiment performed in the high-temperature liquid [3]. From the available evidence [3] the existence of short-range antiferromagnetic order in the liquid with a coherence length of about 5 Å was postulated. This preliminary communication presents some results from a neutron inelastic triple-axis study performed at a temperature just above melting.

The experiment was performed at the IN8 triple-axis spectrometer of the Institut Laue–Langevin (France). The monochromator and analyser were the (002) reflection of pyrolytic graphite, and the momentum-transfer range covered the region $0.35 \leqslant Q \leqslant 4.4$ Å^{-1}. The scans were performed in the constant-energy or constant-Q mode and with a fixed incident wavevector of 4.1 Å^{-1} with the spectrometer in the 'W' (1, −1, 1) configuration. A pyrolytic graphite filter was used in order to avoid the harmonics from the monochromator. Special care was paid to avoiding scattering from the air; the cryostat, with the sample in it, was placed inside an evacuated cylinder of diameter 1 m. Also, a very restrictive collimation had to be used (30′ in pile, 20′ between monochromator and sample, 10′ between sample and analyser and 40′ between analyser

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and detector), which allows an energy resolution at the elastic position of 0.7 THz (full width at half maximum).

The sample container was a cylinder of 10 cm^3 capacity, which allows the in-cell condensation of room temperature O_2 gas from a pressure vessel, directly inside the helium cryostat. The sample container also included five Cd spacers of thickness 0.1 mm, in order to reduce to a minimum the multiple-scattering contribution. Several runs were carried out using the empty cell, which scatters less than 1% of the total intensity.

In order to ensure that the sample remained in the liquid phase, repeated elastic $S(Q, 0)$ scans were carried out and a representative static structure factor is shown below. The temperature stability was better than ± 0.02 K during the experiment. Absorption corrections were performed using a modified version of the Paalman–Pings algorithm [4], and the multiple-scattering contribution was estimated by means of a modification of the Discus Monte Carlo code [5].

The first result indicating the presence of excitations other than those of structural origin was the appearance of a broad, structureless $S(Q, \omega)$ dynamic structure factor with a half-width which, surprisingly, was independent of the wavevector up to $Q = 1.6$ $Å^{-1}$. This result is very different from those characteristic of most molecular liquids [6].

Since no dynamical data are available for this fluid, the structural contribution was estimated from a rescaling of simulation data for liquid nitrogen, for which there is a wealth of dynamics data. In order to estimate the quasi-elastic response, the diffusion coefficient was estimated from that of liquid nitrogen, using a scaling argument as described in [7], and the rotational constants were taken from those measured by optical spectroscopic means [8].

The coherent quasi-elastic resonse was also estimated using a treatment previously employed for the analysis of the quasi-elastic response of a mostly coherent scatterer [9], using the structural, centre-of-mass structure factor given in [3].

In order to account for purely inelastic effects (short-wavelength collective excitations), a simple viscoelastic model was used where the dispersion of the normalized second and fourth frequency moments was taken to be akin to those arising from a simulation in liquid nitrogen rescaled so that the thermodynamic limit reproduced the measured adiabatic sound velocity [10, 11]. A sample spectrum with the quasi-elastic and inelastic contributions estimated as above is shown in figure 1. As can be seen, the residual inelastic intensity (other than structural) corresponds to a broad distribution centred at zero frequency, characteristic of most of the known isotropic antiferromagnets [12], showing a linewidth of about 1.0 THz.

In order to perform a model-free test of the existence of magnetic excitations we have carried out several constant-energy-transfer scans, in order to get some insight into the wavevector dependence of the excitations. The rationale behind this was the fact that, from what is known about collective excitations in liquids, the oscillations appearing in the Q-dependence of this kind of scan should follow, for low energy transfers, the same phase relationships as the quantity $Q^2S(Q, 0)$. Although additional (non-propagating) excitations are expected to appear for larger energy transfers, these are expected to show characteristic features for momentum transfers larger than the maximum of $S(Q, 0)$.

The results for several energy-transfer values are depicted in figure 2. As can be seen upon inspection of the figure, a noticeable peak, not present in the elastic structure factor, is seen for all the curves explored, which, centred about $Q = 1.2$ $Å^{-1}$, shows a width of 1.2 $Å^{-1}$ with a rather smooth dependence on energy transfer. Such an inelastic

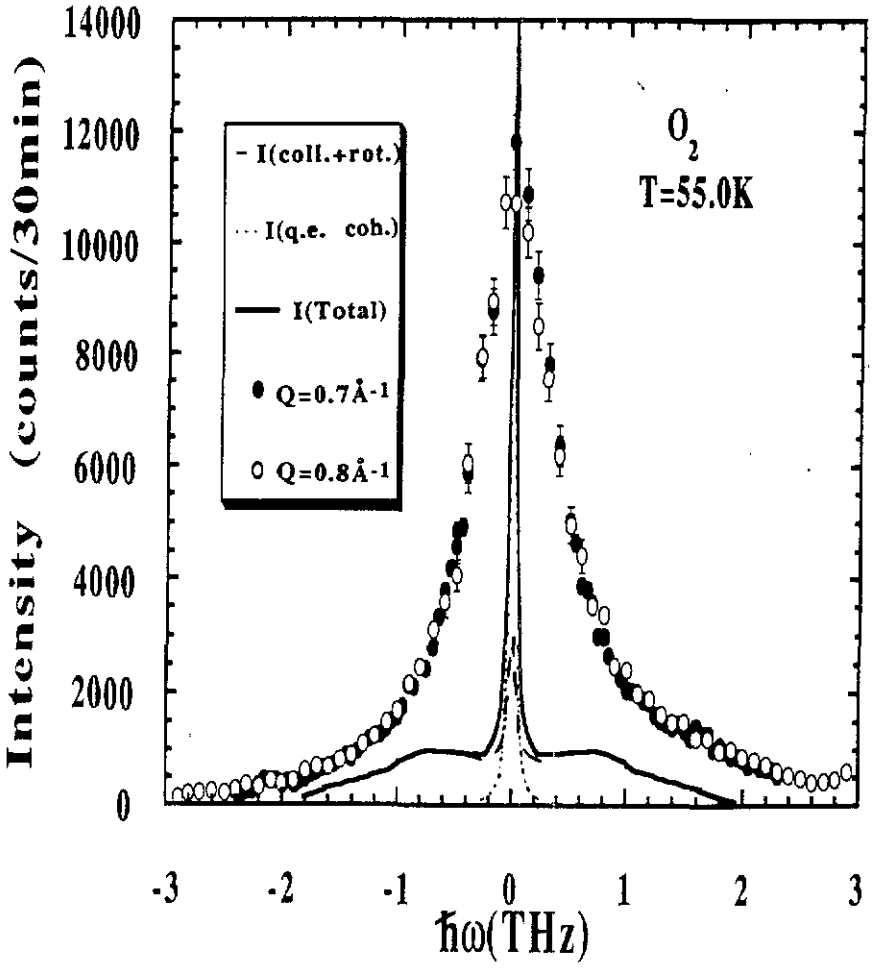

Figure 1. Constant-Q scans at two different momentum transfers, $Q = 0.7$ and 0.8 Å^{-1} for $T = 55.0$K. The full curve indicates the collective excitations, rotations and coherent quasi-elastic scattering. The dotted curve indicates only the coherent quasi-elastic scattering and the broken curve only the collective and rotation scattering. These intensities were calculated as explained in the text, with data scaled from [10] for N_2.

feature is remarkably similar to the one reported for the β-phase [1], and its width indicates a coherence length of about 5.2 Å which can be compared with the 9 Å figure estimated for the solid (β-phase).

The second peak which, at least at low energy transfer, shows the same dependence as the elastic structure factor, denotes the presence of collective excitations of structural nature. In fact, the shape of the curves above 1.4 Å^{-1} could easily be reproduced using a simplified model for the density of states and the structure factors given in [3].

Additional experiments are clearly needed in order to disentangle the dynamics of this liquid. In particular, full polarization analysis experiments are being planned and will be reported in due course.

In summary, we have strong evidence for the presence of magnetic excitations in liquid oxygen. To our knowledge, no other experiment has been reported where the

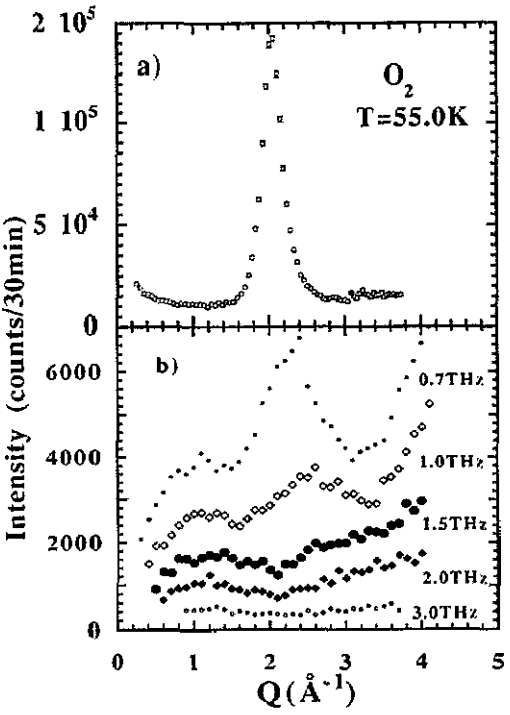

Figure 2. (*a*) Static structure factor and (*b*) wavevector dependence at five different energy transfer values, for O_2 at $T = 55.0$ K. Two types of collective excitation are noticeable, one centred at 2.2 $Å^{-1}$ (sound-wave-like), the second at 1.2 $Å^{-1}$ ('zone boundary'), of magnetic origin.

existence of such a type of dynamic antiferromagnetic correlation on a microscopic scale has been reported for a liquid, and for a temperature as high as $2T_N$ (T_N being $\simeq 30$ K [13]). The present findings have, however, a macroscopic correlate, since it has been known from the early days of magnetic measurements [13] that a surprisingly anomalous behaviour is present after melting of the crystals (the magnetic susceptibility fell by only about 5%). On the other hand, the present results may also serve as a correlate to measurements made on physi-absorbed layers where liquid-like scattering from the high-temperature adsorbate has been reported [14].

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