LETTER TO THE EDITOR

The giant magneto-volume effect in solid oxygen

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Abstract
X-ray diffraction measurements on α-solid oxygen under an applied magnetic
field are reported. The volume of α-solid O_2 is found to expand with increasing
magnetic field: the lattice constants a and b elongate, while the lattice constant
c and the angle β are almost independent of the magnetic field. The maximum
volume expansion observed is about 1% under a 7.5 T field, which is a
giant effect compared to the volume change observed in ferromagnetic metals,
such as Fe, Co and Ni. This finding indicates that a spin-dependent inter-
molecular potential is essential in determining the structure of α-solid O_2.
The experimental results conform with predictions based on a magneto-elastic
interaction derived from an antiferromagnetic exchange coupling of O_2 spins.

The structure of most solids is determined by electric inter-atomic potentials, of a Lennard-
Jones form, and magnetic potentials are not significant. Solid oxygen is one of the rare
exceptions. O_2 molecules carry a magnetic moment and they condense into a solid below
$T_m = 54.8$ K under ambient pressure. Solid O_2 has the three successive temperature-induced
phases below T_m labelled α, β and γ [1]. The α-solid is stable below 23.9 K and the crystal
structure is monoclinic with the space group $C2/m$ [2]. Figure 1 shows the crystal structure of
α-solid O_2. O_2 molecules align with their inter-nuclear axes normal to the ab plane as shown
in figure 1. A magnetic moment coming from the spin-1 state of an O_2 molecule resides at the
centre of the inter-nuclear axis.

The α-solid shows an antiferromagnetic long-range ordering of O_2 magnetic moments.
The antiferromagnetic order is collinear and the one in which a spin is aligned antiparallel to
the neighbouring four spins in the ab plane which in turn is aligned parallel to the neighbouring
spins along the c axis with the spin easy axis parallel to the b axis [3]. As discussed by English
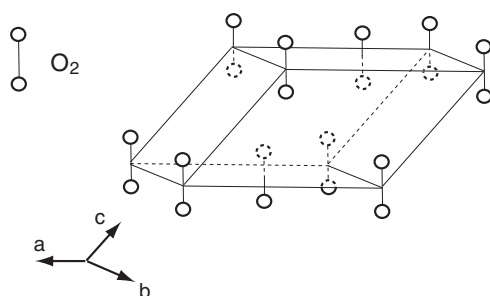
Figure 1. The crystal structure of α-solid O_2.

et al [4], a spin-dependent inter-molecular potential is necessary to account for the crystal and magnetic structures of α-solid O_2, in addition to a Lennard-Jones potential. The authors are successful in predicting the correct magnetic structure in the ab plane, and it is not clear whether the spin-dependent potential is essential in determining the structure along the c axis. Gaididei and Loktev [5] studied theoretically the temperature-induced α–β transition and concluded that thermal properties of the α-phase could be explained by a magneto-elastic interaction. Later, Bar'yakhtar *et al* [6] studied the α–β transition under an applied magnetic field, H, and predicted that the transition temperature decreases with increasing H, because H diminishes the nonisomorphic, α-phase part of the exchange magnetostriction and the corresponding gain in the magneto-elastic energy. On reaching the saturation field, H_s, from the antiferromagnetic to paramagnetic phase the nonisomorphic magnetostriction vanishes and the material reverts to its high symmetry, paramagnetic phase [6].

In this letter we demonstrate that the spin-dependent inter-molecular potential representing a magneto-elastic coupling is essential in determining the structure of α-solid oxygen. We found a giant magneto-volume effect, as determined by an x-ray diffraction measurement. This observation agrees with the field-induced dilation predicted from exchange magnetostriction in the antiferromagnetic α-phase [6].

The x-ray Bragg diffraction measurements were performed at beam line BL19LXU [7] on the third-generation synchrotron SPring-8. Primary x-rays have an energy of 30 keV. A specially designed sample cell, made of aluminium, was inserted to the variable temperature insert of an 8 T superconducting magnet. A gas-handling system connected to the sample cell enabled us to condense O_2 into the cell in a controlled way. The solid O_2 thus obtained was polycrystalline.

Figure 2 shows our diffraction pattern from the solid oxygen in the α-phase, at 1.5 K, in zero field and the pattern is consistent with monoclinic $C2/m$. The lattice parameters in zero field reported here are a bit smaller than those reported before [2] ($a = 5.403$ Å, $b = 3.429$ Å, $c = 5.086$ Å and $\beta = 132.53°$) and we attribute the difference to the energy resolution determined by the angle of a Si monochromator at the beam line.

Data derived from diffraction by α-solid O_2 in an applied magnetic field up to 7.5 T are displayed in figures 3(a)–(d). We used seven diffraction peaks, namely, 001, 002, 020, -201, -202, -312 and -311, to obtain the lattice constants shown in figure 3 from a robust least-squares fitting.

The lattice constants a and b increase with increasing magnetic field, while the lattice constant c changes slightly and the angle β is almost independent of the field. The change in the lattice constant c is about one-third of that of a and b. The maximum volume expansion observed is about 1%. For comparison, it is known that ferromagnetic metals, such as Fe, Co and Ni, show a magneto-volume effect and the volume expansion in Fe is about 0.004% [8]
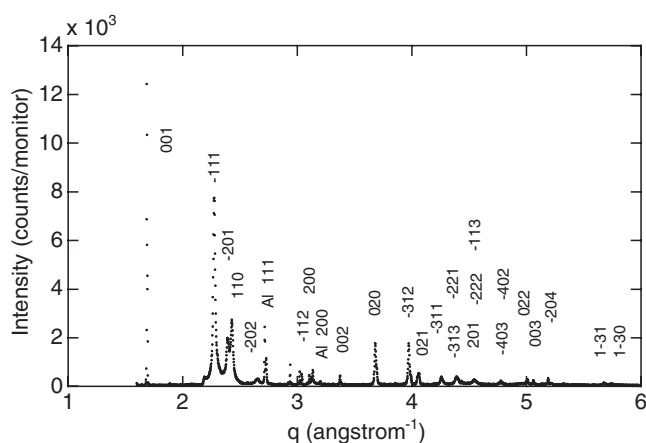
Figure 2. The diffraction pattern from α-solid O_2 obtained at 1.5 K and in zero magnetic field. X-ray primary energy = 30 keV.
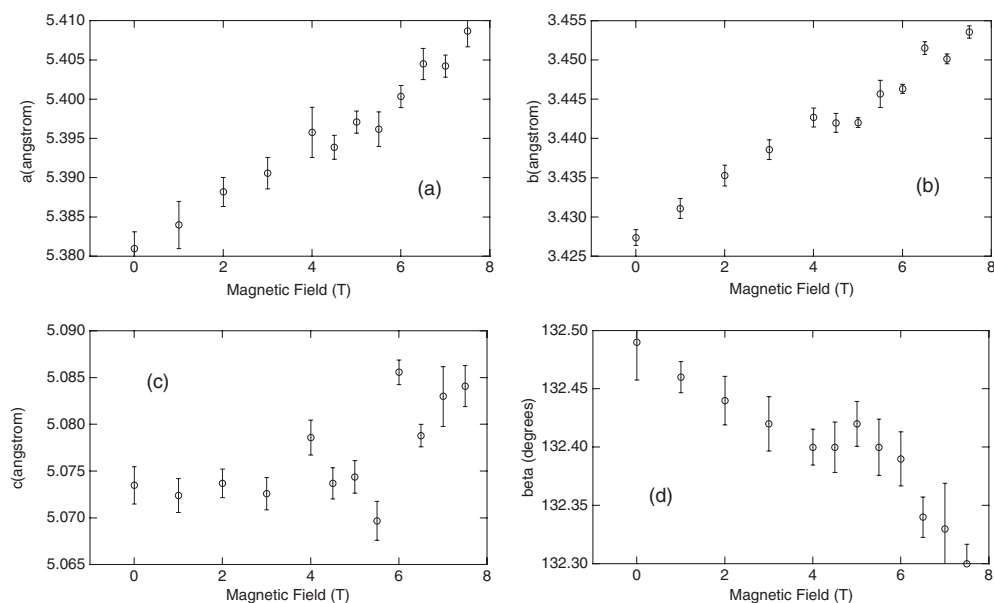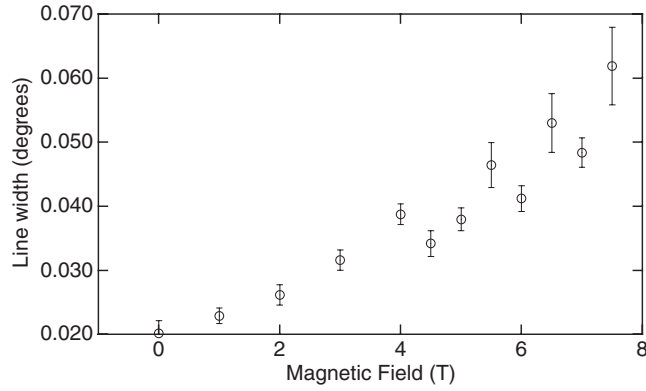

Figure 3. (a)–(d) show the magnetic field dependence of the lattice constants a, b, c and the angle β in $C2/m$ and applied to data for α-solid O_2 obtained at 1.5 K. Note the expanded scales used in panels (c) and (d).

at a field of 8 T.[7] It is interesting to note that a volume expansion has been observed even in liquid oxygen [9] under applied magnetic field, although the amount is much smaller (about 0.02% at 8 T).

The volume of α-solid O_2 shrinks under applied pressure [10], and an external magnetic field apparently plays the role of a negative pressure. Figure 4 shows the magnetic field dependence of the full width at half-maximum of the diffraction peaks. We see the linewidth

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[7] The actual measurement was done up to $\simeq 0.33$ T and a value for the relative volume change with magnetic field was obtained which would give a value $\simeq 0.004\%$ when extrapolated to 8 T.

Figure 4. The magnetic field dependence of an averaged full width at half-maximum of the diffraction peaks in α-solid O_2 obtained at 1.5 K.

increases steadily with magnetic field. This result gives further ground for our claim that a magnetic field plays the role of pressure. For, the increase in the linewidth means solid oxygen experiences microstrains due to the pressure which is similar to the influence of hydrostatic pressure. Both positive and negative pressure are expected to induce microstrain in the material, because the expandability/compressibility is not isotropic.

As described in the first part of this paper, English *et al* [4] are successful in predicting the correct magnetic structure in the *ab* plane of α-solid O_2, using a two-dimensional spin-dependent inter-molecular potential in addition to a Lennard-Jones potential. Gaididei and Loktev have discussed the α–β transition based on the quasi-two-dimensional model [5]. Bar'yakhtar *et al* studied theoretically the effects of H on the phase transition including the effects of the spin-dependent inter-molecular potential in the form of a magneto-elastic coupling [6]. The components of the tensor of small strains caused by the magneto-elastic coupling and H are, in the two-dimensional model,

$$u_{xx} + u_{yy} = A(1 + 2\cos 2\theta) \tag{1}$$

$$u_{xx} - u_{yy} = B(1 - \cos 2\theta) \tag{2}$$

$$u_{xy} = 0 \tag{3}$$

where A (>0) and B are derived from an exchange magneto-elastic interaction. The angle θ is the angle between an O_2 spin and H, and it takes values between $\pi/2$ at $H = 0$, and 0 at $H = H_s$ at which the orthorhombic (nonisomorphic) distortion, equation (2) vanishes. Neglecting the exchange interaction, J_2, between *ab* planes, H_s is $4J_1/g\mu_B$, where J_1 is the exchange interaction in the *ab* plane, $g = 2$ [11] and μ_B is the Bohr magneton. Using the value $J_1 = 17.15$ cm^{-1} [12], we have $H_s \simeq 74$ T which is very large compared to our applied fields. Writing $\theta = \pi/2 - \delta$, $\cos 2\theta$ may be represented by $-1 + 2\delta^2$ in the field range of interest where $\delta \ll 1$, and strains in the α-structure are

$$u_{xx} + u_{yy} \simeq A(-1 + 4\delta^2) \tag{4}$$

$$u_{xx} - u_{yy} \simeq 2B(1 - \delta^2) \tag{5}$$

and the corresponding change in dilation, $\Delta V/V$, is given by

$$\Delta V/V \simeq 4A\delta^2. \tag{6}$$

From the balance of the sublattice magnetization, M_s, of an antiferromagnet subject to H and the molecular field, we have $\cos\theta \propto H/M_s$ which gives a linear relation between δ and H at

low fields. We see from equations (6) and (5) that the ab dilation increases, while the magnitude of the orthorhombic distortion decreases with H. In addition, equations (4) and (5) and the observed elongation imply $A > |B|/2$. In the calculations [5, 6], J_2 was neglected because it is much weaker than J_1 ($J_2/J_1 \sim 0.05$ [12]). We anticipate that this weak inter-plane exchange interaction creates only a weak magneto-elastic coupling between the ab planes and a weakly field-dependent lattice constant c.

Positive dilation in the ab-plane as a consequence of an applied field is also the outcome of a consideration of the magnetic energy and the inter-molecule interaction. An *ab initio* calculation of the interaction [13] shows that it depends on the direction of the magnetic moment relative to the crystal axes, as well as the distance between the molecules. When a field is applied to an antiferromagnet, magnetic moments turn their direction normal to H to gain the magnetic energy, except the few moments pointing close to H. With increasing field, moments pointing close to H keep their zero-field arrangement until a critical field H_c is[8] reached, at which they abruptly turn their direction to normal to H, a phenomenon know as the spin-flop transition [14]. The magnetization process of a polycrystalline sample of α-solid O_2 has been measured by Uyeda *et al* [15]. The magnetization increases gradually from zero with increasing H and the derivative of M with respect to H, dM/dH, shows a peak at $H_c = 6.9$ T at 4.2 K. When H is applied to a polycrystalline α-solid O_2, most of the magnetic moments turn their direction to normal to H. So, a canting of the magnetic moment due to H will increase the lattice energy. In order to release this energy, the distance between the molecules in the ab plane becomes larger, resulting in an elongation of the lattice constants a and b. Since the magnetization change at H_c is very small [15], it is not surprising if we do not detect any anomaly in the lattice constants near H_c.

Our observation of a giant magneto-volume effect poses challenges for *ab initio* calculations of solid oxygen.

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[8] The spin-flop field, H_c, and the saturation field, H_s, should not be confused.