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Title
Magnetism of the Alpha-Beta Transition in Solid Oxygen

Permalink
https://escholarship.org/uc/item/56f2s4b8

Journal
Chemical Physics Letters, 222(4)

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Publication Date
1994-02-01
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February 1994
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MAGNETISM AND THE $\alpha$-$\beta$ PHASE TRANSITION IN SOLID OXYGEN*

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*This work was supported in part by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U. S. Department of Energy under Contract No. DE-AC03-76SF00098.
Magnetism and the $\alpha - \beta$ Phase Transition in Solid Oxygen.

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Abstract

The electronic spectra of $\alpha$ and $\beta$ solid $O_2$ were calculated in a full many-body approach for a cluster consisting of four $O_2$ molecules with periodic boundary conditions. Only the partially occupied $\pi$ orbitals (16 spin-orbitals, 8 electrons) were included. The lowest 81 many-body states, which correspond to neutral, unexcited molecules, describe accurately the magnetic excitations of the solids. The two phases have very different spectra resulting, even at very low temperatures, in a large difference in the (magnetic) entropy. The calculated entropy difference at 23.9 K (the $\alpha - \beta$ phase transition temperature) agrees surprisingly well with the experimentally measured heat of transformation.
The ground state of the oxygen molecule is a spin triplet\(^1\) and, as a consequence, solid \(O_2\) is a molecular crystal with a very rich structure. In particular oxygen is the only known antiferromagnetic, insulating, elemental solid. Therefore, in addition to ordinary low-energy modes characteristic of all van der Waals molecular crystals\(^2\), i.e., phonons and librons, oxygen exhibits magnetic excitations\(^3\)–\(^6\) (spin waves or magnons) peculiar to magnetic solids.

At atmospheric pressure the lowest-temperature \(\alpha\)-phase of oxygen is monoclinic\(^7\) and stable\(^8\) below 23.9 K. It has one molecule per chemical unit cell and space group \(C2/m\). The molecules are orientationally ordered\(^7\)\(^,\)\(^9\) and packed in layers with their axes perpendicular to the \(a - b\) (layer) planes (see Fig. 2 of Ref. 5). In each plane there are four nearest-neighbor molecules, at a distance of 3.20 Å, and two second-nearest-neighbor molecules, at 3.43 Å. The angle between adjacent nearest-neighbor vectors is 64.4°, and the one between adjacent nearest and second-nearest-neighbor vectors is 57.8°. The molecular spins are aligned along the monoclinic axis ±\(b\), with all nearest neighbors in an antiparallel arrangement to each other\(^5\)\(^,\)\(^7\)\(^,\)\(^10\)–\(^12\).

Beta oxygen, which is the stable phase\(^8\) between 23.9 K and 43.8 K, is rhombohedral, with space group \(R3m\) and one molecule per unit cell. The molecules are also packed in planes with their axis perpendicular to them. These layers are the equivalent of the \(a - b\) planes in \(\alpha - O_2\), but with six nearest-neighbor molecules at a distance of 3.30 Å and angles of 60°, i.e., a triangular lattice\(^5\). This arrangement give rise to "frustration"; that is, there is no possibility of having a classical antiferromagnet and still conserve the lattice symmetry. It is impossible for all nearest-neighbor molecular pairs to align themselves in an antiparallel fashion. Susceptibility measurements\(^5\)\(^,\)\(^13\) indicate a behavior characteristic of antiferromagnets, but no long-range order has been observed by neutron diffraction. There is strong evidence of short-range magnetic order\(^10\)–\(^12\)\(^,\)\(^14\). Various models\(^14\)–\(^16\) have been proposed to explain the magnetic structure of \(\beta - O_2\).

The \(\alpha - \beta\) first-order transition at 23.9 K has been extensively studied\(^12\)\(^,\)\(^17\)–\(^20\). Its origin has been speculated to be either elastic or magnetoelastic. The purpose of this contribution is to establish that the magnetic entropy difference between the two phases is sufficient to
explain, quantitatively, the measured heat of transformation.

All phases of solid \( O_2 \) can be viewed as a set of weakly interacting molecules with strong intra-molecular correlations. The dominant (but weak) inter-molecular electronic interactions, therefore, are short ranged. This fact makes solid oxygen an ideal candidate to study its electronic spectra by the so-called small-cluster method\(^{21}\). The method treats one-electron and many-body effects on the same footing, but restricts itself to a "small crystal" (a few unit cells with periodic-boundary conditions) or, equivalently, samples reciprocal space in only a few, symmetry-related, selected points in the Brillouin zone. As treated here the method determines accurately the full many-body states of a periodic cluster of four molecules, including excited electronic states of neutral \( O_2 \) as well as charge-transfer states. Magnetic interactions and excitations within the present model follow naturally from the many-body electronic structure calculation, and do not have to be introduced \textit{a posteriori} in any way. Therefore, this method should provide a good description, qualitative and quantitative, of the magnetic excitations in \( \alpha \) and \( \beta \) oxygen.

Details of the calculation\(^ {22,23} \) are briefly sketched below. For both \( \alpha - O_2 \) and \( \beta - O_2 \) all four molecules in the cluster are in a single \( a - b \) plane. Interplane exchange interactions, which are much weaker\(^ {10,12} \), are completely neglected. Within the cluster molecules are labelled from 1 to 4. In \( \alpha \)-oxygen each molecule, say that labelled 1, has (with periodic boundary conditions included) two each of the molecules 2 and 4 as nearest neighbors, and two of the molecules 3 as second-nearest neighbors. In \( \beta \)-oxygen the six nearest neighbors to molecule 1 are two each of the other molecules, 2, 3, and 4.

Only the partially filled \( \pi \)-orbitals are included explicitly. There are two per molecule, a total of eight in the cluster. The one-particle basis vectors are the mutually orthogonal \( \pi_g \) Löwdin spin orbitals of the \( O_2 \) molecule, two of each spin on each molecule. With this set of sixteen orbitals and with the eight electrons in the cluster, a total of 12870 many-particle states can be obtained. They are then used to construct the Hamiltonian matrix.

The Hamiltonian is
Here \( t_{ij}^{\mu\nu} \) and \( U_{ijkl}^{\mu\nu\lambda\sigma} \) are one- and two-particle matrix elements, respectively; \( c_{i\mu\sigma}^\dagger \) (\( c_{i\mu\sigma} \)) are creation (destruction) operators for an electron in orbital \( \mu \) (corresponding to \( \pi_x \) or \( \pi_y \)), with spin \( \sigma \) (\( \uparrow \) or \( \downarrow \)) on site \( i \) (\( i = 1, 2, 3, 4 \)). The parameters are obtained from fitting the molecular and solid-state spectra\(^{22-24}\) and include intra-site Coulomb and exchange interactions, inter-site hopping parameters between directed orbitals, crystal field potentials, and inter-site Coulomb interactions.

The Hamiltonian was numerically diagonalized for both phases. Full use was made of group-theoretical techniques that take fully into account space and spin symmetries. The largest symmetry-reduced matrix was \((592 \times 592)\). The complete spectra are very rich, and includes energies up to about 60 eV. For the present purposes only the lowest 81 eigenstates, with energies in the meV range, are relevant. They are shown in Figs. 1 and 2 for \( \alpha \) and \( \beta - O_2 \), respectively. All 81 states, in both cases, correspond to various magnetic arrangements (spin waves) of all neutral molecules in the \( 3\Sigma_g^- \) electronic ground state.

The two spectra are very different, reflecting the dissimilar magnetic properties of the two phases. Both phases possess a spin singlet ground state, but whereas in \( \alpha - O_2 \) it is non-degenerate, in \( \beta - O_2 \) it has a space-group-induced two-fold degeneracy. Moreover, the magnetic excitation spectra are strikingly different. In \( \alpha - O_2 \) the 81 states are spread over a broad range, with maximum excitation energy of 94 meV, mean energy of 47.9 meV and a standard deviation of 23.0 meV. On the other hand the spin-wave excitation spectrum of \( \beta - O_2 \) is narrower, and the states, because of the hexagonal symmetry, are highly degenerate. It extends up to 66 meV, has a mean energy of 26.5 meV and a standard deviation of 18.6 meV.

Analysis of spin correlations \( < S_i \cdot S_j > \), for first- and second-nearest neighbors, shows the undisputed antiferromagnetic character of the spin interactions in \( \alpha - O_2 \). For \( \beta - O_2 \) there are short-range antiferromagnetic correlations, thus ruling out the possibility of treating beta oxygen as a paramagnet. The results also indicate appreciable quantum fluctuations.
and a complex set of states in a "frustrated" Heisenberg-type antiferromagnet.

The spectra from Figs. 1 and 2 have been used to calculate the magnetic contributions to the entropies, $S_\alpha(T)$ and $S_\beta(T)$, associated with the magnetic excitations. The entropy difference $\Delta S_{\beta\alpha}(T) = S_\beta(T) - S_\alpha(T)$ at the transition temperature, $T = T_{\alpha\beta} = 23.9$ K, should give the contribution of the magnetic modes to the heat of transformation. From the data of Figs. 1 and 2 one obtains $T_{\alpha\beta} \Delta S_{\beta\alpha} = 0.95$ meV/molecule, which agrees remarkably well with the experimental value $Q_{\beta\alpha} = T_{\alpha\beta} \Delta S_{\beta\alpha} \simeq 0.97$ meV/molecule obtained for the heat of transition$^{25}$.

From the experimental observations it is obvious that the $\alpha$ phase has a lower total energy, since it is the stable phase at $T = 0$. The transformation to the $\beta$ phase can only be driven by (a) a very small total-energy difference between the two phases, and (b) the entropy contribution from the low-lying excited modes. These modes can only be elastic (phonons and librons) or magnetic (magnons or spin waves). The contribution to the heat of transformation at 23.9 K can only thus come from the elastic and magnetic entropies.

The astounding agreement obtained above from the magnetic entropy alone, is probably fortuitous, but easy to understand. The small-cluster approach, used in this calculation, does not yield a good description of the long-wave-length excitation modes. It, therefore, may exaggerate the differences between the $\alpha$ and $\beta$ magnetic entropies, and then account for a larger magnetic share that is the case in reality.

On the other hand, it is very plausible to argue that the difference in entropy contributions at 23.9 K from the elastic and librational modes is either negligible or very small. The structures of $\alpha-O_2$ and $\beta-O_2$ are similar. The speeds of sound in both phases$^{25}$ are almost identical (1645 m/s and 590 m/s for the longitudinal and transverse speeds in the $\alpha$ phase at $T = 23.5$ K; 1633 m/s and 605 m/s in the $\beta$ phase at $T = 24.5$ K), which should result in negligible entropy difference from the acoustic modes (phonons). The librational modes$^{26}$ (two modes at 42 cm$^{-1}$ and 72 cm$^{-1}$ in the $\alpha$ phase at $T = 20$ K; a single doubly degenerate mode at 48 cm$^{-1}$ in $\beta-O_2$ at $T = 25$ K) yield at 23.9 K (and assuming an Einstein spectrum for the librons, an overestimate) a contribution of $Q_{\beta\alpha}(\text{librons}) \simeq 0.17$ meV/molecule,
i.e., only an upper limit of 18 percent of the magnetic contribution, as calculated here.

Several important conclusions can be drawn from these calculations:

(A) Both $\alpha$ and $\beta$ solid oxygen are antiferromagnets, the former a classical one, the latter a "frustrated" one.

(B) "Frustration" causes the spectrum of $\beta - O_2$ to exhibit, in addition to a degenerate ground state, a much lower magnetic excitation energy.

(C) The difference in the magnetic-excitation spectrum is, in turn, responsible for a sizeable difference in magnetic entropy at the transition temperature 23.9 K, sufficient to account for most of the heat of transformation. In other words, the $\alpha$-to-$\beta$ first-order transition in solid molecular oxygen is, essentially, driven exclusively by magnetic effects.

ACKNOWLEDGMENTS

This research was supported, at the Lawrence Berkeley Laboratory, by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division, U.S. Department of Energy, under contract No. DE-AC03-76SF00098. AJR da S acknowledges support from the Brazilian Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq).
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FIGURES

FIG. 1. Spectrum for the lowest 81 states (magnetic excitations) of $\alpha - O_2$. The single, non-degenerate ground-state is indicated by a circle at zero excitation energy.

FIG. 2. Lowest 81 states (magnetic excitations) of $\beta - O_2$. Note that the ground state is doubly degenerate – circle for two states at zero excitation energy – and that there is a singlet excited state at very low energies: 0.80 meV.
FIGURE 1
FIGURE 2