Magnetic coupling and lattice dynamics in solid O₂

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The properties of solid O₂ are studied by means of an integrated lattice-dynamics-spin-wave approach which uses the random-phase approximation. This approach is based on a Hamiltonian from first principles, which includes the structural dependence of the spin coupling parameters. The calculated magnon and libron frequencies in O₂ have been interpretated up to now on the basis of the following phenomenological spin Hamiltonian:

\[ H_{\text{spin}} = - \sum_{i<j} 2J_0 \mathbf{s}(i) \cdot \mathbf{s}(j) + \sum_i \left[ A S^2_{J_x}(i) + B S^2_{J_z}(i) \right] . \]  

The Heisenberg exchange term, with \( J_0 < 0 \) for nearest neighbors, is isotropic in the spin; the other two terms have been added in order to obtain the experimentally observed spin anisotropy. The single-particle term \( A S^2_{J_x}(i) \) keeps the spin momenta perpendicular to the molecular axes (i.e., to the \( x \)-axis); it is probably due to the intramolecular spin-orbit and spin-spin interactions. The term \( B S^2_{J_z}(i) \) imposes the \( a-b \)-plane anisotropy, which forces the spins in the \( \pm b \) directions (i.e., \( \pm z \) directions); this term probably represents the magnetic dipole-dipole interactions between the molecular spin momenta. Using this phenomenological spin Hamiltonian one has made mean-field and spin-wave calculations which yield the magnetic, optical, and thermodynamic properties of O₂. Comparison of the results with experimental data leads to empirical values of the coupling constants \( J, A, \) and \( B \). The situation is unsatisfactory, however, in that various studies yield very different sets of coupling constants (varying typically by factors up to 10), depending on the models used and the experimental data fitted. This discrepancy has most clearly been illustrated in De Fotis's 1981 review, but later studies still show a substantial scattering in the empirical \( J, A, \) and \( B \) values.

In this Rapid Communication, we present a new integrated lattice-dynamics-spin-wave approach. This approach is based on a Hamiltonian from first principles, which is directly related to the properties of the individual O₂ molecules and their interactions. Such a Hamiltonian, which applies not only to \( \alpha \)-oxygen, but to all the condensed phases, is written as follows:

\[ H = H_0 + H_{\text{spin}} . \]  

\[ H_0 = \sum_i \left[ -\frac{k^2}{2M} \nabla^2(i) + \frac{k^2}{2I} L^2(\hat{r}_i) \right] + \sum_{i<j} V(R_{ij}, \hat{r}_i, \hat{r}_j) . \]
From Eq. (1),

\[ H_{\text{spin}} = - \sum_{i<j} 2J(R_{ij}, \mathbf{R}, \mathbf{r}_i, \mathbf{r}_j) \mathbf{S}(i) \cdot \mathbf{S}(j) + \sum_i A_{-m-m}^{m-m} \mathbf{S}(i) \mathbf{S}(m) \]

\[ + \sum_{i<j} S_m(i) T_{-m-m}^{m-m} (R_{ij}) S_m(j) \left[ \frac{1}{m} \frac{1}{m'} \frac{2}{-m-m'} \right] . \]

Equation (2b) denotes the usual spin-independent Hamiltonian, which governs the lattice vibrations for closed-shell molecules. It contains the translational and rotational kinetic energy terms, with \( M \) being the \( O_2 \) mass and \( I \) its moment of inertia, and the potential \( V \), depending on the distance vectors \( \mathbf{R}_{ij} \) and the orientations \( \mathbf{r}_i \) and \( \mathbf{r}_j \) of the molecules in the crystal. Equation (2c) describes the coupling between the \( O_2 \) triplet spin momenta; the structure dependence of the coupling parameters is included explicitly.

(We find it convenient to express this dependence in spherical tensor form, with the larger brackets denoting a 3-j coefficient, and to use the summation convention for \( m \) and \( m' \).) The geometry dependence of the Heisenberg exchange parameter \( J \) is known, analytically, from \( ab \text{ initio} \) calculations on the \( O_2 \) dimer.\(^{13,14} \) The "molecular" spin-anisotropy term depends on the angle between the spin direction \( \mathbf{S}(i) \) and the orientation \( \mathbf{r}_i \) of the molecular axis; this dependence is correctly described by the second-rank tensor \( A \mathbf{m}(\mathbf{R}) - \frac{1}{4} A \sqrt{30} C_{12}^{(4)}(\mathbf{R}) \), with the Racah spherical harmonic \( C_{12}^{(4)} \). For \( A \) we take the free-molecule value \( A = 5.72 \) K. Especially for the third term, the change between the phenomenological spin Hamiltonian (1) and Eq. (2c) is drastic. The \textit{ad hoc} single-particle term \( B S_2^2 \) that imposes the observed spin direction is replaced by a two-body operator which represents exactly the dipole-dipole interactions between the magnetic momenta \( g_e \mu_b S(i) \) and \( g_e \mu_b S(j) \), with \( g_e = 2.0023 \), and \( \mu_b \) being the Bohr magneton. The dipole-dipole interaction tensor is given by

\[ T_m(\mathbf{R}) = -g_e^2 \mu_b \mu_b / \sqrt{30} R^{-3} C_{12}^{(4)}(\mathbf{R}) . \]

When summing this interaction over the lattice, in the calculations described below, we invoke the Ewald method.\(^{15} \)

With this new Hamiltonian (2) we have performed combined lattice dynamics and spin-wave calculations. The formalism used is the random-phase approximation (RPA), which has been applied to spin waves long ago.\(^{16} \) The method has been extended to librons and phonons, using bases of spherical harmonics and three-dimensional (3D) harmonic oscillator functions, respectively, and it has been demonstrated on solid \( N_2 \) that large-amplitude librons, anharmonic phonons, and their coupling are very well described.\(^{17} \) For studying solid \( O_2 \) we have further extended this formalism in order to treat magnons, librons, and phonons simultaneously. The coupling terms included consist of all operators which are bilinear in the magnon, libron, and phonon creation and/or annihilation operators. For the single magnon excitations such terms are absent, however, and thus the main role of the combined formalism is to correctly average ("renormalize") the spin-interaction parameters over the lattice vibrations and, vice versa, to average the effective intermolecular potential for the lattice dynamics over the spin. For the spin-independent potential \( V(R_{ij}, r_i, r_j) \), we have taken the analytic form of the anisotropic-exchange repulsion and the electrostatic-multipole interactions from the \textit{ab initio} calculations,\(^{18} \) while

the attractive dispersion interactions have been chosen to approximate the \( E_g \) libron frequency in \( \beta-O_2 \). The magnetic data presented below and the libron splitting in \( \alpha-O_2 \) are not at all sensitive to this choice. Details will appear in a forthcoming paper.\(^{18} \)

The results for the optical magnon frequencies in \( \alpha-O_2 \) are listed in Table I. The effective nearest-neighbor (NN) exchange interaction equals \( (J_{\text{NN}}) = -10.3 \) K, which corresponds with an increase by 5.5% due to the averaging over the translational vibrations and a decrease by 23% due to the librations, with respect to the value \( J_{\text{NN}} = -12.5 \) K calculated\(^{19} \) for fixed nearest neighbors at \( R_{NN} = 3.20 \) Å. The root-mean-square amplitude of libration, at \( T = 0 \) K, is 11°. The molecular anisotropy along the \( z \) axis is reduced to 94% of the free-molecule \( \alpha \) value by averaging over the librations, while the components along the \( x \) and \( y \) axes, which also result from this averaging, are smaller than 1%. We have checked, in particular, the effect of replacing the term \( B S_2^2 \) in the phenomenological spin Hamiltonian (1) by the explicit form of the dipole-dipole interaction operator in Eq. (2c). This substantial effect is visible in the lower magnon frequency of Table I, which is approximately proportional to \( \sqrt{J_B} \). The higher frequency, which is proportional to \( \sqrt{J_A} \), remains nearly unaffected. The second column of Table I has been obtained by making the spin-wave calculations for the phenomenological Hamiltonian with \( J \) and \( A \) taken as the average values from the first principles calculation and \( B = 0.26 \) K fitted to the spin anisotropy in a classical dipole model.

We have also considered other known magnetic properties\(^{12-15} \) of \( \alpha \)-oxygen by introducing an external magnetic field into our calculations. The mean-field values calculated for the magnetic susceptibility, both parallel and perpendicular to the preferred magnetic \( b \) axis, turn out to be considerably too high. In view of our fairly small \( J \) values, compared with some recent empirical data,\(^{2,4,5} \) this is not surprising. On the other hand, the calculated value for the spin-flop field (6.7 T) agrees well with experiments\(^2 \) and also the Néel temperature \( T_N = 42 \) K obtained from the calculated parallel and perpendicular susceptibility versus temperature curves is fairly realistic. The remaining discrepancies may be due to distortions of the free-molecular charge distributions in the solid, to the inaccuracies in the mean-field and spin-wave models, or to the importance of higher-than-bilinear magnon/phonon or magnon/libron coupling.

<table>
<thead>
<tr>
<th>( \omega ) (cm(^{-1} ))</th>
<th>\text{First principles}</th>
<th>\text{From Eq. (1),} \quad \text{B = 0.26 K}</th>
<th>\text{Experiment (Ref. 1)}</th>
</tr>
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<tr>
<td>6.3</td>
<td>6.4</td>
<td></td>
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<tr>
<td>20.9</td>
<td>20.7</td>
<td>27.5</td>
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The large splitting of the $A_g$-$B_g$ libron frequencies in $\alpha$-O$_2$ appears to have the following explanation. The structural change from $\beta$-O$_2$ to $\alpha$-O$_2$ is small indeed. The magnetic order in these phases is very different, however, which yields a strong discontinuity of the quantity $(S(i) \cdot S(j))$ at the phase transition. For $\beta$-O$_2$ we have found the 120° spin arrangement with $(S(i) \cdot S(j)) = -0.5$, for $\alpha$-O$_2$ the order is antiferromagnetic with $(S(i) \cdot S(j)) = -1$, for nearest neighbors. If we substitute these values into the effective Hamiltonian for the lattice vibrations, the Heisenberg exchange parameter $J(R_{ij}, T_i, T_j)$ gets a very different weight in $\beta$-O$_2$ and $\alpha$-O$_2$. This parameter is extremely anisotropic and, thus, it has a strong influence on the libron frequencies. Use of the analytic representation of $J(R_{ij}, T_i, T_j)$ from the ab initio calculations yields good agreement with experiment, both for the splitting of the peaks in $\alpha$-O$_2$ and for the relative positions of these peaks with respect to the peak in $\beta$-O$_2$ (see Table II). Omitting the Heisenberg exchange term from our calculations, we find a much smaller splitting, just as the earlier lattice-dynamics calculations. This confirms the crucial role of this term: it not only drives the so-called magnetoelastic $\beta$-$\alpha$ phase transition, but it is also responsible for the anomalous libron splitting at this transition.

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