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Magnetic coupling and lattice dynamics in solid O_2

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The properties of solid O_2 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 α oxygen are in satisfactory agreement with experiment and the anomalously large libron splitting at the β-α phase transition is explained.

Solid O_2 is particularly interesting because the O_2 molecules possess an extra degree of freedom, the orientations of their triplet electron spins, in addition to the positional and orientational coordinates which characterize the more common closed-shell molecules. In the condensed phases the molecular spin orientations are coupled by spin-dependent terms in the intermolecular potential. Extra collective excitations (magnons) occur in combination with the phonons and librons, and the various phases of solid O_2 show magnetic as well as structural order. In the α and β phases, which have been studied most extensively,[1-10] the molecules are packed in layers with their axes perpendicular to the layer planes (the a-b planes, see Fig. 2 of Ref. 1). In the β phase the structure of these layers is hexagonal; in the monoclinic α phase the hexagons are slightly distorted. The distorted structure is stabilized by the antiferromagnetic exchange coupling. The α phase is a two-sublattice collinear antiferromagnet, with the spins preferentially aligned in the $\pm\mathbf{b}$ directions. The β phase probably has short-range antiferromagnetic order, with a three-sublattice 120° spin arrangement.

Although it has been concluded[3,8] from the occurrence of the so-called magnetoelastic β-α phase transition that the magnetic coupling and the structure are related, the lattice vibrations in solid O_2 and its magnetic excitations have always been treated separately. Lattice-dynamics calculations[8,11] on α- and β-oxygen have used the standard harmonic model with a spin-independent empirical atom-atom potential. The fitting of the parameters in this potential gave, in general, reasonable agreement with the experimental libron frequencies. One important observation could not be explained, though. In the hexagonal phase one finds a degenerate $\mathbf{q}=0$ libron mode of E_g symmetry with a frequency of about 48 cm^{-1}; in the α phase this mode splits into an A_g-B_g doublet. The structural distortion which marks the β-α phase transition is not very large, however, and so one would expect a small splitting. Indeed, the lattice dynamics calculations have yielded a splitting of at most 10 cm^{-1}. The experimental Raman spectum of α-oxygen shows two peaks, at 43 and 74 cm^{-1}. This splitting is so large that most authors have assumed, therefore, that the A_g-B_g doublet remains very nearly degenerate at 43 cm^{-1}, and they have assigned the peak at 74 cm^{-1} to a two-phonon, two-libron, or libron-magnon transition. Recent experiments[10] indicate, however, that the peak at 43 cm^{-1} probably corresponds with the B_g mode, and the peak at 74 cm^{-1} with the A_g mode. Such an anomalously large libron splitting could not be explained so far.

The magnetic excitations of α-oxygen have been interpreted[1-7] up to now on the basis of the following phenomenological spin Hamiltonian:

$$H_{\mathrm{spin}} = -\sum_{i<j} 2J_{ij}\mathbf{S}(i)\cdot\mathbf{S}(j) + \sum_{i}[AS_x^2(i) + BS_y^2(i)] \quad . \tag{1}$$

The Heisenberg exchange term, with $J_{ij}<0$ 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 $AS_x^2(i)$ 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 $BS_y^2(i)$ imposes the a-b plane anisotropy, which forces the spins in the $\pm\mathbf{b}$ (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 α-O_2. 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,[1] but later studies still show a substantial scattering in the empirical J, A, and B values.[2-7]

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 O_2 molecules and their interactions. Such a Hamiltonian, which applies not only to α-oxygen, but to all the condensed phases, is written as follows:

$$H = H_0 + H_{\mathrm{spin}} \quad , \tag{2a}$$

$$H_0 = \sum_i \left[-\frac{\hbar^2}{2M}\nabla^2(i) + \frac{\hbar^2}{2I}L^2(\hat{\mathbf{r}}_i) \right] + \sum_{i<j} V(\mathbf{R}_{ij}, \hat{\mathbf{r}}_i, \hat{\mathbf{r}}_j) \quad , \tag{2b}$$

$$H_{\text{spin}}=-\sum_{i<j}2J(\mathbf{R}_{ij},\hat{\mathbf{r}}_i,\hat{\mathbf{r}}_j)\mathbf{S}(i)\cdot\mathbf{S}(j)+\sum_i A_{-m-m'}(\hat{\mathbf{r}}_i)S_m(i)S_{m'}(i)\begin{pmatrix}1 & 1 & 2\\ m & m' & -m-m'\end{pmatrix}$$
$$+\sum_{i<j}S_m(i)T_{-m-m'}(\mathbf{R}_{ij})S_{m'}(j)\begin{pmatrix}1 & 1 & 2\\ m & m' & -m-m'\end{pmatrix}\ . \tag{2c}$$

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 $\hat{\mathbf{r}}_i$ and $\hat{\mathbf{r}}_j$ 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,[12] 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 initio* calculations on the $(O_2)_2$ dimer.[13,14] The "molecular" spin-anisotropy term depends on the angle between the spin direction $\mathbf{S}(i)$ and the orientation $\hat{\mathbf{r}}_i$ of the molecular axis; this dependence is correctly described by the second-rank tensor $A_m(\hat{\mathbf{r}})=\frac{1}{3}A\sqrt{30}C_m^{(2)}(\hat{\mathbf{r}})$, with the Racah spherical harmonic $C_m^{(l)}$. 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 *ad hoc* single-particle term $B\,S_y^2$ that imposes the observed spin direction is replaced by a two-body operator which represents exactly the dipole-dipole interactions between the magnetic momenta $g_e\mu_B\mathbf{S}(i)$ and $g_e\mu_B\mathbf{S}(j)$, with $g_e=2.0023$, and μ_B being the Bohr magneton. The dipole-dipole interaction tensor is given by

$$T_m(\mathbf{R})=-g_e^2\mu_B^2\sqrt{30}R^{-3}C_m^{(2)}(\hat{\mathbf{R}})\ .$$

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 $V(\mathbf{R}_{ij},\hat{\mathbf{r}}_i,\hat{\mathbf{r}}_j)$, we have taken the analytic form of the anisotropic-exchange repulsion and the electrostatic-multipole interactions from the *ab initio* calculations,[14] while the attractive dispersion interactions have been chosen to approximate the E_g libron frequency in β-O_2. The magnetic data presented below and the libron splitting in α-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 α-O_2 are listed in Table I. The effective nearest-neighbor (NN) exchange interaction equals $\langle J_{\text{NN}}\rangle=-10.3$ 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[13] for fixed nearest neighbors at $R_{\text{NN}}=3.20$ Å. The root-mean-square amplitude of libration, at $T=0$ K, is 11°. The molecular anisotropy along the x axis is reduced to 94% of the free-molecule A value by averaging over the librations, while the components along the y and z axes, which also result from this averaging, are smaller than 1%. We have checked, in particular, the effect of replacing the term $B\,S_y^2$ 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 $\sqrt{JB}$. The higher frequency, which is proportional to $\sqrt{JA}$, 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[1-9] of α-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[5] 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 I. Optical ($\mathbf{q}=\mathbf{0}$) magnon frequencies in α-O_2.

	Calculated		
	First principles	From Eq. (1), $B=0.26$ K	Experiment (Ref. 1)
ω (cm^{-1})	6.3	4.2	6.4
	20.9	20.7	27.5

TABLE II. Optical ($\mathbf{q}=\mathbf{0}$) libron frequencies.

ω (cm^{-1})		First-principles calculation ($T=0$ K) Putting $J=0$	 Including $J(\mathbf{R}_{ij},\hat{\mathbf{r}}_i,\hat{\mathbf{r}}_j)$	Experiment (Ref. 10)	
α-O_2	B_g	38.9	39.9	42.6/42.0	($T=13/20$ K)
	A_g	50.7	72.2	74.2/72.0	
β-O_2	E_g	42.9	53.6	48.0/42.0	($T=25/40$ K)

The large splitting of the A_g-B_g libron frequencies in α-O_2 appears to have the following explanation. The structural change from β-O_2 to α-O_2 is small indeed. The magnetic order in these phases is very different, however, which yields a strong discontinuity of the quantity $\langle \mathbf{S}(i)\cdot\mathbf{S}(j)\rangle$ at the phase transition. For β-O_2 we have found the 120° spin arrangement with $\langle \mathbf{S}(i)\cdot\mathbf{S}(j)\rangle \approx -0.5$, for α-O_2 the order is antiferromagnetic with $\langle \mathbf{S}(i)\cdot\mathbf{S}(j)\rangle \approx -1$, for nearest neighbors. If we substitute these values into the effective Hamiltonian for the lattice vibrations, the Heisenberg exchange parameter $J(\mathbf{R}_{ij},\hat{\mathbf{r}}_i,\hat{\mathbf{r}}_j)$ gets a very different weight in β-O_2 and α-O_2. This parameter is extremely anisotropic[13,14] and, thus, it has a strong influence on the libron frequencies. Use of the analytic representation of $J(\mathbf{R}_{ij},\hat{\mathbf{r}}_i,\hat{\mathbf{r}}_j)$ from the *ab initio* calculations[14] yields good agreement with experiment, both for the splitting of the peaks in α-O_2 and for the relative positions of these peaks with respect to the peak in β-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 β-α phase transition, but it is also responsible for the anomalous libron splitting at this transition.

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