MAGNETIC AND DYNAMIC PROPERTIES OF SOLID OXYGEN AND THEIR DEPENDENCE ON EXTERNAL MAGNETIC FIELDS

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ABSTRACT

The explicit consideration of the interactions between the triplet ground state O_2 molecules leads to a new lattice and spin hamiltonian for solid oxygen. Especially the coupling parameter $J$ in the Heisenberg effective spin hamiltonian for the exchange interactions is strongly dependent on the positions and the orientations of the molecules. We have developed an integrated lattice dynamics and spin wave formalism which uses the new hamiltonian. The interaction between the lattice modes and the magnons can largely be taken into account by including renormalized coupling terms. Realistic values for the librion splitting in $\alpha$-O_2 and for the magnon frequencies are obtained without empirical fit parameters. The anomalously large librion splitting in $\alpha$-O_2 is attributed to the extremely strong anisotropy of the coupling parameter $J$.

The frequencies of the Raman active librion modes of $\alpha$ and $\delta$-O_2 will be lowered by an external magnetic field. Also the $\alpha$-$\delta$ phase transition temperature is lowered by such a field. We have quantitatively predicted these lowerings.

1. INTRODUCTION

Solid oxygen is one of the most interesting molecular crystals because of its behaviour as a magnetic material. This behaviour is due to the rather unique property of the O_2 molecule of possessing a triplet electronic spin momentum in its ground state. The interactions between the spin momenta in the condensed phase lead to a very rich phase diagram. Most studies have been devoted to the $\alpha$ and $\delta$ phases. Under its own vapour pressure the $\alpha$ phase is stable below 23.9 K and the $\delta$ phase from 23.9 to 43.8 K. The structures are shown in Fig. 1. It is now generally believed that the structural distortion from the geometrically most favourable $\delta$ phase to the $\alpha$ phase is driven by the magnetic interaction between the molecules. The $\alpha$ phase is a two-sublattice antiferromagnet, with the spins aligned parallel to the $a$-$b$-axis. The $\delta$ phase is assumed to have an antiferromagnetic three-sublattice structure, the angle between the sublattice magnetizations being 120°.

The theoretical approaches that have been made for $\alpha$ and $\delta$-O_2 fall into two categories. On the one hand, one has tried to understand the elastic and optical properties via standard harmonic lattice dynamics calculations.
Fig. 1. Crystal structures of (a) α and (b) β-oxygen.

ignoring the open shell character of $O_2$. Such calculations cannot explain the splitting of the optical librion mode at the phase transition from β to α-$O_2$.

In view of the small structural distortion this splitting is very large (more than 30 cm$^{-1}$). On the other hand, one has interpreted the magnetic properties of α-$O_2$ by means of spin wave calculations based on a pure spin hamiltonian:

$$H_{\text{spin}} = -2 \sum_{\mu \nu} J_{\mu \nu} \hat{S}_\mu \cdot \hat{S}_\nu + \frac{1}{2} \left( A \hat{S}_\mu^2 + B \hat{S}_\nu^2 \right)$$

(1)

The first term is the usual Heisenberg exchange term and the single-particle anisotropic spin terms were included in order to explain the experimental data. The parameters $J_{\mu \nu}$, $A$, and $B$ have been regarded as empirical constants.

The main drawback of this hamiltonian is that one obtains very different sets of parameters from different experiments.

From ab initio electronic structure calculations in our institute (refs. 1,2) it has been found that $J_{\mu \nu}$ depends very sensitively on the positions and orientations of the molecules P and P'. This being the case it is no longer justified a priori to perform separate lattice dynamics and spin wave calculations.
We have developed an integrated lattice dynamics and spin wave formalism that includes the coupling between phonons, librons and magnons (refs. 3-4). We start from a hamiltonian which is based on first principles. Apart from a spin-independent potential \( V_{pp'} \), we include the geometry-dependence of \( J_{pp'} \). Moreover, the second sum in Eq. (1) has been replaced by operators that represent explicitly the intramolecular spin-spin and spin-orbit interactions and the intermolecular spin-spin (magnetic dipole-dipole) interactions.

2. THEORY

The hamiltonian that we propose to use for solid oxygen reads as follows:

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

\[
H_0 = \sum_p \left( \tilde{J}_p + \gamma \frac{\partial }{\partial \omega_0^p} \right) + \sum_{p' \neq p} V_{pp'} \left( \omega_{pp'} \right)
\]

\[
H_{\text{spin}} = -2 \sum_{pp'} J \left( \tilde{r}_{pp'}, \omega_{pp'} \right) \tilde{s}_p \cdot \tilde{s}_{p'}
\]

The first two terms in the spin-independent hamiltonian \( H_0 \) are the kinetic energies of the translational \( \left( \tilde{J}_p \right) \) and orientational \( \left( \tilde{J}_p \right) \) vibrations of the molecules. The last term is the spin-independent (anisotropic) intermolecular potential. In the earlier (harmonic) lattice dynamics calculations (refs. 5-7) one has used only this hamiltonian \( H_0 \), with the potential \( V \) estimated by an empirical atom-atom model.

The spin-dependent hamiltonian has been obtained from first principles. The first term represents the exchange interaction between the open-shell \( \text{O}_2 \) molecules. This interaction can be written as a Heisenberg effective spin operator with the triplet spin momenta \( \tilde{s}_p \). The coupling parameter \( J \) is strongly dependent on the molecular orientations \( \left( \omega_0^p \right) \) and positions \( \left( \tilde{J}_p \right) \). This dependence has been obtained from ab initio calculations (refs. 1-2), just as the spin-independent potential \( V \). The second term represents the
intramolecular spin-orbit and spin-spin coupling with the second rank tensor:

\[ A_m(\alpha) = \frac{1}{3} A \sqrt{\frac{\sigma}{2}} C^{(2)}_m(\alpha) \]  

(5)

and the molecular coupling constant \( A = 5.712 \text{ K} \). The last term represents the intermolecular spin-spin coupling with the magnetic dipole-dipole interaction tensor:

\[ T_m(\alpha, \beta) = -\sqrt{\frac{\sigma}{8}} \sigma^2 \frac{1}{8} r_{\alpha\beta}^{-3} C^{(2)}_m(\alpha, \beta) \]  

(6)

Just as the phenomenological spin-hamiltonian (1), our expression (6) contains two anisotropic spin terms, but in our case each term has a direct origin in the molecular properties.

Given this hamiltonian with the terms in Eq. (6) depending both on the structural coordinates \( \alpha \) and \( \beta \) and on the spin coordinates \( \alpha \beta \), we have made an integrated lattice dynamics and spin wave calculation. Rather than using the standard harmonic lattice dynamics theory, we have applied a new method (refs. 3, 4) that is suitable also for strongly anharmonic motions. This new method is based on the Random Phase Approximation (RPA) just as the spin wave theory and, thus, it could rather easily be integrated with the latter. In the original lattice dynamics scheme, as it has been applied to solid nitrogen (ref. 8), we have included phonon-libron coupling; in the case of oxygen phonon-magnon and libron-magnon couplings are included as well. For details we refer to refs. 4 and 8.

3. LATTICE DYNAMICS OF THE \( \alpha \) AND \( \beta \)-PHASE

Let us first consider the results for \( \alpha-O_2 \). We find twice as many lattice modes (phonons and librons) as the earlier lattice dynamics calculations because we have used the magnetic unit cell. The mixing between the lattice modes and the magnons is in general very small. Only at those (isolated) points in the Brillouin zone where there is a forbidden crossing, mixing occurs and the branches involved interchange their character. This means that the librons/phonons and the magnons can be calculated separately. However, one has to retain the Heisenberg exchange interactions in the intermolecular potential for the librons/phonons with the spin factor \( \sigma^2 \), \( \sigma^2 \), averaged over the spin states. Similarly, for the spin waves one has to average the coupling coefficients in the spin hamiltonian over the lattice vibrations.

The agreement of the calculated magnon frequencies with the experimental ones is very satisfactory, especially if one considers that none of the
TABLE 1
Optical \( (q = 0) \) magnon frequencies in \( \alpha - O_2 \).

<table>
<thead>
<tr>
<th>( \omega (\text{cm}^{-1}) )</th>
<th>calculated ( \text{from Eq. (4)} )</th>
<th>semi-empirical ( \text{from Eq. (1) with } B = 0.26 \text{ K} )</th>
<th>experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.7</td>
<td>4.7</td>
<td>6.4</td>
<td></td>
</tr>
<tr>
<td>22.2</td>
<td>22.7</td>
<td>27.5</td>
<td></td>
</tr>
</tbody>
</table>

Parameters in the spin-dependent hamiltonian have been fitted (see Table 1). We have compared the first-principles hamiltonian with the phenomenological hamiltonian \( \text{Eq. (1)} \). The first anisotropy parameter in Eq. (1) has been taken equal to the free molecule value, \( A = 5.712 \text{ K} \), and for the second parameter, we have taken the value \( B = 0.26 \text{ K} \) that yields the classical spin dipole anisotropy field. We see in Table 1 that there is a substantial difference in the lower magnon frequency. We therefore conclude that it is not justified to replace the exact magnetic dipole-dipole interaction by an effective single-molecule term.

TABLE 2
Optical \( (q = 0) \) libron frequencies in \( \alpha \) and \( \beta - O_2 \) from pure libron calculations \( (\text{cm}^{-1}) \).

<table>
<thead>
<tr>
<th>Putting</th>
<th>including ( J = 0 )</th>
<th>( J(T_{pp}, J, J_{sp}) )</th>
<th>experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \alpha - O_2 : B_g )</td>
<td>38.9</td>
<td>39.9</td>
<td>42.6/42.0 (( T = 13/20 \text{ K} ))</td>
</tr>
<tr>
<td>( \beta - O_2 : B_g )</td>
<td>42.9</td>
<td>53.6</td>
<td>48.0/42.0 (( T = 25/40 \text{ K} ))</td>
</tr>
</tbody>
</table>

The optical Raman active libron modes in the \( \alpha \) and \( \beta \)-phase have led to a controversy. In the hexagonal \( \beta \)-phase these modes are degenerate and of \( B_g \) symmetry. In the monoclinic \( \alpha \)-phase the two libron modes are non-degenerate and of \( B_g \) and \( A_g \) symmetry. Two peaks have been observed by Raman spectroscopy which are 32 cm\(^{-1} \) apart. Lattice dynamics calculations have never yielded a splitting of more than 10 cm\(^{-1} \), which appears to be reasonable because of the small distortion of \( \alpha - O_2 \) with respect to \( \beta - O_2 \). One has therefore assigned the lower Raman peak of \( \alpha - O_2 \) to the accidentally degenerate libron modes and the higher peak to a two phonon/libron or libron-magnon transition. The weak point is that at various temperatures and pressures no indication of the doublet
Fig. 2. Orientational dependence of J.
Fig. 3. Variation of the potential energy of the $\alpha$-O$_2$ crystal along the normal coordinates $L_a$ and $L_b$ of the $B_g$ and $A_g$ optical librations, respectively. The dashed curves denote the potential without the Heisenberg exchange contribution; in the solid curves this contribution has been added.

The character of the lowest peak in $\alpha$-O$_2$ has been observed. Recent measurements suggest that the lower frequency peak corresponds to the $B_g$ mode and the higher one to the $A_g$ mode. The explanation of the large splitting can be inferred from Table 2. The large splitting is caused by the extremely anisotropic Heisenberg exchange parameter $J$ (see Fig. 2). The older lattice dynamics calculations have always neglected the Heisenberg exchange interaction. Fig. 3 illustrates the effect of this interaction. It stabilizes the $\alpha$-phase and it increases the stiffness of the potential in the $A_g$ direction much more than in the $B_g$ direction.
4. MAGNETIC FIELD EFFECTS

The responses of the spin systems of α and δ-O₂ to an external magnetic field have been calculated using the MF approximation. Our magnetic susceptibilities are considerably too high. This might indicate that our values of J are too small. However, we obtain fairly good values for the optical magnon frequencies in α-O₂ with the same values. Moreover, one would expect that if the absolute value of J would be substantially in error, then the absolute values of its main anisotropy components would be incorrect too. The latter, however, determine the optical libron frequencies in α-O₂, which were found to be in very good agreement with the Raman spectra. Therefore we believe that the error is due to the approximations made by the MF model.

We have calculated also the Néel temperature. Although the α-phase is not stable above 23.9 K (at low pressure) and no direct comparison can be made, our value of \( T_N = 49.5 \) K is not far from estimated values. In high magnetic fields along the b-axis the spin momenta in α-O₂ change direction by 90°. This spin-flop takes place at a field of 7.5 ± 0.5 Tesla. Our calculations yield a spin-flop field of 7.1 Tesla at 0 K.

As the α-phase is stabilized with respect to the δ-phase by the magnetic interactions, one expects that an external magnetic field B will affect the phase transition temperature. If we assume that the magnetic susceptibility is field independent and that the change in phase transition temperature is small, then it is easy to derive (ref. 9) that:

\[
\Delta T = -\frac{\Delta \chi}{2\beta S} S^2
\]  

(7)

with:

\[
\Delta \chi = \chi_\delta(T_\alpha) - \chi_\alpha(T_\alpha)
\]

\[
\Delta S = S_\delta(T_\alpha) - S_\alpha(T_\alpha)
\]

\[
\Delta T = T_\alpha(B) - T_\alpha(0)
\]

We know that \( \Delta \chi > 0 \) and \( \Delta S > 0 \) so that the phase transition temperature is lowered. Using the experimental magnetic susceptibilities and heat of transition we find that the α-δ transition temperature is lowered by an amount of 1.83 mK/Teila². Because of the spin-flop in α-O₂ the actual shift at higher magnetic field strengths will be
smaller. The resulting $\Delta T$ is about 1.2 K at 30 Tesla.

Another interesting phenomenon occurs because of the anisotropy of the magnetic susceptibility. The shift in the transition temperature will range for single crystals, depending on the direction of the magnetic field, from $-2.88 \text{ mK/Tesla}^2$ to $-1.25 \text{ mK/Tesla}^2$ in low fields. In powder samples the $\alpha$-$\beta$ phase transition in a magnetic field will take place over a range of temperatures, see Fig. 4.

Fig. 4. Magnetic field strength dependence of the $\alpha$-$\beta$ phase transition temperature. The dashed curve depicts the average transition temperature. The solid curves indicate the range of transition temperatures in a powder sample. Note the effect of the spin-flop in $\alpha$-$\beta$ at 7.5 Tesla.

The most direct demonstration of the importance of the coupling between the magnetic and structural phenomena in solid oxygen would be the measurement of an effect of external magnetic fields on some properties that are normally determined by a spin-independent intermolecular potential. We have calculated
the effect of a magnetic field on the optical libron modes in α and θ-O₃ that are observed by Raman spectroscopy.

![Graph showing the effect of magnetic field on optical libron frequencies](image)

Fig. 5. Magnetic field induced lowering of the optical libron frequencies in α-O₃.

The magnetic structure of α-O₃ is fairly rigid. So one needs high fields to distort it to an appreciable extent and the resulting shifts will not be large. Fig. 5 shows these shifts for the optical Bg and Ag librons. They vary only slightly for different field directions. There will be a discontinuity at 7.5 Tesla, due to the spin-flop if the field is along the b-axis. However, this discontinuity is too small to be visible.

We have assumed for θ-O₂ that the spins adopt the three-sublattice structure. A magnetic field along the c-axis gives every spin the same c-component, which yields not a very favourable situation. Consequently the effect on the Bg mode will be small. If the field is parallel to the ab-plane, the spin momenta can have all possible angles relative to this field. There are two extreme cases, i.e. a magnetic field parallel and antiparallel,
respectively, to one of the sublattice magnetizations. In both cases the magnetic structure can easily be distorted and the libron shifts are larger. The effects on the \( E_g \) mode frequency in \( \delta - O_2 \) are displayed in Fig. 6.

5. CONCLUSIONS

A substantial coupling between the magnetic properties and the lattice vibrations in solid \( O_2 \) is caused by the large anisotropy and the dependence on the intermolecular distance of the Heisenberg exchange coupling parameter. The actual mixing between phonons/librons and magnons is, however, small and so lattice dynamics and spin wave calculations can be made separately. A crucial difference with the older lattice dynamics calculations is that we have...
retained the spin terms, in particular the Heisenberg exchange term, with averaged spin operators. In our spin wave calculations the coupling parameters in the spin hamiltonian have been obtained by averaging the ab initio parameter functions over the lattice vibrations. Another essential improvement is that we have taken the exact two-body spin operator for the magnetic dipole-dipole interaction instead of an effective one-body operator.

The optical magnon frequencies from the spin wave calculations on α-O₂ are in fair agreement with the values from infrared and Raman spectroscopy. The lattice dynamics calculations have led to a unique assignment of the Raman libron peaks in α and β-O₂. The large splitting between the peaks in α-O₂ has been attributed to the extremely strong anisotropy of the Heisenberg exchange coupling parameter.

We expect a shift of the optical libron frequencies in a magnetic field because of this strong anisotropy of the Heisenberg exchange coupling parameter. We have predicted the largest shift for the B₈ libron frequency in β-O₂, when the magnetic field is parallel to the ab-plane (2.9 cm⁻¹ at 30 Tesla). The shifts for the B₈ and A₈ modes in α-O₂ are somewhat smaller (1.5 and 2.5 cm⁻¹, respectively, at 30 Tesla). Also the α-β phase transition temperature will be lowered by an external magnetic field by 1.2 K at 30 Tesla.

ACKNOWLEDGEMENT

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REFERENCES

DISCUSSION

PRESS - The question I have is related with this orientation-dependent interaction. A parallel arrangement of dumbbells is not the signature of electrostatic quadrupole-quadrupole interaction, but rather is reminiscent of the stacking of pencils. From this I would conclude that hard-core-repulsion is the dominant interaction, or is it important to include higher-order multipoles?

VAN DER AVOIRD - The quadrupole moment of O₂ is small indeed, about 4 times smaller than for N₂ and also the higher multipole interactions may be neglected. So it is true that the parallel packing of O₂ molecules is mainly determined by their short range repulsion. This packing is further stabilized by the nearest neighbour Heisenberg exchange interactions between the O₂ molecules in the different antiferromagnetic sublattices.

HOLZAPFEL - Since your calculations use ab initio potentials, you should be able to calculate high pressure behaviour. Have you tried this?

VAN DER AVOIRD - Yes, we are able to do this, although for very high pressures the three-body interactions will become important as well. We intend to study the high pressure phases of solid O₂ in the near future.

LYNDEN-BELL - Why do the magnetic spins lie in the planes of molecules and not perpendicular to these planes?

VAN DER AVOIRD - The spins in α-O₂ and β-O₂ are forced to lie in the a-b plane by the anisotropic spin interaction originating from intramolecular spin-orbit and spin-spin coupling (the second term in our spin-hamiltonian). In α-O₂ the preferred magnetization direction is parallel to the b-axis. This is caused by the magnetic dipole-dipole, i.e. the intramolecular spin-spin, interactions (the third term in our spin-hamiltonian).