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A symmetry analysis of the lattice vibrations/spin waves of α -O₂

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Abstract. After determining the magnetic space group of α -O₂, we have made a symmetry analysis of the phonons, librations, and magnons in the context of the random-phase approximation, and determined at which points in the Brillouin zone there is a mixing of the magnons and the librations/phonons. It is shown that the time reversal operator yields doubly degenerate modes at some points on the boundary of the Brillouin zone. We have derived the selection rules for infrared and Raman spectroscopy. The magnons appear to be both infrared and Raman active via their coupling to the magnetic dipole field of the radiation.

1. Introduction

Solid oxygen is a unique system. It combines the properties of a molecular crystal with those of a magnetic material. The coupling of the structural and magnetic interactions leads to very interesting but also very complex phenomena. This is also apparent from the phase diagram [1]; already at low pressures there are three phases instead of the ordinary one or two.

Experimental research on solid oxygen dates back to 1914 [2]. However, the interpretation of even these early and also of later measurements is still controversial (see [3] and references therein). This is in part due to the fact that they have been done on powder samples. Only recently have the first experiments on single crystals of α -O₂ been reported [4].

Until recently theoreticians have been treating the structural and magnetic properties separately [5–11]. In our institute we have developed a formalism to describe the coupling between the spin waves and the lattice vibrations [12, 13]. It is an extension of a formalism we developed to describe phonons, librations and their coupling in solid nitrogen [14, 15]. Our calculations were the first to yield accurate values for the libration and magnon frequencies from a first-principles (spin-dependent) intermolecular potential. Furthermore, they yielded detailed information on the coupling between magnons and librations/phonons.

In the literature, only the symmetry assignment of the optical phonons and librations can be found [16], based on the harmonic approximation [17]. A symmetry analysis for classical spin waves has been given by Sahni and Venkataraman [18], but it has never been applied to solid oxygen. In this paper we will investigate the symmetries of the

librons, phonons, magnons and their coupling. As we need a theory for the symmetry assignment that can describe this coupling, we will use here the random-phase approximation (RPA), i.e. the method we have used in the calculations mentioned above. For a detailed description of the RPA formalism we refer the reader to [13] and [15]. We will also determine the selection rules for infrared and Raman spectroscopy, and suggest an experiment with polarised infrared radiation.

2. The magnetic space group of α -O₂

The non-magnetic space group of α -O₂ as determined by x-ray diffraction measurements is C2/m (see figure 1) [19]. This group is not appropriate, however, for a group theoretical analysis that includes the magnetic properties. For this purpose, we have to determine the magnetic space group of α -O₂, which is determined by the magnetic structure as obtained from neutron diffraction measurements [20].

Figure 1. The structure of α -O₂. The magnetic unit cell is shown. α -O₂ is an antiferromagnet with magnetic moments (anti) parallel to the b -axis.

α -O₂ is an antiferromagnet. The magnetic space group can be derived from C2/m by adding to the operations that connect molecules of the different magnetic sublattices an operation θ that reverses spins (a magnetic sublattice is defined as a set of molecules with translational symmetry in which each molecule has the same magnetic moment in magnitude and direction). We thus obtain the magnetic space group P_A2/m [21]. We write its elements as $\{\alpha|\mathbf{R}\}$ and $\{\alpha\theta|\mathbf{R} + \mathbf{r}(\theta)\}$, where α is an element of the non-magnetic point group C_{2h}, $\mathbf{R}$ is a primitive translation, and $\mathbf{r}(\theta)$ is an intermolecular vector between nearest neighbours. This magnetic space group has as subgroup of index 2 the non-magnetic space group P2/m.

3. The equation of motion

The RPA formalism is based on the following equation of motion [13, 15]

$$[\hat{H}, \hat{\Xi}] = \hbar\nu\hat{\Xi} \quad (1)$$

where $\hat{H}$ is the Hamiltonian of the system, $\hat{\Xi}$ is an excitation operator that yields an

excited state when it is applied to the crystal ground state, and $h\nu$ is an excitation energy. We will associate with every element $\{\alpha|\mathbf{R}\}$ or $\{\alpha\theta|\mathbf{R} + \mathbf{r}(\theta)\}$ of the magnetic space group of α -O₂ an operator $\hat{O}(\{\alpha|\mathbf{R}\})$ or $\hat{O}(\{\alpha\theta|\mathbf{R} + \mathbf{r}(\theta)\})$ that operates on the same Hilbert space as the Hamiltonian, and that commutes with the Hamiltonian. Suppose we have a complete set of excitation operators $\{\hat{\Xi}_i\}$. Then every operator $\hat{O}(\{\alpha|\mathbf{R}\})\hat{\Xi}_i\hat{O}(\{\alpha|\mathbf{R}\})^{-1}$ and $\hat{O}(\{\alpha\theta|\mathbf{R} + \mathbf{r}(\theta)\})\hat{\Xi}_i\hat{O}(\{\alpha\theta|\mathbf{R} + \mathbf{r}(\theta)\})^{-1}$ is also an excitation operator with the same excitation energy as $\hat{\Xi}_i$. If we express these operators as linear combinations of operators of the set $\{\hat{\Xi}_i\}$, we obtain co-representations of the magnetic space group [22]. Assuming that there is no accidental degeneracy, the co-representations are irreducible. The irreducible co-representations of P_A2/m thus give us the degeneracies and symmetries of the lattice vibrations/spin waves of α -O₂. In what follows we will determine these irreducible co-representations, and how they relate to RPA.

4. The symmetries of the single-molecule mean field states

In the RPA formalism the Hamiltonian and the excitation operators are expressed in terms of mean field excitation operators (cf equation (6)) [13, 15]. These are in turn defined in terms of single-molecule mean field states. We thus start by looking at the symmetries of the single-molecule mean field states.

The transformation properties of these states under the grey point group $\{\alpha, \alpha\theta|\alpha \in C_{2h}\}$ are determined by a group of operators isomorphic to this point group. The operators corresponding with the elements of C_{2h} are defined as follows [23]:

$$\hat{O}(\alpha)\psi(x) = \psi(\alpha^{-1}x) \quad (2)$$

for librational ($x = (\theta, \varphi)$) or translational states ($x = \mathbf{r}$). If we write the spin states in the standard representation [24] then they transform as spherical harmonics under rotations. They are invariant under inversion.

The operator that yields the reversal of the spin momenta is the time reversal operator that is given by [24]

$$\hat{O}(\theta) = \hat{K}_0 \exp(-i\pi\hat{S}_y) \quad (3)$$

where $\hat{K}_0$ is the complex conjugation operator. Again the spin states must be in standard representation. We note that the operators of equation (2) are unitary, whereas $\hat{O}(\theta)$ is anti-unitary.

The symmetries of the single-molecule mean field states can be determined by inspection of the results of the mean field calculations. However, we can also use some physical arguments. The $S = 1$ spin states transform according to the irreducible representation $D^{(1)+}$ of the direct product of the rotation group and the group C_i [24]. This representation decomposes under C_{2h} into $2B_g + A_g$. The mean field spin ground state must have B_g symmetry because the state of A_g symmetry (i.e., $|m_s = 0\rangle$) has no spin momentum along the monoclinic axis. The two excited mean field spin states must then be of A_g and B_g symmetry.

The total single-molecule state must be symmetric under permutation of the nuclei (nuclear spin momentum $I = 0$ for $^{16}\text{O}_2$). The electronic ground state ($^3\Sigma_g^-$) is odd under this permutation, and the vibrational and translational factors are even, so that the librational states are ungerade. Librational states with A_u symmetry have a nodal plane perpendicular to the monoclinic axis. The equilibrium orientation is also perpendicular to the monoclinic axis, and therefore the librational mean field ground state will have

B_u symmetry. The librational mean field excited states have A_u and B_u symmetry. The translational mean field ground state will have no nodal plane and thus have A_g symmetry. The first three translational excited states will have one nodal plane and thus have A_u symmetry (a nodal plane perpendicular to the monoclinic axis) and B_u symmetry (the nodal plane contains the monoclinic axis; there are two of these states). The operator $\hat{O}(\theta)$ has no effect on the librational and translational mean field states as they are real. It interchanges the corresponding mean field spin states of the two magnetic sublattices.

5. Transformation properties of the mean field (de)excitation operators

The mean field crystal states are defined in terms of the single-molecule mean field states

$$\Psi_{\{m\}\{n\}\{k\}} \equiv \prod_P \psi_{m_P}^{(L)}(\Omega_{R_P}) \psi_{n_P}^{(T)}(\mathbf{r}_{R_P}) \psi_{k_P}^{(S)}(\sigma_{R_P}). \quad (4)$$

The superscripts denote the types of motions; L stands for librations, T for translations and S for spin. Furthermore, I_P and R_P denote the sublattice to which molecule P belongs and the position of the molecule, respectively. We can define a group of operators, called the symmetry group of the Hamiltonian, that determines the transformation properties of these states under P_A2/m , as follows

$$\hat{O}(\{\alpha|\mathbf{R}\})\Psi_{\{m\}\{n\}\{k\}} \equiv \hat{O}(\alpha) \prod_P \psi_{m_P}^{(L)}(\Omega_{\{\alpha|\mathbf{R}\}R_P}) \psi_{n_P}^{(T)}(\mathbf{r}_{\{\alpha|\mathbf{R}\}R_P}) \psi_{k_P}^{(S)}(\sigma_{\{\alpha|\mathbf{R}\}R_P}) \quad (5a)$$

$$\begin{aligned} \hat{O}(\{\alpha\theta|\mathbf{R} + \mathbf{r}(\theta)\})\Psi_{\{m\}\{n\}\{k\}} &\equiv \hat{O}(\alpha) \prod_P \psi_{m_P}^{(L)}(\Omega_{\{\alpha\mathbf{R} + \mathbf{r}(\theta)\}R_P}) \psi_{n_P}^{(T)}(\mathbf{r}_{\{\alpha\mathbf{R} + \mathbf{r}(\theta)\}R_P}) \\ &\times \psi_{k_P, I_{P,c}}^{(S)}(\sigma_{\{\alpha\mathbf{R} + \mathbf{r}(\theta)\}R_P}) \end{aligned} \quad (5b)$$

where $\hat{O}(\alpha)$ is defined by equation (2) but now it operates on all single molecule mean field states, and $I_{P,c}$ denotes the sublattice that is not given by I_P . The operators in equation (5a) are unitary, whereas those in equation (5b) are anti-unitary. We obtain the mean field crystal ground state Ψ_0 if we put all m s, n s and k s in equation (4) equal to zero. We note that this state, combined with all electronic states of the molecules, is invariant under P_A2/m . We get singly excited mean field crystal states by taking one of the m s, n s and k s not equal to zero. Using the singly excited mean field crystal states we can define the following operators:

$$\begin{aligned} \hat{a}_{L,P,m}^\dagger &\equiv \left[\prod_{P' \neq P} \otimes \hat{\mathbf{I}}_{P'} \right] \otimes |\psi_m^{(L)}(\Omega_{R_P}) \psi_0^{(T)}(\mathbf{r}_{R_P}) \psi_0^{(S)}(\sigma_{R_P})\rangle \\ &\times \langle \psi_0^{(L)}(\Omega_{R_P}) \psi_0^{(T)}(\mathbf{r}_{R_P}) \psi_0^{(S)}(\sigma_{R_P}) | \end{aligned} \quad (6)$$

(and analogous operators for the translation and the spin). These operators yield singly excited mean field crystal states when working on the mean field crystal ground state Ψ_0 . They transform as

$$\hat{a}_{K,P,m}^\dagger \xrightarrow[\{\alpha\theta|\mathbf{R} + \mathbf{r}(\theta)\}]{\{\alpha|\mathbf{R}\}} \hat{O}\left(\begin{matrix} \{\alpha|\mathbf{R}\} \\ \{\alpha\theta|\mathbf{R} + \mathbf{r}(\theta)\} \end{matrix}\right) \hat{a}_{K,P,m}^\dagger \hat{O}^\dagger\left(\begin{matrix} \{\alpha|\mathbf{R}\} \\ \{\alpha\theta|\mathbf{R} + \mathbf{r}(\theta)\} \end{matrix}\right). \quad (7)$$

We adapt these operators to the translational symmetry of the crystal

$$\hat{a}_{q,K,l,m}^\dagger \equiv \frac{1}{\sqrt{N}} \sum_{P \in \text{sublattice } l} \exp(i\mathbf{q} \cdot \mathbf{R}_P) \hat{a}_{K,P,m}^\dagger \quad (8)$$

Figure 2. The first Brillouin zone of α -O₂. The line ΓZ is the monoclinic axis. The line ΓB is perpendicular to the ab plane of the crystal.

where N denotes the number of unit cells, and $\mathbf{q}$ is a wavevector in the first Brillouin zone (see figure 2). The transformation properties of the translationally adapted operators under P_A2/m are given by

$$\hat{O}(\{\alpha|\mathbf{R}\})\hat{a}_{\mathbf{q},K,I,m}^+\hat{O}^\dagger(\{\alpha|\mathbf{R}\}) = S_{\alpha Km} \exp(-i\alpha\mathbf{q} \cdot \mathbf{R})\hat{a}_{\alpha\mathbf{q},K,I,m}^+ \quad (9a)$$

$$\begin{aligned} \hat{O}(\{\alpha\theta|\mathbf{R} + \mathbf{r}(\theta)\})\hat{a}_{\mathbf{q},K,I,m}^+\hat{O}^\dagger(\{\alpha\theta|\mathbf{R} + \mathbf{r}(\theta)\}) \\ = S_{\alpha Km} \exp[i\alpha\mathbf{q} \cdot (\mathbf{R} + \mathbf{r}(\theta))]\hat{a}_{-\alpha\mathbf{q},K,I_c,m}^+ \end{aligned} \quad (9b)$$

where $S_{\alpha Km} = \pm 1$ (see table 1), and I_c denotes the sublattice that is not given by I . In deriving equation (9b) we have used that $\hat{O}(\{\alpha\theta|\mathbf{R} + \mathbf{r}(\theta)\})$ is anti-unitary and that also for an anti-unitary operator $\hat{A}$

$$\hat{A}(|\psi\rangle\langle\varphi|)\hat{A}^\dagger = (\hat{A}|\psi\rangle)(\langle\varphi|\hat{A}^\dagger) \quad (10)$$

holds. We observe that the values for $S_{\alpha Km}$ are not the characters of the irreducible

Table 1. The factor $S_{\alpha Km}$ in equation (9).

K	Symmetry of $\psi_m^{(K)}$	$\alpha \in C_{2h}$			
		E	C_2	I	σ
L	A_u	1	-1	1	-1
	B_u	1	1	1	1
T	A_u	1	1	-1	-1
	B_u	1	-1	-1	1
S	A_g	1	-1	1	-1
	B_g	1	1	1	1

representations of C_{2h} which are spanned by the states ψ_m . The reason for this is that the single-molecule mean field ground states do not all have A_g symmetry.

The excitation operators of equation (6) play the same role in the RPA formalism as the displacement coordinates in the harmonic approximation. In particular their transformation properties are the same.

6. The transformation properties of the RPA matrix and its eigenvectors

We can now determine the transformation properties of the RPA matrix. Let us first write the Hamiltonian in second-quantised form

$$\hat{H} = \langle \Psi_0 | \hat{H} | \Psi_0 \rangle + \sum_q \left(\sum_{KK'} \sum_{IJ} \sum_{mn} {}^q V_{IJ}^{KK'}(m, n) \hat{a}_{qKIm}^\dagger \hat{a}_{qK'Jn} \right. \\ \left. + \sum_{\substack{KK' \\ K \leq K'}} \sum_{IJ} \sum_{mn} {}^q W_{IJ}^{KK'}(m, n) \hat{a}_{qKIm}^\dagger \hat{a}_{-qK'Jn}^\dagger + \text{HC} \right). \quad (11)$$

This Hamiltonian must be invariant under $P_A 2/m$. Using equation (9a) we find for the coefficients

$${}^{\alpha q} V_{IJ}^{KK'}(m, n) = {}^q V_{IJ}^{KK'}(m, n) S_{\alpha Km} S_{\alpha K'n} \quad (12a)$$

$${}^{\alpha q} W_{IJ}^{KK'}(m, n) = {}^q W_{IJ}^{KK'}(m, n) S_{\alpha Km} S_{\alpha K'n} \quad (12b)$$

and using equation (9a) we find

$$-{}^{\alpha q} V_{I_c J_c}^{KK'}(m, n)^* = {}^q V_{IJ}^{KK'}(m, n) S_{\alpha Km} S_{\alpha K'n} \quad (13a)$$

$$-{}^{\alpha q} W_{I_c J_c}^{KK'}(m, n)^* = {}^q W_{IJ}^{KK'}(m, n) S_{\alpha Km} S_{\alpha K'n}. \quad (13b)$$

The RPA equation is an eigenvalue equation of the RPA matrix $\mathbf{R}(q)$, which can be obtained by substituting

$$\hat{\Xi}_q^\chi = \sum_{KIm} (c_{qKIm}^{(\chi+)} \hat{a}_{qKIm}^\dagger + c_{qKIm}^{(\chi-)} \hat{a}_{-qKIm}) \quad (14)$$

into equation (1) [13, 15]. Defining

$$\tilde{\Gamma} \left(q; \begin{matrix} \{\alpha | \mathbf{R}\} \\ \{\alpha \theta | \mathbf{R} + \mathbf{r}(\theta)\} \end{matrix} \right) \equiv \begin{pmatrix} \Gamma \left(q; \begin{matrix} \{\alpha | \mathbf{R}\} \\ \{\alpha \theta | \mathbf{R} + \mathbf{r}(\theta)\} \end{matrix} \right) & 0 \\ 0 & \Gamma \left(q; \begin{matrix} \{\alpha | \mathbf{R}\} \\ \{\alpha \theta | \mathbf{R} + \mathbf{r}(\theta)\} \end{matrix} \right) \end{pmatrix} \quad (15)$$

with

$$\Gamma(q; \{\alpha | \mathbf{R}\})_{KIm, K'Jn} = \exp(-i\mathbf{q} \cdot \mathbf{R}) S_{\alpha Km} \delta_{KK'} \delta_{IJ} \delta_{mn} \quad (16a)$$

$$\Gamma(q; \{\alpha | \mathbf{R} + \mathbf{r}(\theta)\})_{KIm, K'Jn} = \exp[-i\mathbf{q} \cdot (\mathbf{R} + \mathbf{r}(\theta))] S_{\alpha Km} \delta_{KK'} \delta_{IJ_c} \delta_{mn} \quad (16b)$$

we can derive using (12) and (13)

$$\tilde{\Gamma}(q; \{\alpha | \mathbf{R}\}) \mathbf{R}(q) \tilde{\Gamma}(q; \{\alpha | \mathbf{R}\})^\dagger = \mathbf{R}(\alpha q) \quad (17a)$$

$$[\tilde{\Gamma}(q; \{\alpha \theta | \mathbf{R} + \mathbf{r}(\theta)\}) K_0] \mathbf{R}(q) [\tilde{\Gamma}(q; \{\alpha \theta | \mathbf{R} + \mathbf{r}(\theta)\}) K_0]^\dagger = \mathbf{R}(-\alpha q). \quad (17b)$$

Equation (17) shows that the eigenvectors for the RPA matrix $\mathbf{R}(q)$ yield bases for

the irreducible co-representations of the group of $\mathbf{q}$. Bases for the irreducible co-representations of P_{A2}/m are obtained by collecting those solutions of the RPA equations that correspond with the different wavevectors of a star.

If we place the coefficients $c_{\mathbf{q}Klm}^{(\chi^\pm)}$ of equation (14) in a column vector $\mathbf{c}_{\mathbf{q}}$ we find using equation (9) that

$$\mathbf{c}_{\mathbf{q}} \xrightarrow{\{\alpha|\mathbf{R}\}} \hat{\Gamma}(\mathbf{q}; \{\alpha|\mathbf{R}\})\mathbf{c}_{\mathbf{q}} \quad (18a)$$

$$\mathbf{c}_{\mathbf{q}} \xrightarrow{\{\alpha\theta|\mathbf{R}+\mathbf{r}(\theta)\}} \hat{\Gamma}(\mathbf{q}; \{\alpha\theta|\mathbf{R}+\mathbf{r}(\theta)\})K_0\mathbf{c}_{\mathbf{q}} \quad (18b)$$

if $\alpha\mathbf{q} = \mathbf{q} + \mathbf{Q}$ and $\alpha\mathbf{q} = -\mathbf{q} + \mathbf{Q}$, respectively, where $\mathbf{Q}$ is a primitive translation of the reciprocal lattice. Actually these transformations led us to equations (15)–(17). If $\mathbf{q}$ lies on the zone boundary equation (16b) is not necessarily the correct expression for $\hat{\Gamma}(\mathbf{q}; \{\alpha\theta|\mathbf{R}+\mathbf{r}(\theta)\})$. However, this is really immaterial. In what follows we will only need to know the irreducible representations of non-magnetic space groups.

7. The symmetries of the lattice vibrations/spin waves

We can now determine the symmetries of the lattice vibrations/spin waves for every wavevector $\mathbf{q}$. There are essentially three steps. First, we have to determine the group of $\mathbf{q}$. Secondly, we have to determine the irreducible representations with wavevector $\mathbf{q}$ of the subgroup of this subgroup that consists of all non-magnetic elements. Thirdly, we have to check whether the magnetic elements yield extra degeneracies.

The subgroup of the second step is a symmorphic space group. The irreducible representations are found by looking up the irreducible representations of the point group of the elements for which $\alpha\mathbf{q} = \mathbf{q} + \mathbf{Q}$ holds and then multiply with $\exp(-i\mathbf{q} \cdot \mathbf{R})$. The irreducible co-representations that give the symmetries of the lattice vibrations/spin waves are determined in the third step.

We know from group theory that the irreducible co-representations of a magnetic group are characterised by the irreducible representations of the subgroup of all non-magnetic elements that they subduce [22]. There are three possibilities. If the irreducible co-representation is of the first kind it subduces one irreducible representation; if it is of the second kind it subduces two equivalent irreducible representations and if it is of the third kind it subduces two non-equivalent irreducible representations. There is a doubling of the degeneracy if the irreducible co-representation is of the second or third kind. Fortunately, the following simple character test enables us to classify the irreducible co-representation.

$$\sum_{\substack{\alpha, \mathbf{R} \\ \alpha\mathbf{q} = -\mathbf{q} + \mathbf{Q}}} \chi(\alpha\theta|\mathbf{R}+\mathbf{r}(\theta))^2 = M, -M, \text{ or } 0 \quad (19)$$

where M is the number of terms in the summation and χ is the character of an irreducible representation. The different results of the summation hold for an irreducible co-representation of the first, second and third kind, respectively. We note that we only need to know the irreducible representations of a non-magnetic space group.

As the third step we thus take all irreducible representations that we have found in the second step and apply the character test above. The result indicates from what kind of irreducible co-representation the irreducible representation is subduced. The final results for the irreducible co-representations of the groups of $\mathbf{q}$ are shown in table 2. The

Table 2. The symmetry of the lattice vibrations/spin waves (see [21] for the notation of the irreducible co-representations).

Point in the Brillouin zone	$\{\alpha \alpha q = q + Q\}$	Symmetry of the single-molecule mean field state that is excited					
		Librations		Translations		Spin	
		A_u	B_u	A_u	B_u	A_g	B_g
Γ	C_{2h}	Γ_4	Γ_1	Γ_2	Γ_3	Γ_4	Γ_1
Λ	C_2	Λ_2	Λ_1	Λ_1	Λ_2	Λ_2	Λ_1
A	C_{2h}	A_2	A_1	A_2	A_1	A_2	A_1
B	C_{2h}	B_4	B_1	B_2	B_3	B_4	B_1
C	C_{2h}	C_1	C_1	C_2	C_2	C_1	C_1
D	C_{2h}	D_2	D_1	D_1	D_2	D_2	D_1
E	C_{2h}	E_1	E_1	E_2	E_2	E_1	E_1
Y	C_{2h}	Y_2	Y_1	Y_2	Y_1	Y_2	Y_1
Z	C_{2h}	Z_2	Z_1	Z_1	Z_2	Z_2	Z_1
U	C_2	U_1	U_1	U_1	U_1	U_1	U_1
V	C_2	V_2	V_1	V_1	V_2	V_2	V_1
W	C_2	W_1	W_1	W_1	W_1	W_1	W_1
		Librons		Phonons		Magnons	

points in the plane through C, D, E, and Z, and on the lines through Y and C, and A and E have only irreducible co-representations of the third kind. All other irreducible co-representations are of the first kind. Those of the first kind are one-dimensional and those of the third kind are two-dimensional. The symmetry assignments of the phonons and librons are the same as we would have obtained when working with the harmonic approximation and two molecules per unit cell [17]. We can visualise the irreducible co-representations of the third kind as follows. Imagine that only the molecules of one sublattice participate in an excitation. The excitation has a certain point group symmetry. The operation $\{\theta|r(\theta)\}$ translates the excitation to the other sublattice, thereby changing its symmetry (see figure 3 for two examples).

8. Selection rules for infrared and Raman spectroscopy

A practical application of the group theoretical analysis is the determination of the selection rules for infrared and Raman spectroscopy. According to the symmetry analysis of α -oxygen based on the harmonic approximation, two libron modes, one with A_g and one the B_g symmetry, should be Raman active. No modes should be infrared active [16]. This analysis, however, does not apply to magnons.

If we restrict ourselves to one-phonon, -libron, and -magnon modes then only optical ($q = 0$) modes can be infrared or Raman active [25]. The dominant interaction with radiation fields for infrared adsorption is normally the electric dipole interaction. Other interactions that are linear in the field strength are the magnetic dipole and the electric quadrupole interactions. We can neglect the last interaction because of the long wavelength of the infrared radiation [26]. The electric dipole operator has one component with A_u and two components with B_u symmetry. The optical phonons thus may be infrared active by coupling to the electric dipole field (the modes Γ_2 and Γ_3 transform

Figure 3. Signs of the coefficients in the basis vectors of the irreducible co-representations Y_1 of the Y point (a), and C_1 of the C point (b). The basis vectors are expressed in terms of the excitation operators of equation (6). The symmetries of the basis vectors with respect to C_{2h} are given to show the sticking of different irreducible representations of $C2/m$. (Only operators with A_g symmetry are considered.)

under C_{2h} as A_u and B_u , respectively). The magnetic dipole operator has one component with A_g and two components with B_g symmetry. The optical librons and magnons thus may be infrared active by coupling to the magnetic dipole field (the modes Γ_1 and Γ_4 transform under C_{2h} as A_g and B_g , respectively). The intensity in Raman scattering is quadratic in the electric and magnetic dipole operators [27]. The relevant entities are the electric polarisability, the magnetic susceptibility and a mixed susceptibility term which is a combination of an electric and a magnetic transition dipole. The operators pertaining to the former two can be decomposed into parts having A_g and B_g symmetry, and the operators pertaining to the mixed term into parts having A_u and B_u symmetry. All modes thus may be Raman active.

From this analysis it seems that more modes are infrared or Raman active than are actually observed experimentally. Optical phonons are observed neither in infrared nor in Raman spectra. The reason for this is as follows. In table 2 we can observe that the

optical phonons do not couple to the magnons. This means that they can be labelled according to the non-magnetic space group $C2/m$ of α -O₂. Their wavevector then will lie on the boundary of the Brillouin zone corresponding to the structural unit cell. In other words, the excitations on nearest neighbours for the optical phonons are out of phase, and consequently the optical phonons will be neither infrared nor Raman active.

As the coupling between the librations and the magnons is small [13], this holds also for half of the librations. The other two libration modes, which are Raman active, are not observed in infrared spectra because the magnetic transition dipole moments are probably too small. The $q = 0$ magnons are observed in infrared as well as in Raman spectra. As has been pointed out above, they are infrared active because they couple to the magnetic dipole field. The magnetic transition dipole moments for the magnons are large. Therefore, it is probably the magnetic susceptibility that leads to the observation of magnon excitations in Raman experiments.

9. Conclusions

We have derived the symmetries of the lattice vibrations/spin waves of α -oxygen by looking at the solutions of the RPA equations. Because of the non-zero electronic spin momentum of the O₂ molecules, a magnetic space group is required to describe the symmetry of α -O₂. The symmetry group of the Hamiltonian consequently contains anti-unitary operators. This in turn leads to the use of co-representations.

The results differ in several aspects from those which are obtained when neglecting the magnetic structure of α -O₂. Except for the Γ , C and E point in the Brillouin zone, the magnons couple to the librations and the phonons. For the Γ , C and E point the magnons only couple to the librations. At the boundary of the Brillouin zone the lattice vibrations/spin waves may become degenerate due to the time reversal symmetry. The results as shown in table 2 confirm the results of the numerical calculations we have made [13]. There are some slight errors in the dispersion curves in figure 3 of [13]. Some forbidden crossings were not detected due to the smallness of the coupling between the magnons and the phonons/librations.

The selection rules derived from the group theoretical analysis for infrared and Raman spectroscopy agree with experiment. The magnon peaks in infrared spectra can be explained by the coupling of the magnons to the infrared radiation via the magnetic dipole interaction. Inspection of the results of the numerical calculation [13] shows that the magnons at 6.4 and 27.3 cm⁻¹ have B_g symmetry. This means that no adsorption should be observed in an experiment with a single crystal and polarised infrared radiation with the magnetic dipole field parallel to the monoclinic axis. On the other hand, the libration at 42 cm⁻¹ [28] may be observed in this experiment, depending on the strength of the libration-magnon coupling. The libration at 72 cm⁻¹ [28] may be observed if the infrared radiation is polarised with the magnetic dipole field perpendicular to the monoclinic axis. It would be interesting to perform these experiments.

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