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Magnetic-Structure-Factor Calculations in Paramagnetic γ-Oxygen

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We introduce a simple model to interpret the results of a polarized-neutron study of paramagnetic solid $\gamma-O_2$ carried out at 46 °K. The model is based on the assumption of a rotational motion of the molecules around the lattice sites, and agreement with the experimental results presented in the preceding paper is quite satisfactory. The function $w(\hat{a})$ which is used to describe the motion of the molecule as a whole may depend strongly upon temperature. Its qualitative behavior is discussed particularly in the $T=0$ °K and $T=\infty$ limits for an ideal O_2 crystal having the paramagnetic γ structure over the whole temperature range.

I. INTRODUCTION

In the preceding paper[1] (referred to as I), the results of a polarized-neutron diffraction study of paramagnetic γ-oxygen are described. The main interest for this lies in the fact that no detailed studies of materials containing unpaired p electrons have previously been made, and also that in oxygen these electrons occupy molecular rather than atomic orbitals.

At atmospheric pressure three modifications of solid oxygen are known, two paramagnetic and one antiferromagnetic.[2-6] The cubic γ phase is stable in the temperature range 54.4–43.8 °K, the rhombohedral β phase in the range 43.8–23.9 °K and the monoclinic α phase from 23.9 down to 4.2 °K. The latter is antiferromagnetic. Previous x-ray studies have shown the space group of γ-O_2 to be $Pm3n$, with eight molecules per unit cell, centered at the $2(a)$ sites at $(0, 0, 0)$ and the $6(d)$ sites at $(0, \frac{1}{4}, \frac{1}{2})$ with point symmetries $m3$ and $\bar{4}2m$, respectively.[7-9] These studies revealed that the electron density has an approximately spherical distribution around the $2(a)$ sites, but an oblate spherical distribution around the $6(d)$ sites (Fig. 1). This is readily deduced from the fact that some reflections are observed which would be forbidden if there were perfect spherical disorder. The x-ray studies indicated that the disorder could be reasonably well described on the basis of free spherical rotation in the $2(a)$ sites and statistical disorder about the $6(d)$ sites. A more definitive result was given by the neutron study in which structure refinement yielded excellent agreement with a model in which there is statistical disorder in $16(i)$ and $24(k)$ positions together with quite large and anisotropic temperature factors which can be interpreted in terms of molecular librations.

In the present paper we develop a simplified model which incorporates the essential features of the crystal structure and allows a satisfactory explanation of the observed magnetic data without requiring an explicit knowledge of the thermal motion or positional parameters as a function of temperature. Numerical calculations of the magnetic structure factors have been made on the basis of this model with the Gaussian Meckler wave function.[10]

Other phases of solid O_2 have also been studied. The crystal and magnetic structure of the α phase have been determined by Alikhanov and coworkers.[5] The form-factor values for the two magnetic reflections observed in this phase are in reasonable agreement with theory.[11]

II. THEORY

As is well known, the magnetic scattering cross section for polarized neutrons can be written in terms of the structure factor according to the following formula:

$$\frac{d\sigma}{d\Omega} \propto \hat{p} \cdot \left[\vec{F}_M(\vec{k}) - \hat{k}(\vec{F}_M(\vec{k}) \cdot \hat{k})\right] , \tag{1}$$

where $\hat{p}$ is a unit vector in the direction of the neutron polarization, $\vec{k}$ is the momentum transfer, and $\vec{F}_M(\vec{k})$ is the magnetic structure factor. From a knowledge of the cross section it is possible to determine the structure factors. Our purpose in this paper is to calculate and compare these with the experimental values.

If we assume that the electron wave function is essentially the same as that of the free molecule, the structure factor can be written as a sum over all the molecules in the unit cell:

$$\vec{F}_M(\vec{k}) = \sum_j e^{i\vec{k}\cdot\vec{R}_j} \mu_j \vec{f}_j(\vec{k})\, e^{-W_j(\vec{k},T)} , \tag{2}$$

where $\vec{R}_j$ is the position vector of the molecular

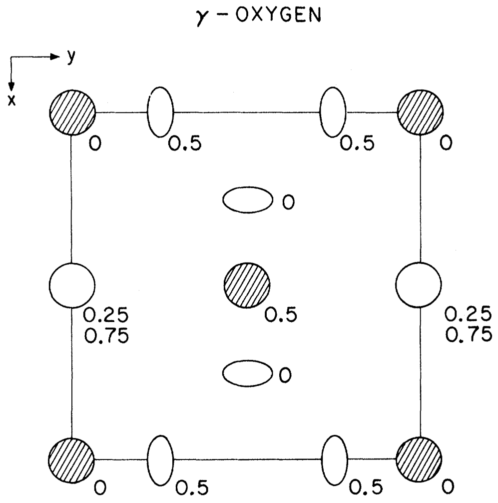

FIG. 1. Projection of the unit cell of γ-O_2 on (001) showing the rotational symmetry of each molecule.

center, $\vec{f}_j(\vec{k})$ is the form factor of the jth molecule, μ_j is the corresponding magnetic moment, and $e^{-W_j(\vec{k},T)}$ the Debye-Waller factor.

As has been shown by Trammel,[12] there are in general both spin and orbital contributions to the magnetic scattering. In the case of oxygen it is possible to see by simple symmetry arguments that the orbital scattering vanishes, and that only the z component of the spin form factor differs from zero.[13] We will accordingly use the symbols $F(\vec{k})$ and $f_j(\vec{k})$ to denote the z component of the structure factor and the form factor of the jth molecule, respectively.

The form factor is the Fourier transform of the spin density, and in order to interpret the experimental data we observe that if $\hat{a}$ is the direction of the molecular axis the spin density at a point $\vec{r}$ will depend on both $\vec{r}$ and $\hat{a}$. Of course, the molecules in the solid will not all have a common fixed direction, and we assume that each molecule has a probability $w(\hat{a})$ of pointing parallel to $\hat{a}$. This can be regarded in two ways; either each molecule is rotating with a probability $w(\hat{a})$ of being found in the $\hat{a}$ direction, or alternatively each molecule has a different fixed direction and $w(\hat{a})$ is proportional to the number of molecules pointing paralled to $\hat{a}$.

An analogous interpretation can be given for gaseous O_2. In this case all the directions are equally probable and $w(\hat{a})$ is a constant. In solid γ-O_2 we have to consider two different functions $w(\hat{a})$ which must be compatible with the point symmetry $m3$ and $\bar{4}2m$ of the $2(a)$ and $6(d)$ sites, respectively. For the sake of simplicity, we assume a spherical and ellipsoidal distribution, and we accordingly require $w(\hat{a})$ to be constant for the $2(a)$ sites and to have spheroidal symmetry at the $6(d)$ sites.

Comparison with experiment will be made in terms of the averaged density

$$\rho(\vec{r}) = \langle \rho(\vec{r}, \hat{a}) \rangle = \int w(\hat{a})\, \rho(\vec{r}, \hat{a})\, d\hat{a} \quad , \tag{3}$$

or alternatively by the averaged form factor

$$f(\vec{k}) = \int e^{i\vec{k}\cdot\vec{r}} \rho(\vec{r}) d\vec{r} = \int \int e^{i\vec{k}\cdot\vec{r}}\, w(\hat{a}) \rho(\vec{r}, \hat{a})\, d\vec{r}\, d\hat{a}$$

$$= \int f(\vec{k}, \hat{a}) w(\hat{a}) d\hat{a} \quad . \tag{4}$$

In this section we make an analysis in spherical harmonics of the spin density and the form factor. We will show that once the spherical harmonic components of $w(\hat{a})$ and $\rho(\vec{r}, \hat{a})$ are known, the form factor can easily be calculated and the numerical work is reduced to the computation of a few integrals involving Bessel functions.

Let us first develop the spin density and the probability function in spherical harmonics,

$$\begin{aligned} \rho(\vec{r}, \hat{a}) &= \sum_{l m} \rho_{l m}(\vec{r})\, Y_{l m}(\hat{a}) \quad , \\ w(\hat{a}) &= \sum_{l m} w_{l m}\, Y^{*}_{l m}(\hat{a}) \quad , \end{aligned} \tag{5}$$

where

$$\rho_{l m}(\vec{r}) = \int \rho(\vec{r}\, , \hat{a})\, Y^{*}_{l m}(\hat{a})\, d\hat{a} \quad ,$$

$$w_{l m} = \int w(\hat{a})\, Y_{l m}(\hat{a})\, d\hat{a} \quad .$$

In order to derive the last result, use has been made of the orthogonality properties

$$\begin{aligned} &\int Y^{*}_{l m}(\hat{a})\, Y_{l' m'}(\hat{a})\, d\hat{a} = \delta_{l, l'}\, \delta_{m, m'} \, , \\ &Y^{*}_{l m}(\hat{a}) = (-1)^m\, Y_{l m}(\hat{a}) \quad . \end{aligned} \tag{6}$$

It is easy to calculate

$$\rho(\vec{r}) = \sum_{l m} w_{l m} \rho_{l m}(\vec{r}) \quad . \tag{7}$$

Similarly we obtain

$$f(\vec{k}) = \sum_{l m} w_{l m} A_{l m}(\vec{k}) \quad , \tag{8}$$

where

$$A_{l m}(\vec{k}) = \int f(\vec{k}\, , \hat{a})\, Y^{*}_{l m}(\hat{a})\, d\hat{a} = \int e^{i\vec{k}\cdot\vec{r}} \rho_{l m}(\vec{r}) d\vec{r} \quad . \tag{9}$$

In the last expression we use the following expansion[14]:

$$e^{i\vec{k}\cdot\vec{r}} = 4\pi \sum_{l' m'} i^{l'}\, j_{l'}(kr)\, Y^{*}_{l' m'}(\hat{r})\, Y_{l' m'}(\hat{k}) \quad . \tag{10}$$

It is then easy to show that

$$\begin{aligned} A_{l m}(\vec{k}) &= 4\pi \sum_{l' m'} i^{l'}\, Y_{l' m'}(\hat{k}) \int j_{l'}(kr)\, \rho_{l m}(\vec{r}) \\ &\qquad Y^{*}_{l' m'}(\hat{r}) r^2\, dr\, d\hat{r} \\ &= 4\pi \sum_{l' m'} i^{l'}\, Y_{l' m'}(\hat{k}) \int j_{l'}(kr)\, \rho_{l m; l' m'}(r)\, r^2\, dr \quad , \end{aligned} \tag{11}$$

where

$$\rho_{lm;\,l'm'}(r)=\int \rho_{lm}(r,\hat{r})\,Y^{*}_{l'm'}(\hat{r})\,d\hat{r}\ .$$

The problem is now reduced to the calculation of the functions $\rho_{lm;l'm'}(r)$ and of a radial integral involving spherical Bessel functions.

A great simplification is introduced by the use of a symmetry property of $\rho(\vec{r},\hat{a})$. Let us consider two identical molecules pointing in the direction $\hat{a}$ and $\mathcal{R}\hat{a}$, where $\mathcal{R}$ is a rotation operator. It is obvious that the spin density of the first molecule calculated at a point $\vec{r}$ will be equal to that of second molecule at a point $\vec{r}\,'=\mathcal{R}\vec{r}$ (with $|\vec{r}\,'|=|\vec{r}|$):

$$\rho(\vec{r},\hat{a})=\rho(\mathcal{R}\vec{r},\ \mathcal{R}\hat{a})\ . \tag{12}$$

In particular if $\hat{a}=\mathcal{R}^{-1}(\hat{a})\hat{z}$ (where $\hat{z}$ is the unit vector parallel to the z axis of the reference frame) we will have

$$\rho(\vec{r},\hat{a})=\rho(\bar{\mathcal{R}}(\hat{a})\vec{r},\hat{z})=\rho(\vec{r}\,',\hat{z})\ . \tag{13}$$

We expand both members in spherical harmonics and use the addition theorem for them:

$$\begin{aligned}\rho(\vec{r},\hat{a})&=\sum_{lm'}\rho_{lm'}(\vec{r})\,Y_{lm'}(\hat{a})=\rho(\vec{r}\,',\hat{z})\\&=\sum_{lm}\rho_{lm}(\vec{r},\hat{z})\,Y_{m}(\hat{r}\,')\\&=\sum_{mm'}\rho_{lm}(r,z)\,D^{l}_{0m'}(\hat{a})\,D^{l}_{m'm}(\hat{r})[(2l+1)/4\pi]^{1/2},\end{aligned} \tag{14}$$

with standard notation[15] for the D functions. $\rho_{lm}(\vec{r})$ has been previously defined, and

$$\rho_{lm}(r,\hat{z})=\int\rho(\vec{r}\,',\hat{z})\,Y^{*}_{lm}(\hat{r}\,')\,d\hat{r}\ .$$

The last equality in formula (14) has been obtained by using an application of the addition theorem for spherical harmonics.[15] By comparing the two expansions we obtain

$$\rho_{lm}(\vec{r})=\sum_{m'}\bar{\rho}_{lm'}(r,\hat{z})\,D^{l}_{mm'}(\hat{r})[(2l+1)/4\pi]^{1/2}\ . \tag{15}$$

The result (15) is important because it shows that we do not need to know the spin density $\rho(\vec{r},\hat{a})$ for any $\hat{a}$ direction. It is sufficient if we know it just for a molecule whose axis points in the $\hat{z}$ direction.

Further simplification is obtained if we consider the $m=0$ component

$$\rho_{l0}(\vec{r})=\sum_{m}\rho_{lm}(r,\hat{z})\,Y^{*}_{lm}(\hat{r})=\rho_{l0}(r,\hat{z})\,Y_{l0}(\hat{r})\ . \tag{16}$$

The last equality follows from the symmetry of the molecule with respect to its axis (which coincides with the z axis of the reference frame).

If we analyze the form factor in terms of spherical harmonics, we may easily show that

$$A\rho_{0}(\vec{k})=4\pi i^{l}\,Y_{l0}(\hat{k})\int j_{l}(kr)\,\rho_{l0}(r,\hat{z})\,r^{2}dr\ . \tag{17}$$

III. TEMPERATURE DEPENDENCE

We will compare our theory with the results of a neutron experiment on γ-O_2 performed at 46 °K. An obvious question is how the temperature enters into our theory and how this affects the structure factors. The effect of the molecular motion is contained in the Debye–Waller factors of formula (2). If we neglect the vibrorotational motion of the molecule, there are only two sources of the possible dependence of the neutron scattering cross section on temperature: the contribution from the excited states of the molecule and its rotational motion around the site.

Let us examine the two sources separately. We exclude first the rotational motion by considering a crystal with atoms (not molecules) fixed at the lattice sites. The elastic-magnetic-scattering cross section for unpolarized neutrons[16] is

$$\frac{d\sigma}{d}=\left(\frac{\gamma e^{2}}{mc^{2}}\right)^{2}\sum_{\lambda\lambda'}P_{\lambda}\,\langle\lambda\,|[\vec{Q}-\hat{k}(\hat{k}\cdot\vec{Q})]^{\dagger}|\lambda'\rangle\times\langle\lambda'|\vec{Q}-\hat{k}(\hat{k}\cdot\vec{Q})|\lambda\rangle\ , \tag{18}$$

where the sum is over all (ground and excited) states of the atom. In the absence of orbital scattering

$$\vec{Q}=\sum_{i}e^{i\vec{k}\cdot\vec{r}_{i}}\vec{s}_{i}\ , \tag{19}$$

$\vec{r}_i$ and $\vec{s}_i$ being the position and the spin of ith electron. P_λ is the probability of the state $|\lambda\rangle$ being occupied, which is given by the Boltzmann factor. Then it is apparent that only the ground state has a high probability of being occupied and also that the transition probability $P_g\,\langle\lambda'|\,Q|g\rangle$ is negligible when $|\lambda'\rangle$ differs from $|g\rangle$. Then only the form factor $\langle g|\vec{Q}|g\rangle$ contributes significantly to the scattering. The same applies to the molecule, pointing in a fixed direction. Hence we can use the same $\rho(\vec{r},\hat{a})$ at any temperature.

So far we have only considered the motion of the electrons in a fixed molecule. The motion of the molecule as a whole is described by $w(\hat{a})$. Since the motion is essentially thermal, particularly so in a scheme such as ours in which interactions between the molecules are disregarded, it is clear that w depends upon the temperature T as well as $\hat{a}$.

We will now examine the qualitative behavior of $w(T,\hat{a})$ as a function of temperature. We recall that $w(\hat{a})$ is the probability that the axis points between $\hat{a}$ and $\hat{a}+d\hat{a}$. It is consequently related to the inverse of the time the molecular axis spends within such a solid angle. This time depends on the rotational (and eventually vibrational and vibrorotational) energy of the molecule in the direction $\hat{a}$. If f is the degree of freedom, the mean value of the energy in $\hat{a}$ space is approximately $E_{\text{av}}\sim\frac{1}{2}fk_{B}T$. The molecules which have this energy for any $\hat{a}$ direction have spherical rotational motion: $w(T,\hat{a})=1/4\pi$ independent of temperature, while for the aspherical molecules $E(T,\hat{a})=E_{\text{av}}(T)+\Delta E(T,\hat{a})$.

Hence w depends effectively on T and $\hat{a}$. The asphericity is determined by the parameter η:

$$\eta = \frac{1}{4\pi}\int \frac{\Delta E(\hat{a})}{E(T, a)}\, d\hat{a} = \frac{1}{4\pi}\int \frac{\Delta E(\hat{a})}{\frac{1}{2} f k_B T + \Delta E(\hat{a})}\, da$$

and is therefore an order parameter equal to 1 for $T = 0$ °K and 0 for $T \to \infty$. This has the advantage that it provides a convenient way of allowing for thermal motion without the necessity of having to know the thermal and positional parameters as a function of temperature. We therefore expect that the ellipsoidal motion of these molecules at the temperature of the experiment should become spherical at the upper limit. Conversely their asphericity should be much stronger at $T = 0$ °K.

This is of course only a qualitative discussion. Our purpose in fact is not to calculate the temperature dependence of the function $w(\hat{a})$ from first principles, but simply to show that such dependence can be built phenomenologically in it by fitting the parameters w_{lm} with experiments done at different temperatures. In particular, on the basis of the above arguments we expect that in the limit $T \to \infty$, $w_{lm} = 0$ for $l, m \neq 0$; whereas w_{00} is temperature independent, being given at any temperature by the normalization condition for $w(\hat{Q})$.

The vibrational effect is contained in the Debye-Waller factor, which is very difficult to calculate from first principles. In order to interpret the γ-O_2 experiment performed at 46 °K, we can assume either that w_{lm} depends phenomenologically on temperature, and put some model-dependent Debye-Waller factor in formula (2), or equivalently we can correct the experimental data by the same Debye-Waller factor and set it equal to unity in formula (2). We have followed the second procedure and applied it to the two models described in paper I.

IV. APPLICATION TO γ-O_2

In the last section we showed how it is possible to calculate the effective form factor by the use of a development in spherical harmonics once the spin density $\rho(r, \hat{z})$ and the probability function $w(\hat{a})$ are known.

We assume that $w(\hat{a})$ has either spherical or ellipsoidal symmetry according to which sites are occupied. Hence

$$\begin{aligned} &w_{lm} = 0 \text{ if } l,\ m \neq 0 \text{ for the } a \text{ sites },\\ &w_{lm} = 0 \text{ if } m \neq 0 \text{ for the } d \text{ sites }. \end{aligned} \qquad (20)$$

This allows us to use the simpler formulas (16) and (17).

We assume the Meckler[10] electronic ground state for the O_2 molecule and the spin density given by Kleiner[13] in terms of the Meckler atomic orbitals

$$\rho(r, \hat{z}) = A(|\phi|^2 + |\phi'|^2) + 2B\phi^*\phi' , \qquad (21)$$

where ϕ and ϕ' are the atomic $2p^{\pm}$ orbitals calculated at $-\frac{1}{2}R$ and $\frac{1}{2}R$ (R being the internuclear distance with $\vec{R} = R\hat{z}$), and B is taken equal to $-A$.

The $2p^{\pm}$ orbitals are taken to have a Gaussian form

$$2p^{\pm} = (x \pm iy)\, e^{-br^2} . \qquad (22)$$

This is the choice which has been made for the gaseous molecule,[10] and we assume that the wave function does not change very much in the solid. The Gaussian form has been chosen because the analytical calculation is simplified and the numerical computation is accordingly reduced. More realistic wave functions would involve linear combinations of Gaussians with different parameters. We will see, however, that a good fit with the experimental data can be obtained in terms of a single Gaussian.

From the definitions of ϕ and ϕ' we obtain

$$\rho(r, \hat{z}) \propto r^2 e^{-2br^2}\left[Y_{00}(\hat{r}) - \tfrac{1}{5} Y_{20}(\hat{r})\right] \times\left[\left(e^{-2b\vec{r}\cdot\vec{R}} + e^{2b\vec{r}\cdot\vec{R}}\right) + 2B\right] . \qquad (23)$$

We generalize Eq. (10) to exponentials with real argument. If $\vec{R}$ is parallel to $\hat{z}$ the expansion is

$$e^{-2brR\hat{r}\cdot\hat{z}} = 4\pi \sum_l \left[(2l+1)/4\pi\right]^{1/2} i^l j_l(i2brR)\, Y_{l0}(\hat{r}) . \qquad (24)$$

After straightforward algebra involving the use of the addition theorem for spherical harmonics we obtain

$$\rho_{l''0}(r, \hat{z}) \propto r^2 e^{-2br^2}\left\{ A\sum_l \left[\delta_{l''l} - (2l+1)^{1/2}(2l''+1)^{1/2}\begin{pmatrix} 2 & l & l'' \\ 0 & 0 & 0 \end{pmatrix}^2 (2l+1)^{1/2} \times\left[j_l(i2brR) + j_l(-i2brR)\right]\right] + 2B\left(\delta_{l''0} - \frac{1}{\sqrt{5}}\,\delta_{l''2}\right)\right\} . \qquad (25)$$

A Fourier transform yields the expression

$$A_{l''0}(\vec{k}) \propto 4\pi i^{l''} Y_{l''0}(\hat{k})\left\{ A\sum_l \left[\delta_{ll''} - (2l+1)^{1/2}(2l''+1)^{1/2}\begin{pmatrix} 2 & l & l'' \\ 0 & 0 & 0 \end{pmatrix}^{1/2} (2l+1)^{1/2}\int j_{l''}(kr)\left[j_l(i2brR)\right.\right.\right.$$

$$+j_l\,(-i2brR)]\,r^4 e^{-2br^2}\,dr\Big] + 2B\left(\delta_{l''0} - \frac{1}{\sqrt{5}}\,\delta_{l''2}\right)\int j_{l''}(kr)\,r^4 e^{-2br^2}\,dr\Big\} \ . \qquad (26)$$

The constant factor common to all the components A_{l0} can be determined if the form factor is taken to be unity at $k=0$. If we put $A_{l0}(k)=f_{l0}(k)\,Y_{l0}(\hat{k})$ we can write

$$f(\vec{k}) = \sum w_{l0} f_{l0}(k)\, Y_{l0}(\hat{k}) \ . \qquad (27)$$

The functions $f_{l0}(k)$ play the same role as the $\langle j_l \rangle$ functions in the theory of transition metals,[16–18] and the ones which are significant in the present problem are plotted in Fig. 2.

V. CALCULATION OF MAGNETIC STRUCTURE FACTORS AND COMPARISON WITH EXPERIMENTAL VALUES

We are now able to calculate the form factor in the case of spherical and ellipsoidal symmetry when the asymmetry axis of the ellipsoid is directed along the z crystallographic axis. This happens in γ-O_2 for the sites $(0, 0, 0)$ and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ with spherical symmetry and the sites $(\frac{1}{2}, 0, \frac{1}{4})$ and $(\frac{1}{2}, 0, \frac{3}{4})$ with ellipsoidal symmetry.

In the first case we have simply $f(k)=w_{00}A_{00}(k)$; in the second case

$$f(\vec{k}) = \sum_l w_{l0} A_{l0}(\vec{k})$$
$$\simeq w_{00}A_{00}(k) + w_{20}A_{20}(\vec{k}) + w_{40}A_{40}(\vec{k}) \ .$$

In the other $6(d)$ positions $\pm(\frac{1}{4}, \frac{1}{2}\ 0)$ and $\pm(0, \frac{1}{4}, \frac{1}{2})$ the form factors also have ellipsoidal symmetry with axes pointing in the x and y directions, respectively, and can be deduced by application of the proper rotations.

Let us call $w^i(\hat{a})$ and $\rho^i(\vec{r})$ the probability and the mean-spin-density function when the major axis of the ellipsoid points in the ith direction (i stands for x, y, z). Then

$$w^i(\hat{a}) = \mathcal{R}_i\, w^z(a) = w^z(\mathcal{R}_i a) \ . \qquad (28)$$

By definition and formulas (12) and (25) we have

$$\rho^i(\vec{r}) = \int w^i(\hat{a})\,\rho(\vec{r}, \hat{a})\,d\hat{a} = \int w(\mathcal{R}_i\hat{a})\,\rho(\mathcal{R}_i\vec{r}, \mathcal{R}_i\hat{a})\,d\hat{a}$$
$$= \int w(\hat{a})\,\rho(\mathcal{R}_i\vec{r}, \hat{a})\,d\hat{a} = \rho^z(\mathcal{R}_i\vec{r}) \ . \qquad (29)$$

The last two equalities follow from the unitary nature of $\mathcal{R}_i$ and from the definition of $\rho(\vec{r})$.

We can express the result (29) for the form factor by making explicit use of the Cartesian components of the vector $\vec{k}$:

$$f^x(k_x, k_y, k_z) = f^z(k_z, k_y, k_x) \ ,$$
$$f^y(k_x, k_y, k_z) = f^z(k_x, k_z, k_y) \ . \qquad (30)$$

It is now an easy matter to calculate the structure factor:

$$F(k_x, k_y, k_z) = \sum_j e^{i\vec{k}\cdot\vec{R}_j}\,\mu_j f_j(k)\,e^{-W_j(k,T)} = \{\mu_{sp}[1 + e^{ia(k_x+k_y+k_z)/2}]f_{sp}(|\vec{k}|)\,e^{-W_{sp}(|\vec{k}|,T)} + \mu_z[e^{ia(k_x/2+k_y)/2}$$
$$+ e^{ia(3k_x/2+k_y)/2} f^z(k_z, k_y, k_x) + e^{ia(k_y/2+k_z)/2} + e^{ia(3k_y/2+k_z)/2} f^z(k_x, k_z, k_y)$$
$$+ e^{ia(k_x+k_z/2)/2} + e^{ia(k_x+3k_z/2)} f^z(k_x, k_y, k_z)]\,e^{-W_{asp}(\vec{k},T)}\} \ , \qquad (31)$$

where $f_{sp}(|\vec{k}|)$ is the form factor calculated for the molecules with spherical symmetry, a is the lattice parameter, μ_{sp} and μ_z are the magnetic moments at the sites with spherical and ellipsoidal symmetry, respectively.

In order to avoid the difficulty of calculating the Debye–Waller factors, we compared our theory to the F_M experimental data extrapolated to 0 °K by the E and H models introduced in I by assuming a different statistical disorder in calculating the nuclear structure factor F_N.

We computed numerically the $A_{2l,0}$ components up to $l=4$ and found that only A_{00}, A_{20}, and A_{40} are significant. We have assumed $A=-B$ as proposed by Kleiner for gaseous oxygen. The Gaussian b parameter has been varied in order to obtain better agreement with experiment, and a value of 1.125 a.u. was found to be satisfactory. This may be compared with the value of 0.8 a.u. used for the free molecule.[13] We have restricted our fit to the first 18 reflections since the Gaussian wave function is not very accurate at low r (and hence high k), μ_{sp}, μ_z, and $w_{2l,0}$ were taken as free parameters, while $w_{00}=1/4\pi$ from the normalization condition.

Since the lattice sites have different symmetries the two magnetic moments μ_{sp} and μ_z can differ. However, the total cell moment $\mu = 2\mu_{sp} + 6\mu_z$ is expected to be comparable to the value $1.15\mu_B$ obtained by extrapolation of the susceptibility measurements[3] at 80 kOe. Such a conclusion is in agreement with the values $\mu_{sp} = 0.115 \pm 0.002\ \mu_B$ and $\mu_z = 0.102 + 0.002\ \mu_B$ found in the fit to the E model, and $\mu_{sp} = 0.113 \pm 0.002\ \mu_B$ and $\mu_z = 0.104 \pm 0.002\ \mu_B$ to the H model. The parameters w_{20} and w_{40} have been found, respectively, as follows:

$$w_{20} = 1.32 \pm 0.041, \quad w_{40} = 0.62 \pm 0.10 \quad \text{for the E model,}$$

$$w_{20} = 1.20 \pm 0.07, \quad w_{40} = 0.61 \pm 0.02 \quad \text{for the H model.}$$

In both cases the fit is very good, perhaps slightly better for the latter, and the values agree within error for the two models considered.

Comparison of the theoretical and experimental values of F_M is given in Table I and Fig. 3 for both models. We obtained $\chi^2 = 11.6$ for the E model and $\chi^2 = 9.1$ for the H model. Table I lists both the

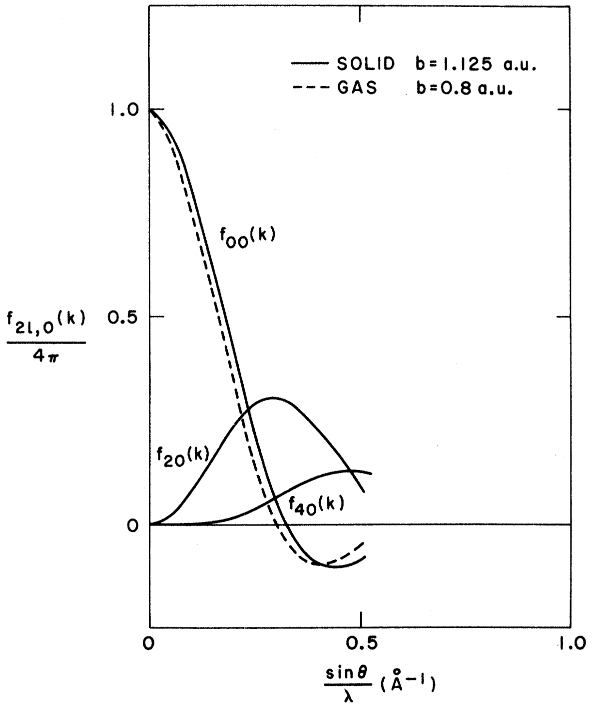

FIG. 2. Plots of $f_{l0}(k)$ of importance in the present problem.

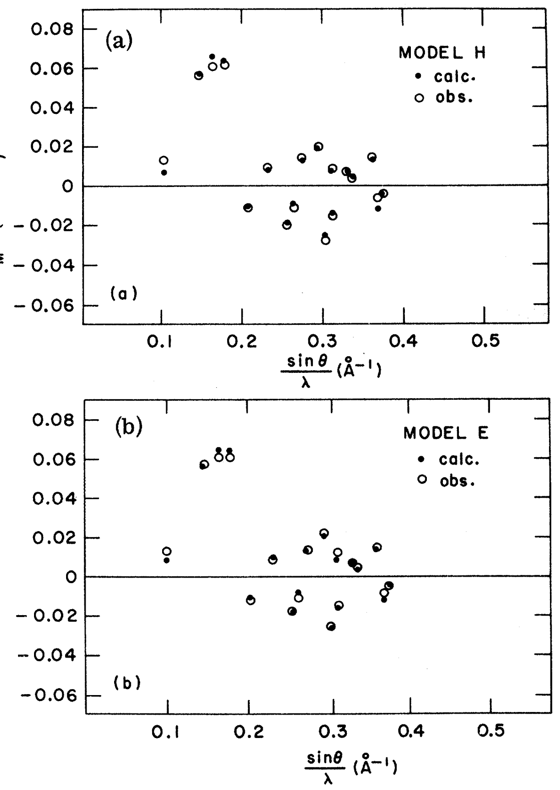

FIG. 3. Comparison between experimental and calculated magnetic structure factors: (a) model H, (b) model E.

TABLE I. Comparison of the calculated magnetic structure for γ-O_2 and the experimental values corrected for the Debye–Waller factor for models H and E. Units are in 10^{-12} cm.

	Experimental	Calculated		
(*hkl*)	F_M	F_M	F_s	F_{as}
		Model H		
(110)	0.0125 ± 0.0023	0.0066	0.0039	0.0027
(200)	0.0564 ± 0.0028	0.0573	0.0745	−0.0172
(210)	0.0612 ± 0.0036	0.0655	0.0632	0.0022
(211)	0.0612 ± 0.0087	0.0637	0.0581	0.0056
(220)	−0.0110 ± 0.0018	−0.0107	0.0018	−0.0126
(310)	0.0088 ± 0.0014	0.0085	0.0014	0.0071
(222)	−0.0200 ± 0.0014	−0.0191	−0.0209	0.0018
(320)	−0.0113 ± 0.0019	−0.0090	−0.0178	0.0088
(321)	0.0135 ± 0.0027	0.0130	0.0147	−0.0018
(400)	0.0196 ± 0.0020	0.0198	0.0159	0.0038
(410)	−0.0276 ± 0.0060	−0.0248	0.0000	−0.0248
(411)	−0.0153 ± 0.0026	−0.0152	0.0001	−0.0153
(330)	0.0087 ± 0.0014	0.0076	0.0001	0.0075
(420)	0.0076 ± 0.0013	0.0067	−0.0015	0.0082
(421)	0.0039 ± 0.0015	0.0036	−0.0032	0.0068
(422)	0.0137 ± 0.0022	0.0135	−0.0003	0.0139
(430)	−0.0061 ± 0.0047	−0.0119	0.0000	−0.0119
(431)	−0.0048 ± 0.0010	−0.0048	−0.0004	−0.0044
		Model E		
(110)	0.0130 ± 0.0024	0.0080	0.0055	0.0026
(200)	0.0570 ± 0.0029	0.0561	0.0746	−0.0185
(210)	0.0611 ± 0.0036	0.0646	0.0622	0.0024
(211)	0.0611 ± 0.0087	0.0642	0.0582	0.0060
(220)	−0.0124 ± 0.0020	−0.0110	0.0026	−0.0136
(310)	0.0083 ± 0.0014	0.0096	0.0019	0.0077
(222)	−0.0181 ± 0.0013	−0.0186	−0.0202	0.0016
(320)	−0.0110 ± 0.0018	−0.0081	−0.0175	0.0094
(321)	0.0137 ± 0.0028	0.0130	0.0148	−0.0018
(400)	0.0222 ± 0.0038	0.0202	0.0158	0.0044
(410)	−0.0258 ± 0.0056	−0.0269	0.0000	−0.0269
(411)	−0.0152 ± 0.0026	−0.0161	0.0002	−0.0163
(330)	0.0119 ± 0.0020	0.0084	0.0002	0.0082
(420)	0.0064 ± 0.0011	0.0064	−0.0015	0.0080
(421)	0.0042 ± 0.0016	0.0037	−0.0032	0.0069
(422)	0.0147 ± 0.0024	0.0138	−0.0004	0.0142
(430)	−0.0082 ± 0.0063	−0.0125	0.0000	−0.0125
(431)	−0.0050 ± 0.0011	−0.0050	−0.0050	−0.0045

spherical and aspherical contributions to the total structure factor of the cell,

$$F = F_{\mathrm{sp}} + F_{\mathrm{asp}} \quad , \tag{32}$$

with

$$F_{\mathrm{sp}} = f_0(k)\, Y_{00}(\hat{k}) w_{00} \sum_i \left(\mu_{\mathrm{sp}}\, e^{i\vec{k}\cdot\vec{r}_i^{(a)}} + \mu_z\, e^{i\vec{k}\cdot\vec{r}_i^{(d)}}\right),$$

$$F_{\mathrm{asp}} = \mu_z \sum_{l\neq 0} w_{2l,0} f_{2l,0}(k)\, Y_{2l,0}(\hat{k}) \sum_i e^{i\vec{k}\cdot\vec{r}_i^{(}} \quad .$$

The F_{asp} term arises only from molecules with ellipsoidal rotational symmetry. This contribution is essential in order to account for the reflections for which the spherical contribution alone would be rigorously zero by symmetry arguments as can be seen from Table I.

For the limit $T \to \infty$, $w_l m$ should be zero for l, $m \neq 0$, as discussed qualitatively in Sec. III. In this limiting case, the magnetic structure factor F is simply equal to F_{sp}, as can be easily seen from Eq. (32) by setting $w_{2l,0} = 0$ for $l \neq 0$.

VI. CONCLUSIONS

The polarized-neutron-diffraction data from paramagnetic γ-O_2 have been explained by a simple model which takes into account the different symmetry of the molecules present in the unit cell. The approximately ellipsoidal symmetry around the d sites introduces an aspherical contribution to the structure factor, which does not appear in the calculation for gaseous oxygen.

Thus the directional dependence of $f(\vec{k})$ is due not only to the electron motion but also to that of the molecule as a whole. In the spherical molecules the asphericity due to the electron motion is averaged by the molecular rotation, but in the others both contribute.

We have seen that only the $l = 2$ and 4 terms contribute significantly to the fit. This situation is similar to that predicted and observed in the d transition metals and alloys having cubic symmetry.[18,19]

The b parameter of our Gaussian wave function is larger than the one used by Meckler for gaseous oxygen. This is an indication that the wave function is more contracted in the solid as compared to the free molecule, although a Gaussian wave function is probably not the best choice. However, we have not attempted to use a better one, since the agreement with experiment over the first 18 reflections is quite satisfactory and gives useful physical information on the system in a simple way. The model used involves a probability function $w(\hat{a})$ related to the rotational motion of the molecule as a whole. For this reason it may depend on temperature and we have discussed its qualitative behavior in this respect.

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[1] D. E. Cox, E. J. Samuelsen, and K. H. Beckurts, preceding paper, Phys. Rev. B 7, 3102 (1973).

[2] A. S. Borovic-Romanov, M. P. Orlova, and P. G. Strelkov, Dokl. Akad. Nauk SSSR 99, 699 (1954).

[3] E. Kanda, T. Haseda, and A. Otsubo, Physica 20, 131 (1954); Sci. Rept. Res. Inst. Tohuko Univ. 7, 1 (1955).

[4] M. F. Collins, Proc. Phys. Soc. 89, 415 (1966).

[5] R. A. Alikhanov, E. B. Vul, and J. G. Fedorov, Acta Cryst. 21, Suppl. A92 (1966); R. A. Alikhanov, Zh. Eksp. Teor. Fiz. Pis'ma Red. 5, 430 (1967) [JETP Lett. 5, 349 (1967)].

[6] C. S. Barrett, L. Meyer, and J. Wassermann, J. Chem. Phys. 47, 592 (1967).

[7] T. H. Jordan, W. E. Streib, H. W. Smith, and W. N. Lipscomb, Acta Cryst. 17, 177 (1964).

[8] H. W. Smith, Ph.D. thesis (Harvard University, 1966) (unpublished).

[9] T. H. Jordan, W. E. Streib, and W. N. Lipscomb, J. Chem. Phys. 41, 760 (1964).

[10] A. Meckler, J. Chem. Phys. 21, 1750 (1953).

[11] R. A. Alikhanov, I. L. Ilyina, and L. S. Smirnov, Phys. Status Solidi B 50, 385 (1972).

[12] G. T. Trammel, Phys. Rev. 92, 1387 (1953).

[13] W. H. Kleiner, Phys. Rev. 97, 411 (1955).

[14] J. L. Powell and B. Crasemann, *Quantum Mechanics* (Addison-Wesley, Reading, Mass., 1962).

[15] A. R. Edmonds, *Angular Momentum in Quantum Mechanics* (Princeton U. P., Princeton, N. J., 1964).

[16] S. W. Lovesey, J. Phys. C 2, 470 (1969).

[17] D. F. Johnston, Proc. Phys. Soc. 88, 37 (1966); D. F. Johnston and D. E. Rimmer, J. Phys. C 2, 1151 (1969); S. W. Lovesey and D. E. Rimmer, Rept. Progr. Phys. 32, 333 (1969).

[18] R. E. Watson and A. J. Freeman, Acta Cryst. 14, 27 (1961).

[19] A. Paoletti, Rivista Il Nuovo Cimento 2, 451 (1970).