

Magnetic form factor of the O₂ molecule

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The polarized neutron data of Cox *et al.* on γ -O₂ are reanalyzed using the spherical harmonic expansion technique of Leoni and Sacchetti. The results are found to be in good agreement with the spin density derived from Gaussian atomic orbitals. Several errors in the work of Leoni and Sacchetti, as well as in the interpretation of neutron scattering measurements on α -O₂, are discussed.

The magnetic form factor, defined as the Fourier transform of the spin density, is an important connection between the electronic structure of a magnetic system and the neutron scattering cross section. From the viewpoint of electronic structure, the simplest magnetic systems are probably the condensed phases of oxygen. It is therefore particularly important to compare theory and experiment for this model system. Several groups have measured the magnetic form factor, and all have claimed good agreement with theory.¹⁻⁴ In the course of neutron scattering measurements on α - and β -oxygen, I have discovered serious errors in the interpretation of several of these measurements.⁵ It is the purpose of this paper to rectify these errors, and provide a comprehensive comparison with theory.

The magnetic form factor has been determined by two experimental techniques: measuring the intensity of magnetic reflections in antiferromagnetic α -O₂, and by using polarized neutrons to observe the magnetic-nuclear interference in a magnetized sample of paramagnetic γ -O₂. Because of the weakness of the crystal binding-energy scale relative to the atomic orbitals which are responsible for the magnetism, one expects that the molecular form factor will be independent of the crystal structure. Consequently, the measurements on α and γ phases should agree, and one can speak simply of the molecular form factor without reference to a specific crystal structure. I will discuss the α -O₂ measurements at the end of this paper; for now, I note that, because only a few magnetic reflections are seen, relatively little information is available. In contrast, in their experiment on γ -O₂, Cox, Samuelsen, and Beckurts (CSB) were able to determine the ratio of magnetic to nuclear amplitudes for 27 Bragg reflections.² This enabled them to construct a Fourier synthesis map of spin density in the magnetized sample. However, the spin distribution was severely smeared by the librational motion of the molecules, thereby limiting the extent to which these results could be compared with theory.

In order to account for the distribution of molecular orientations in γ -O₂, Leoni and Sacchetti (LS) expanded the form factor and orientation distribution in spherical harmonics, and fitted the measurements of CSB.³ However, as discussed below, the LS calculations contain conceptual and computational errors that render the claimed satisfactory agreement with experiment fortuitous. I re-

capitulate their analysis as follows.

Define $w(\hat{\mathbf{a}})d\Omega$ to be the probability that the molecular axis is in an element of solid angle $d\Omega$ about the direction $\hat{\mathbf{a}}$. Expanding $w(\hat{\mathbf{a}})$ in spherical harmonics,

$$w(\hat{\mathbf{a}}) = \sum_{l,m} w_{lm} Y_{lm}(\hat{\mathbf{a}}), \quad (1)$$

where

$$w_{lm} = \int d\Omega w(\hat{\mathbf{a}}) Y_{lm}^*(\hat{\mathbf{a}}). \quad (2)$$

The normalization of $w(\hat{\mathbf{a}})$ implies $w_{00} = (4\pi)^{-1/2}$. If the form factor $f(\mathbf{K})$ depends only on the magnitude of \mathbf{K} and the angle β between \mathbf{K} and $\hat{\mathbf{a}}$, it can be expanded in Legendre polynomials:

$$f(\mathbf{K}) = \sum_{l=0}^{\infty} (2l+1) i^l A_l(K) P_l(\cos\beta),$$

where

$$A_l(K) = \frac{1}{2^l l!} \int_0^\pi \sin\beta d\beta P_l(\cos\beta) f(\mathbf{K}).$$

In the present case, the symmetry when nuclei are interchanged implies that only even l need be considered.

If one now considers the averaged form factor $f_{av}(K)$ of an ensemble of molecules with orientational probability distribution $w(\hat{\mathbf{a}})$, the addition theorem of spherical harmonics may be applied to show that

$$f_{av}(\mathbf{K}) = 4\pi \sum_{l,m} i^l w_{lm} A_l(K) Y_{lm}(\hat{\mathbf{K}}). \quad (3)$$

The crystal structure of γ -O₂ is shown in Fig. 1(b). It is an A15 structure with two different orientational distributions at the two molecular sites. CSB carried out a crystallographic refinement of the structure and concluded that the I molecules form a bcc lattice of molecules predominantly oriented along $\langle 111 \rangle$ directions and the axes of the II molecules are generally perpendicular to the rows of molecules. CSB proposed two models, labeled E and H, for the static orientational disorder of the II molecules. In model E, the average molecular orientation is along one of the $\langle 100 \rangle$ directions, with a large librational amplitude. Model H differs by having molecules statistically disordered, 22° from the $\langle 100 \rangle$ directions. See Ref. 2 for full details.

The application of the orientationally averaged form

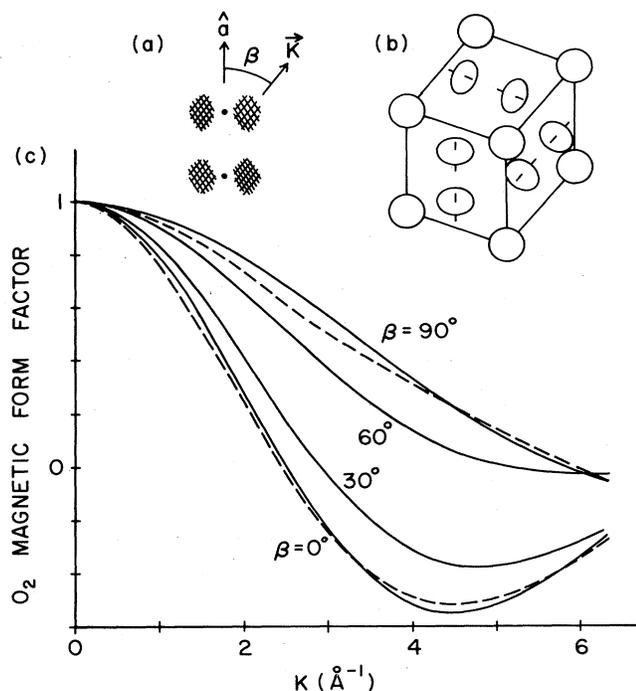


FIG. 1. (a) Sketch of O₂ molecule, indicating region of concentration of P atomic orbitals, responsible for magnetic interactions. (b) Crystal structure of γ -O₂. I molecules form a bcc lattice (center site not shown) and II molecules occupy sites on cube faces. (c) Calculated magnetic form factor for O₂ molecule. Dashed line illustrates results of Meier and Helmholdt at $\beta=0^\circ$ and 90° (from Ref. 4).

factor to the interpretation of the diffraction experiment of CSB may require some clarification. Short-range orientational correlations would be seen as diffuse scattering between the Bragg peaks. Dynamical effects of molecular orientation, having perhaps the energy scale of librations, will cause inelastic scattering. To the extent that the data of CSB-measured elastic Bragg scattering, it is the time averaged, long-distance limit, i.e., the single-site average orientational distribution, which is measured. It is therefore appropriate to use the form factor of Eq. (3) in calculating the structure factor for a given reflection in the crystal. The magnetic structure factor is then given by

$$F_{\text{mag}}(\mathbf{K}) = 4\pi P \sum_{j,l,m} \mu_j i^l (w_{lm})_j A_l(K) Y_{lm}(\hat{\mathbf{K}}, \hat{\mathbf{z}}_j) e^{i\mathbf{K}\cdot\mathbf{r}_j}, \quad (4)$$

where \mathbf{r}_j is the position of the center of the j th molecule in the unit cell, $\hat{\mathbf{z}}_j$ is the direction of the symmetry axis, and $Y_{lm}(\hat{\mathbf{K}}, \hat{\mathbf{z}}_j)$ is a spherical harmonic calculated for polar angle equal to the angle between $\hat{\mathbf{K}}$ and $\hat{\mathbf{z}}_j$, and azimuthal angle between $\hat{\mathbf{K}}$ and any cube axis. The magnetic scattering length P is 0.27×10^{-12} cm for spin 1 and g factor 2, and μ_j is the magnetization in units of the Bohr magneton. This is equivalent to LS Eq. (31).

CSB did not measure F_{mag} directly, but instead reported $\gamma(\mathbf{K}) = F_{\text{mag}}(\mathbf{K})/F_{\text{nuc}}(\mathbf{K})$. On the basis of models E

and H, they calculated F_{nuc} for each reflection. To the extent that the thermal motion smears F_{nuc} and F_{mag} identically, $\gamma(\mathbf{K})$ will be unaffected by this correction, and F_{mag} obtained by multiplying the calculated F_{nuc} by experimental γ will accurately reflect the magnetic structure of a hypothetical crystal free from thermal disorder. In this way, they intended to preserve the essential structure of $w(\hat{\mathbf{a}})$, while compensating for the large thermal motion.

In their interpretation of these corrected experimental F_{mag} , LS regarded the orientational distribution of molecule II as adjustable parameters. This is incorrect, as the orientational distributions are fixed by the structural models of CSB. In addition, they regarded molecule I as spherically symmetric, so that only w_{00} is nonzero for molecule I. Equation (2) shows that w_{lm} is bounded by Y_{lm} , whereas the converged values of LS grossly exceed these limits. Their fits to the magnetic amplitudes can therefore not be regarded as reliable.

The first calculation of the O₂ magnetic form factor was given by Kleiner,⁶ who showed that the density of atomic $P \pm$ orbitals is an accurate representation of the spin density. Following Kleiner, I used Meckler's⁷ Gaussian wave functions for O₂, which give a spin density proportional to

$$\rho(r, \theta) \propto r^2 \sin^2 \theta e^{-2br^2} [\cosh(2brR_0) \cos \theta - 1].$$

Here r and θ are polar coordinates centered between the nuclei, $R_0 = 1.21$ Å is the internuclear separation, and the parameter b controls the spatial extent of the atomic P orbitals. The form factor $f(\mathbf{K}) = \int d^3\mathbf{r} e^{i\mathbf{K}\cdot\mathbf{r}} \rho(\mathbf{r})$ calculated numerically is shown in Fig. 1(c). As discussed below, the best fit to experiment is for $b = 4.1 \pm 0.2$ Å⁻². For comparison, the calculated form factor of Meier and Helmholdt for three Gaussian orbitals matched to a self-consistent field calculation is also shown. The agreement between these two calculations is satisfactory. Alikhanov *et al.* calculated the same quantity, but their results differ significantly.⁸

In order to calculate the scattering amplitudes from Eq. (4), $A_l(K)$ was determined for $l=0-6$ by matching the calculated $A(K)$ at four angles. Expansion in Legendre polynomials on a finer grid gave the same results. The $A_l(K)$ agree with those calculated by Kleiner, but differ substantially from the results of LS Fig. 2. Evidently, there is an error in the derivation or evaluation of LS Eq. (26) for $A_l(K)$. This error, combined with the fitted w_{20} and w_{40} led LS to reasonable agreement with the experimental data, despite the fact that the calculated form factor is incorrect. The $A_l(K)$ for the nuclear amplitudes are given by $2j_l(KR_0/2)$.

Using these $A_l(K)$ and the disorder parameters w_{lm} for CSB models E and H at zero temperature, I have calculated the nuclear and magnetic structure factors. The error in truncating the series for $A(K)$ at $l=4$ is at most 4%, determined by comparing the nuclear structure factors from the spherical harmonic expansion with those given in CSB Table IX. For reasons which will be clear below, I compare the ratio of the amplitudes to the experimentally measured values rather than comparing calculated F_{mag} to those derived by CSB. The magnetization at the two in-

dependent sites and the b parameter were varied to obtain the best fit. The relevant w_{lm} are listed in Table I and the calculated ratios for each reflection are given in Table II. Two reflections, (432) and (521), gave ratios quite different from experiment. No adjustment of parameters was able to bring them into line, so I excluded them from the fit. The quality of fit is measured by the parameter χ^2 , defined as

$$\chi^2 = \sum_j \left[\frac{\gamma_{\text{meas}}(\mathbf{K}_j) - \gamma_{\text{model}}(\mathbf{K}_j)}{\sigma_j} \right]^2 / (N - m - 1),$$

where N is the number of data points (24) and m is the number of independent parameters (3). When the calculations were extended to $l=6$, the fits did not improve significantly. In the present case, the standard errors of the experimental points are dominated by counting statistics, and so one would expect $\chi^2 \sim 1$ for a perfect fit to the model. The agreement for model H is satisfactory, and model E significantly worse.

One potential source of systematic error is the some-

TABLE I. Disorder parameters for CSB models E and H, and for direct refinement with spherical harmonic orientation distributions. Bottom two rows show the range of orientation probabilities calculated from the specified disorder parameters.

	Model E	Model H	Direct
$w_{40}\text{I}$	-0.329	-0.329	-0.019±0.029
$w_{44}\text{I}$	-0.198	-0.198	-0.011
$w_{20}\text{II}$	-0.315	-0.315	-0.257±0.010
$w_{40}\text{II}$	0.317	0.317	0.111±0.025
$w_{44}\text{II}$	0.443	0.021	0.085±0.023
Site I	-0.20 +0.26	-0.20 +0.26	-0.65 + 0.88
Site II	-0.19 +0.67	-0.08 +0.30	-0.27 + 0.30

what arbitrary nature of the CSB models of orientational disorder. If the ratios of magnetic to nuclear structure factor were indeed independent of the degree of orientational disorder, the two models would describe the data

TABLE II. Ratios of magnetic/nuclear structure factors for 26 Bragg reflections in $\gamma\text{-O}_2$. Experimental values are from Ref. 2, Table IX. Numbers in parentheses are relative deviation from the experimental values. The last three rows show magnetization of the two sublattices, in units of the Bohr magneton, and goodness of fit parameter for the fits. All quoted errors are standard deviations.

K	Experimental	Model E	Model H	Direct
110 ^a	0.1090±0.0200	0.0901(-0.9)	0.0788(-1.5)	0.0837(-1.3)
200	0.0200±0.0010	0.0198(-0.2)	0.0198(-0.2)	0.0197(-0.3)
210	0.0169±0.0010	0.0162(-0.7)	0.0164(-0.5)	0.0168(-0.1)
211	0.0169±0.0024	0.0169(0)	0.0168(0)	0.0170(0)
220	0.0149±0.0024	0.0081(-2.8)	0.0107(-1.8)	0.0097(-2.2)
310	0.0215±0.0035	0.0253(1.1)	0.0222(0.2)	0.0206(-0.3)
222	0.0098±0.0007	0.0111(1.8)	0.0104(0.9)	0.0101(0.5)
320	0.0078±0.0013	0.0084(0.5)	0.0083(0.4)	0.0088(0.8)
321	0.0074±0.0015	0.0091(1.1)	0.0092(1.2)	0.0093(1.2)
400	0.0058±0.0010	0.0055(-0.3)	0.0065(0.7)	0.0065(0.7)
410	0.0138±0.0030	0.0105(-1.1)	0.0099(-1.3)	0.0104(-1.1)
411	0.0110±0.0019	0.0075(-1.8)	0.0077(-1.7)	0.0091(-1.0)
330	0.0121±0.0020	0.0072(-2.4)	0.0107(-0.7)	0.0101(-1.0)
420	0.0042±0.0007	0.0052(1.4)	0.0041(-0.1)	0.0042(0.1)
421	0.0024±0.0009	0.0034(1.1)	0.0038(1.6)	0.0034(1.1)
422	0.0080±0.0013	0.0062(-1.4)	0.0069(-0.8)	0.0074(-0.5)
430	0.0044±0.0034	0.0059(0.5)	0.0086(1.2)	0.0074(0.9)
431	0.0098±0.0021	0.0110(0.6)	0.0115(0.8)	0.0087(-0.5)
432 ^b	-0.0110±0.0050	0.0135(4.9)	-0.1435(-26.5)	-0.0819(-14.2)
521 ^b	-0.0019±0.0025	0.0587(24.2)	0.0208(9.1)	0.0443(18.5)
600	0.0063±0.0009	0.0097(3.8)	0.0054(-1.0)	0.0082(2.1)
442	-0.0048±0.0021	-0.0046(0.1)	-0.0063(-0.7)	-0.0091(-2.0)
532	0.0158±0.0016	0.0097(-3.8)	0.0154(-0.2)	0.0126(-2.0)
621	0.0046±0.0015	0.0047(0.1)	0.0029(-1.2)	0.0036(-0.6)
542	0.0101±0.0031	0.0035(-2.1)	0.0063(-1.2)	0.0070(-1.0)
444	0.0075±0.0008	0.0041(-4.3)	0.0085(1.3)	0.0079(0.5)
μ I		0.109±0.006	0.106±0.003	0.106±0.003
μ II		0.089±0.004	0.090±0.002	0.0092±0.002
χ^2		4.17	1.26	1.46

^a See footnote 9.

^b Not included in fits.

equally well. This is particularly worrisome in view of the fact that of the 26 peaks for which γ was determined, F_{nuc} was not directly measured for eight. It is therefore possible that the assigned F_{nuc} has large systematic errors for these reflections. Consequently, I have fitted F_{nuc} from CSB Table IV directly to a model where the molecular disorder is entirely specified by a spherical harmonic series. The symmetry of the molecular environment has been incorporated as follows. The environment of the I molecules has T point group symmetry. When combined with the inversion symmetry of the molecule, this yields octahedral symmetry for $w(\hat{\mathbf{a}})$. Therefore, w_{lm} is nonzero only for l even and m a multiple of four. Furthermore, $w_{20}=0$, and $w_{44}=w_{4-4}=(\frac{5}{14})^{1/2}w_{40}$ and $w_{64}=w_{6-4}=- (\frac{7}{2})^{1/2}w_{60}$. The II molecules have D_4 point group symmetry, which gives the same set of w_{lm} nonzero. I fitted 29 reflections (including three duplicates measured in two different zones) up to (444) from CSB Table IV.¹⁰ Following CSB, I did not fit the four strongest reflections because of possible extinction effects. The disorder parameters w_{lm} for $l=0,2,4$ were varied, as well as isotropic Debye-Waller factor. The rms thermal amplitudes of the molecular centers are $0.52 \pm 0.01 \text{ \AA}$ for the I molecules and $0.50 \pm 0.01 \text{ \AA}$ for the II molecules. Fits to all 40 reflections were somewhat worse. The results for l truncated at 4 are given in Table I. The R factor, defined as

$$R = \frac{\sum_j |F_{\text{obs}}(\mathbf{K}_j) - F_{\text{model}}(\mathbf{K}_j)|}{\sum_j |F_{\text{obs}}(\mathbf{K}_j)|},$$

is 0.117. A fit including w_{60} and w_{64} terms was only slightly better, with $R=0.115$. As a probability distribution, $w(\hat{\mathbf{a}})$ must be positive throughout its domain. Table I shows that for all models there are regions in which the $w(\hat{\mathbf{a}})$ reconstructed by Eq. (1) from w_{lm} is negative, evidently due to truncation of the spherical harmonic series. However, the direct fit of w_{lm} violates this requirement significantly more than models E and H.

The fit to $\gamma(\mathbf{K})$ for this directly modeled set of disorder parameters is listed in Table II. χ^2 is 1.46 for this model, which is essentially as good as for model H of CSB. Table II shows that the troublesome (432) and (521) reflections are still substantially incorrect for the directly measured orientational disorder model.

As a final attempt to understand this discrepancy, the w_{lm} were adjusted to obtain the best fit of $\gamma(\mathbf{K})$. χ^2 for the 26 ratios is 4.30. While this is no worse a fit than model E, this set of disorder parameters cannot be taken as an acceptable description of the molecular disorder. When applied to the experimental nuclear structure factors from CSB Table IV, the R factor is 0.30, significantly worse than for other models.

The (432) and (521) reflections were among the weakest studied in the polarization analysis data set of CSB.¹⁰ Furthermore, CSB Table IX shows that these two reflec-

tions are particularly sensitive to the extrapolation to zero temperature. Their low intensity implies that the structure factor is very near zero due to phase cancellation from different regions of the unit cell. It is likely that the structural model is inadequate to describe them.

In summary, the spherical harmonic expansion technique of LS is useful for interpretation of the magnetic structure of $\gamma\text{-O}_2$, when correctly applied. A magnetic form factor derived from Gaussian P atomic orbitals gives satisfactory agreement with the experimental results.

I conclude with some brief comments on the measurements of antiferromagnetic Bragg peaks in $\alpha\text{-O}_2$. The diffraction measurements have been carried out on powder samples, in which there is a distribution of orientations of sample crystallites. Alikhanov *et al.* argued that one should compare the spherically averaged form factor to experimentally determined intensities.¹ This is incorrect. The O_2 molecules in a powder sample are in individual crystallites. Any crystallite which is aligned with the incoming beam and the detector so as to meet the diffraction condition is made up of molecules with a specific orientation to the Bragg wave vector. For a given reflection, the angle β between \mathbf{K} and $\hat{\mathbf{a}}$ is well determined (neglecting thermal libration within the crystallite). For the (101) reflection, $K=1.31 \text{ \AA}^{-1}$ and $\beta=62.4$, for which $f=0.84$. For the (100), $K=1.58 \text{ \AA}^{-1}$, $\beta=47.5$, and $f=0.70$. If one assumes that the spins are directed along the monoclinic b axis, the structure factors of the two reflections are equal. In this case, neglecting thermal motion and Lorentz factor, the ratio of intensities of these two magnetic Bragg peaks should be 1.45. The measured values in the literature are all somewhat higher than this value: 2.2 by Collins,¹² 2.0 by Alikhanov *et al.*,¹ 3.3 by Meier and Helmholtz,⁴ and 2.2 by Stephens *et al.*⁵ The spread in the experimental values is rather large, pointing up the significance of preferred sample orientation.⁴ Meier and Helmholtz argue that the spins are oriented slightly away from the symmetry direction, based on the ratio of these two magnetic peak intensities and the observation of several other extremely weak magnetic peaks.⁴ Molecular librations are significant in $\alpha\text{-O}_2$, in the range $9^\circ\text{--}20^\circ$ rms.¹³ In view of these difficulties of interpretation, the strength of antiferromagnetic Bragg peaks in $\alpha\text{-O}_2$ does not seem to provide a reliable measurement of the molecular form factor.

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The form factor, not the orientational average, was compared with experiment [R. Meier (personal communication)]; the text of this paper was not clear on this point.

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- ⁸The scale of K on the calculated form factor of Alikhanov *et al.* (Ref. 1) is incorrect by a factor of 0.53, suggesting that they confused atomic units with Angstrom units. It is clear that the form factor for $\beta=0$ must be zero at a wave vector near $\pi/R_0=2.6 \text{ \AA}^{-1}$. Meier and Helmholdt (Ref. 4) also noted a discrepancy with Ref. 1.
- ⁹In the course of this work, it became obvious that γ must be 0.109 for the (110) reflection, not 0.0109 as printed in CSB Table IX. In the same line, F_{mag} for model H should be 0.0125. D. Cox confirms both misprints.
- ¹⁰The fits were done with a least-squares algorithm, with standard errors set proportional to the observed amplitude. The best fit parameters yield rms $(F_{\text{obs}} - F_{\text{model}})/F_{\text{obs}} = 17\%$. Fits including $l=6$ have an rms deviation of 15%.
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