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Neutron-diffraction experiments were performed on polycrystalline samples of α-O_2 at 6 and 22 K and on β-O_2 at 30 K. A large amount of preferred orientation was observed in all samples. For the first time a *quantitative* analysis was carried out to determine the magnetic structures with the use of the Rietveld profile refinement technique. The magnetic structure of α-O_2 is collinear antiferromagnetic with the moments directed nearly along the monoclinic b axis. In β-oxygen only short-range order is present, and the local magnetic structure is described as consisting of three antiferromagnetically coupled (120°) sublattices.

INTRODUCTION

Several investigations have been carried out to determine the structure of the solid α phase ($T = 0-24$ K) and β phase ($T = 24-44$ K) of oxygen. Owing to a relatively large decrease in volume when transforming from the high-temperature γ phase ($T = 44-54$ K) down to the β phase, no single crystals have been obtained. α-O_2 was found to have $C2/m$ (C_{2h}^3) symmetry from x-ray[1] and neutron diffraction,[2] whereas β-O_2 is rhombohedral [$R\,3m$ (D_{3d}^5)] as was determined by neutron[3,4] and electron diffraction.[5,6] Other interesting x-ray studies have been published by DeFotis[7] and Krupskii *et al.*[8]

The crystallographic structures of both phases seem to be well known, although absence of free precession in β-O_2 as suggested by Krupskii[8] is questionable. The magnetic structures are not well known. It has been stated from qualitative arguments that the α phase has a collinear antiferromagnetic structure with the moments directed along the monoclinic b axis, but no accurate analysis has been carried out so far.[8] Evidence for deviations from this direction will be presented. In the literature no definite statements could be made concerning the magnetic structure of β-O_2 except for suggestions, such as no long-range order (LRO),[9] evidence for LRO,[10] or favoring of a three-sublattice structure in which neighboring spins make an angle of 120°.[11-16]

EXPERIMENTAL

The polycrystalline samples were prepared by condensing gaseous oxygen (Matheson Gas Products, 99.999% pure) from a storage vessel at 1 atm. into the liquid phase in a thin-walled stainless-steel cylindrical sample cell. The dimensions of the sample were approximately 20 mm diam and 60 mm in height. When the appropriate amount of liquid had been collected the sample holder was isolated from the gas supply. Since we wanted to avoid

preferred orientation the samples were cooled quickly. The sample cell was mounted in a cryostat and provided with a heater and a gold-iron Chromel thermocouple, both connected to a temperature controller. The thermocouple was calibrated against a germanium thermometer. The temperature was kept constant within ±0.1 K when recording a diffractogram.

Neutron-diffraction data were collected on the powder diffractometer at the HFR reactor at Petten at 6, 22, and 30 K. Neutrons of wavelength 2.5906(3) Å were obtained by reflection from the (111) planes of a copper crystal. The λ/n contamination had been reduced to less than 1 part in 10^3 using a pyrolytic graphite filter. Soller slits with a horizontal divergence of 30' were placed between the reactor and monochromator and in front of the four ^{3}He counters. Since absorption was negligible, the data were not corrected for this effect.

CRYSTAL STRUCTURES OF α- AND β-OXYGEN

Diffractograms of α-O_2 at 6.0 and 22.0 K are shown in Figs. 1 and 2. Peaks at $2\theta \simeq 78°$ and 93° are due to the cryostat and sample holder. As in previous investigations the space group $C2/m$ was found. The structures have been refined using the Rietveld profile-refinement technique.[17] The coherent scattering length used for the O atom is 0.580×10^{-14} m. It should be noted that the experimental (001) reflection was extremely sensitive to the orientation of the sample; its intensity varied up to a factor of 3. Annealing or traversing the α-β transition back and forth a number of times decreased this factor to a value of 2. A 30% difference in relative intensities between different specimens was observed by Collins;[9] the particular effect of preferred orientation on the (001) reflection was also noted by Barrett.[1] Therefore this reflection was not included in the refinement. We also observed the two small unidentified peaks mentioned by Barrett[1] [lying on both sides of the ($\bar{1}$11) reflection], which cannot be indexed.
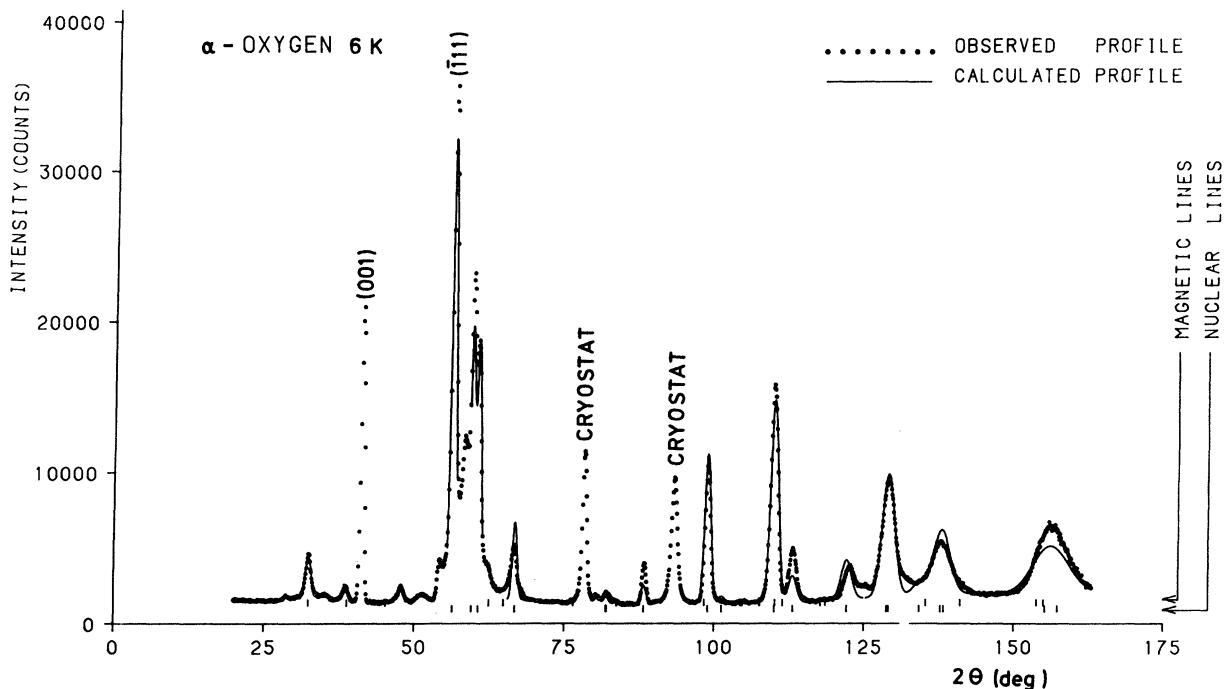
FIG. 1. Diffraction diagram of α-O_2 at 6.0 K. Solid lines are calculated data.

The results of the refinements are given in Table I, for α-O at 6 K and in Table II for 22 K. The peaks at $2\theta = 48°$ and $51°$ will be discussed together with the magnetic structure. The fact that the oxygen molecules are not tilted with respect to the normal of the ab plane (i.e., molecular axis perpendicular to this plane, Fig. 5) can be understood by noting that the exchange interaction has an optimum at zero tilt.[18]

The diffractogram of β-O_2 is shown in Fig. 3. The two unidentified peaks in the α-O_2 diffractograms are also observed here. The space group is found to be $R\bar{3}m$ (D_{3d}^5). The results of the refinement are listed in Table III (the
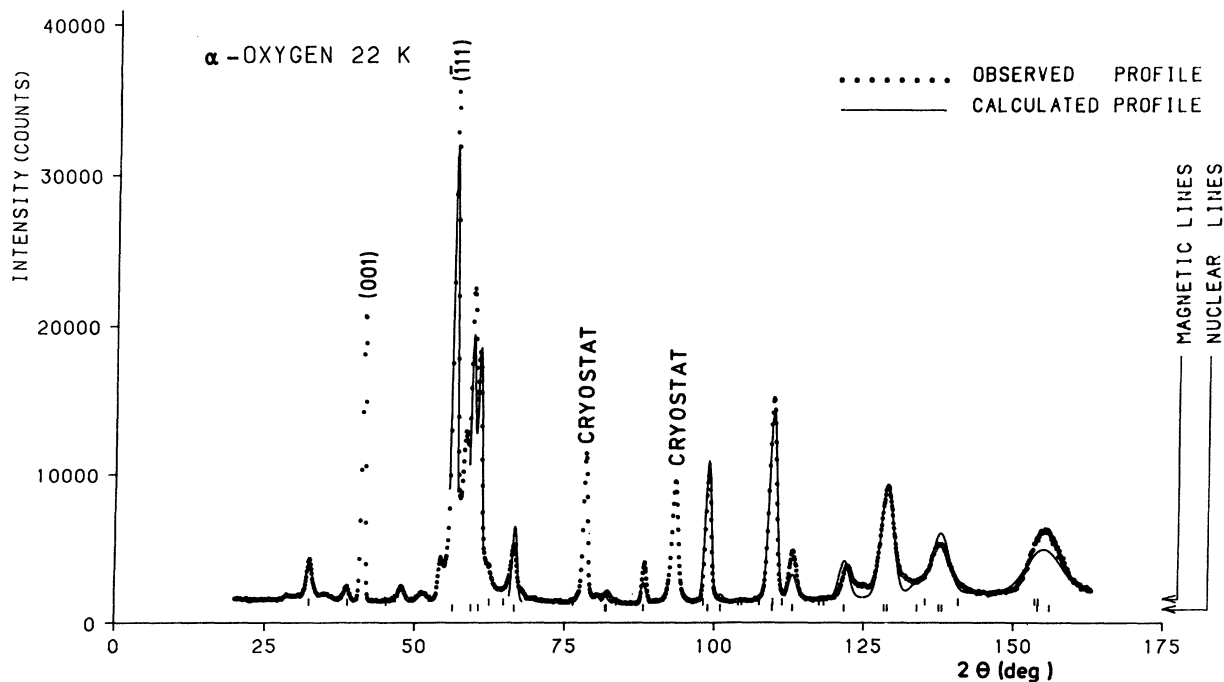

FIG. 2. Diffraction diagram of α-O_2 at 22 K. Solid lines are calculated data.

TABLE I. Experimental and calculated $(I_{tot} = I_{nuc} + I_{mag})$ results for α-O_2 at 6 K. All calculated data are results from the refinement. For the magnetic moment only x and y components (i.e., ab plane) were relaxed. A nonzero z component is not excluded, but standard deviations in calculated results then considerably increase. For the definition of the R factors see text. I should be replaced by I_{nuc} and I_{mag}, respectively.

h	k	l	2θ	I_{nuc}	I_{mag}	I_{tot}	I_{obs}
-1	0	1	31.66	0	31 342	31 342	30 603
1	0	0	38.04	0	8 335	8 335	9 387
0	1	0	44.47	0	940	940	1189
-1	1	1	55.55	311 636	0	311 636	327 116
-2	0	1	58.73	178 835	0	178 835	210 736
1	1	0	59.85	167 449	0	167 449	161 264
0	1	1	61.64	0	274	274	259
-1	0	2	64.08	0	0	0	0
-2	0	2	65.96	50 287	0	50 287	49 148
1	0	1	75.71	0	7	7	0
2	0	0	81.16	3 952	0	3 952	7 758
-1	1	2	81.25	748	0	748	1 602
-2	1	2	82.97	0	1049	1 049	2 114
0	0	2	87.45	13 153	0	13 153	22 931
2	1	0	97.53	0	4	4	0
0	2	0	98.11	124 258	0	124 258	101 352
-2	0	3	100.43	5 199	0	5 199	1 426
-3	0	1	103.57	0	155	155	0
0	1	2	103.90	0	287	287	289
-1	2	1	106.78	0	434	434	1 036
-3	1	2	109.22	213 108	0	213 108	209 609
-3	0	3	109.32	0	19	19	18
1	2	0	110.61	0	73	73	73
0	2	1	112.29	30 179	0	30 179	56 390
-1	0	3	116.92	0	845	845	1 664
-2	1	3	117.74	0	15	15	15
-3	1	1	121.27	55 345	0	55 345	52 920
-3	1	3	127.97	14 081	0	14 081	16 206
-2	2	1	128.29	198 262	0	198 262	210 727
2	0	1	133.42	24 993	0	24 993	34 812
-1	2	2	134.54	0	0	0	0
-2	2	2	136.97	83 199	0	83 199	75 638
-1	1	3	137.48	66 877	0	66 877	63 479
1	0	2	140.27	0	1405	1 405	3 250
1	2	1	152.99	0	0	0	0
3	0	0	154.17	0	38	38	43
-4	0	3	154.39	107 399	0	107 399	124 485
-4	0	2	156.47	124 819	0	124 819	159 213

Relative atom positions: $x = 0.105$, $z = 0.171$ (yields $d_{atom\text{-}atom} = 1.28$ Å)

Debye-Waller factor: $B = 1.05$ Å^2

Components of magnetic moment: $M_x = (0.28 \pm 0.20)\mu_B$, $M_y = (1.62 \pm 0.06)\mu_B$

Total magnetic moment: $M = (1.64 \pm 0.06)\mu_B$

Cell parameters: $a = 5.389$ Å; $b = 3.433$ Å, $c = 5.071$ Å, $\beta = 132.27°$ (present work)

                          $a = 5.376$ Å, $b = 3.425$ Å, $c = 5.065$ Å, $\beta = 132.17°$ (Ref. 8)

R factor (nuclear) $= 11.4$

R factor (magnetic) $= 13.7$

lattice has been described in the hexagonal setting). The (003) reflection shows a strong effect of preferred orientation and has been omitted from the refinement; it seriously influences the R factors, which are defined by

$$R = 100\sum_i |I_i(\text{obs}) - I_i(\text{calc})| \Big/ \sum_i I(\text{obs}) .$$

Therefore the statement by Krupskii et al.,[8] based on a comparison between calculated and observed x-ray intensities including the (003) reflection, that best agreement is obtained when the molecular axes are parallel to the hexagonal axis (contrary to the qualitative arguments given by Barrett[19] and Alikhanov[8]), cannot be regarded as definite.

TABLE II. Results from refinement for α-O_2 at $T = 22$ K.

Relative atom positions: $x = 0.106$, $z = 0.173$ (yields $d_{\text{atom-atom}} = 1.29$ Å)
Debye-Waller factor: $B = 1.54$ Å^2
Components of magnetic moment: $M_x = (0.34 \pm 0.16)\mu_B$, $M_y = (1.51 \pm 0.06)\mu_B$
Total magnetic moment: $M = (1.55 \pm 0.03)\mu_B$

Cell parameters:	$a = 5.403$ Å,	$b = 3.433$ Å,	$c = 5.079$ Å,	$\beta = 132.32°$ (present work, $T = 22$ K)
	$a = 5.403$ Å,	$b = 3.249$ Å,	$c = 5.086$ Å,	$\beta = 132.53°$ (Ref. 1, $T = 23$ K)
	$a = 5.404$ Å,	$b = 3.424$ Å,	$c = 5.083$ Å,	$\beta = 132.28°$ (Ref. 8, $T = 23$ K)

R factor (nuclear) $= 11.1$
R factor (magnetic) $= 20.4$

MAGNETIC FORM FACTOR OF THE O_2 MOLECULE

When dealing with a molecule the absence of spherical symmetry must be accounted for. The only parameter involved when calculating the magnetic form factor f as a function of $\sin\theta/\lambda$ is the angle ϕ between the scattering vector and the molecular axis. A similar calculation was carried out by Alikhanov et al.[20] using one Slater-type orbital (STO) for each (atomic) p orbital. However, their results are incorrect as we will show below.

In our LCAO-MO (linear combination of atomic orbitals—molecular orbitals) approach a 3-GTO (GTO denotes Gaussian-type orbital) expansion of Clementi's STO SCF AO's (self-consistent-field atomic orbitals) method was used from Ref. 21. No appreciable difference in form-factor values was obtained when using a 5-GTO expansion. The form factors have been calculated with the formulas given by Stewart.[22] The calculation has been checked for the C_{2p}-C_{2p} MO form factors. The results are shown in Fig. 4, where Alikhanov's numbers are also displayed. At first sight it looks as if Alikhanov et al. have made a mistake by averaging over the amplitudes of the form factor (calculating $\langle f \rangle^2$), instead of averaging the intensities, i.e., calculating $\langle f^2 \rangle$. It can be noted that for smaller values of $\sin\theta/\lambda$ there is but a small difference between $\langle f \rangle^2$ and $\langle f^2 \rangle$ as was noted before by Kleiner.[23]
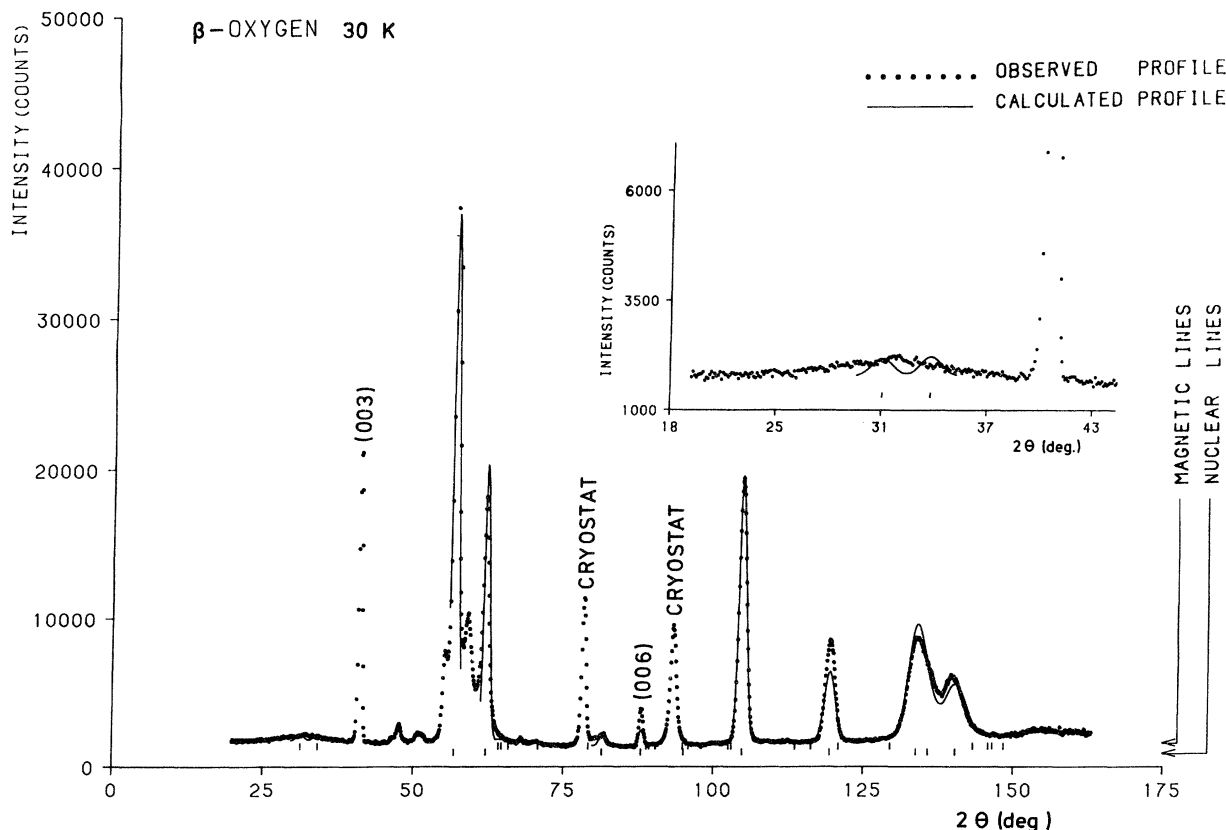

FIG. 3. Diffraction diagram of β-O_2 at 30.0 K. Solid lines are calculated data. The inset shows the diffuse magnetic scattering centered around $2\theta = 32°$.

TABLE III. Experimental and calculated $(I_{tot}=I_{nuc}+I_{mag})$ results for β-O$_2$ at $T=30$ K. Calculated results are from the refinement procedure.

h	k	L	2θ	I_{nuc}	I_{mag}	I_{tot}	I_{obs}
1	0	0	30.52	0	6429	6429	10641
1	0	1	33.38	0	6906	6906	7374
1	1	1	56.02	435924	0	435924	493575
−1	−1	2	61.33	219060	0	219060	200151
2	0	0	63.43	0	771	771	6465
1	0	4	63.96	0	0	0	0
2	0	1	65.11	0	990	990	0
2	0	2	70.02	0	354	354	528
1	1	4	80.61	8586	0	8586	15654
0	0	6	87.17	11083	0	11083	18975
2	1	0	88.08	460	462	462	240
2	0	4	88.55	0	0	0	0
2	1	1	89.59	0	636	636	72
2	1	2	94.13	0	240	240	96
−1	−1	5	94.26	3015	0	3015	1107
1	0	6	95.08	0	66	66	0
2	1	3	101.76	0	36	36	0
2	0	5	102.24	0	0	0	0
3	0	0	104.02	271185	0	271185	267051
2	1	4	112.85	0	0	0	0
1	0	7	115.54	0	264	264	0
3	0	3	118.65	104862	0	104862	132594
2	0	6	120.13	0	24	24	0
2	1	5	128.72	0	0	0	192
−2	−2	1	132.99	231240	0	231240	214245
1	1	7	134.97	84939	0	84939	90246
2	2	2	139.55	155283	0	155283	165093
3	1	0	142.49	0	114	114	108
3	1	1	145.04	0	168	168	168
1	0	8	145.72	0	612	612	636
2	0	7	147.60	0	174	174	186

Relative atom positions: $z=0.05430$ (yields $d_{atom-atom}=1.23$ Å)

Debye-Waller factor: $b=0.97$ Å^2

Cell parameters: $a=3.289$ Å; $c=11.281$ Å (present work, $T=30$ K)

                        $a=3.286$ Å, $c=11.286$ Å (Ref. 8, $T=30$ K)

R factor (nuclear) $=9.9$

R factor (magnetic) $=50.1$

Our calculated $\langle f^2 \rangle$ is in good agreement with the calculations of Kleiner and the experimental gas-phase data from Powles et al.[24] Therefore we conclude that the results of Alikhanov et al. are incorrect and that Kleiner's results were incorrectly depicted in Ref. 20.

MAGNETIC STRUCTURE OF α-OXYGEN

Two magnetic reflections have been observed in previous studies.[4,9] Our data show an additional number of weak magnetic reflections (Table I). The peaks at $2\theta=48°$ and 51° could not be accounted for; the latter was also observed in the neutron-diffraction study by Collins but not in detailed x-ray studies.[1]

The small intensity of the (010) reflection was qualitatively interpreted before (see, e.g., Refs. 1 and 7) as being due to moments directed along the monoclinic b axis [Fig. 5(a)]. This has not been determined unambiguously, for instance, because the behavior of the magnetic form factor should be taken into account correctly. Therefore we carried out a quantitative analysis. The fact that only $1.6\mu_B$ is found for the total moment per molecule can be ascribed to zero-point spin reduction and strong preferred orientation. The data indicate (Table I) that the moments are not completely directed along the b axis.

Calculations of the exchange parameter[14,25] show that the interaction between the layers is quite small and fer-
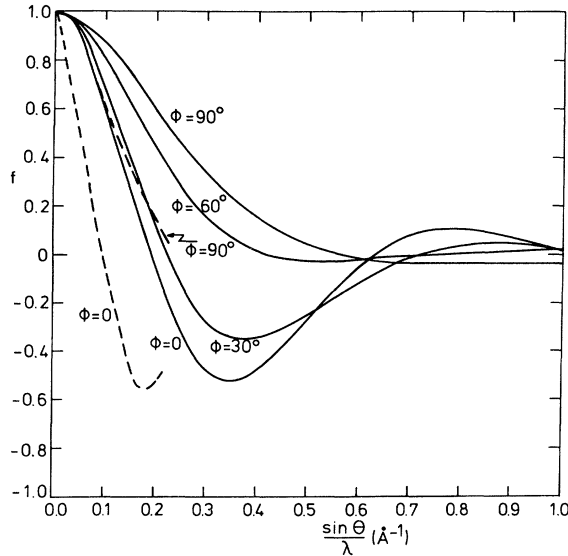
FIG. 4. Magnetic form factor of the O_2 molecule. ϕ is the angle between the scattering vector and the molecular axis. Dashed curves are from Alikhanov (Ref. 16), solid curves are present results.

FIG. 6. β-O_2 crystallographic (left) and magnetic (right) structures.

romagnetic. This suggests a ferromagnetic ordering with the four nearest-neighbor out-of-plane molecules [Fig. 5(b)]. A structure refinement rejected such a magnetic structure. The calculations in Ref. 14 cannot be expected to be very reliable for very small J values. Stephens et al.[15] stated that the magnetic structure can be qualified as two-dimensional (2D). Our neutron data at 22 K show that no appreciable spin disordering has occurred as compared to the 6-K data. Stephens et al. already noted the difficulty that $T_{\alpha\beta}$ (monolayer), the α-β transition temperature in a monolayer (2D) system, is much lower than $T_{\alpha\beta}$ (bulk), and that $T_{\alpha\beta}$ even exhibits a discontinuity when increasing the number of layers.[26] Since $T_{\alpha\beta}$ is determined by the competition between magnetic and lattice energies, it could be inferred that the halving of the transition temperature can be understood by noting that $\Delta E_{\alpha\beta}$ (lattice) is different for the monolayer and bulk. The magnetic behavior can still be 2D then. However,
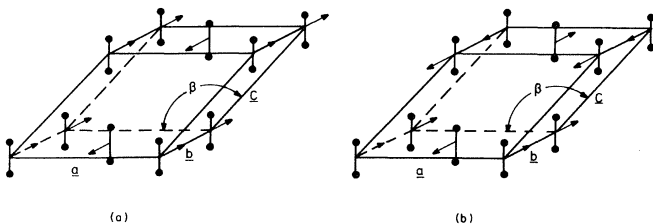
lattice-energy calculations based on a Lennard-Jones potential[27] show that the change in $\Delta E_{\alpha\beta}$(lattice) is much too small, being in disagreement with specific-heat data.[26] A continuous change in $T_{\alpha\beta}$, going from monolayer to bulk, would also be expected. Therefore we conclude that α-O_2 is a 3D magnetic system.

MAGNETIC STRUCTURE OF β-OXYGEN

A magnetic three-sublattice structure with neighboring spins making angles of 120° (Fig. 6) is very favorable from a point of view of minimum energy and in agreement with susceptibility data.[14] No quantitative analysis of neutron-diffraction data of β-oxygen has been carried out thus far. Therefore we tried such a model in the refinement procedure. Nuclear reflections have reflection conditions $h - k = 3n$ and simultaneously $h + k + 1 = 3m$, whereas for the magnetic reflections $h - k \neq 3n$ is prescribed. We have included zero coupling between adjacent hexagonal layers since three neighboring moments in a certain layer produce a zero molecular field at the nearest lattice point in the next layer. The only observable diffraction peaks that resulted from the calculation are at $2\theta = 31.3°$ and 34.2° (Table III). A magnetic moment of $1\mu_B$ per molecule was obtained when the calculated and experimental data were compared (Fig. 3). The experimental diffractogram, however, clearly shows diffuse scattering in this region, implying that LRO is absent and $1.0\mu_B$ per molecule is an underestimate. The width of this diffuse band implies a correlation length of about 12 Å (i.e., four nearest-neighbor distances), still large enough to yield a high-field magnetization curve resembling a LRO system.[10] Whether the diffuse scattering is due to elastic, quasielastic, or inelastic scattering cannot be decided on the basis of our data. A static kind of disorder is consistent with both the (nearly) temperature independence of the diffuse scattering noted by Stephens et al.[15] between 27 and 41 K and the temperature dependence of the powder susceptibility.[10]

FIG. 5. (a) α-O_2 structure with magnetic moments directed along the b axis and antiferromagnetic coupling between the layers; this arrangement is observed experimentally. (b) Same as (a) but weak ferromagnetic coupling between nearest neighbors in different layers, excluded by the present diffraction data.
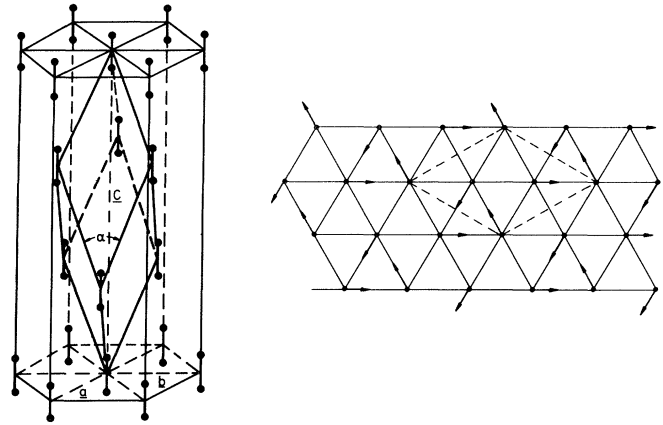
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