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Magnetism of solid oxygen

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Magnetic susceptibilities of single-crystal γ-O_2 and preferentially oriented polycrystalline samples of β-O_2 and α-O_2 have been measured, employing a mutual-inductance bridge method. The susceptibility of paramagnetic γ-O_2 is isotropic and exhibits a temperature dependence which is not strictly Curie-Weiss, due to short-range correlations and partially hindered rotation. The susceptibility of β-O_2 exhibits very little anisotropy, but has an unusual temperature dependence which is probably due to the novel behavior of the lattice constants, modulation of in-plane and out-of-plane exchange interactions, and short-range order. The susceptibility of antiferromagnetic α-O_2 is anisotropic, and data from five differently oriented samples have been analyzed in terms of principal antiferromagnetic susceptibilities. The data are consistent with the assumption that the easy axis is the twofold axis, $\vec{b}_\alpha$, though the direction $\vec{a}_\alpha$ cannot be excluded. A comprehensive analysis of the present susceptibility results and other magnetic, spectroscopic, and thermal measurements is made, with special reference to α-O_2. The perpendicular susceptibility implies an unreasonably large Néel temperature, 211 K, and a correspondingly large intersublattice exchange interaction, $|J_2|/k = 19.8$ K. The effects of anisotropy and zero-point spin deviations do not reduce this estimate by more than 15%. The temperature dependence of the parallel susceptibility suggests a much smaller value for the effective exchange interaction, $|J|/k = 5.3$ K, and appears to be well accounted for assuming a single spin-wave excitation. Antiferromagnetic resonance frequencies are analyzed and shown to yield, on assuming a dominant anisotropy equal to that of the free molecule, $|J_2|/k = 4.3$ K. An approximate separation of lattice and magnetic heat capacities is effected, and a value $|J|/k = 3.0$ K deduced. The data appear to require the assumption of two spin-wave modes. Except for the perpendicular susceptibility, experimental results suggest a Néel temperature between 30 and 40 K. Mean-field and other theories lead to similar estimates, assuming that $|J|/k$ is between 3 and 4 K. The effect of the anisotropy on T_N is minor, and no significant spin-shortening effect is predicted. Other experimental results are considered, and a disparate set of estimates for the exchange interaction and zone-boundary spin-wave energies is discussed. Including the effects of intrasublattice exchange interactions within the context of a two-sublattice model does not seem sufficient to remove the various discrepancies. An approximate calculation of relative overlap integrals and exchange interactions between different pairs of molecules in α-O_2 is made. It is suggested that a multisublattice model for the magnetic structure, and possibly one involving noncollinear sublattices, may provide an eventual resolution of the various difficulties. A "quasi-two-dimensional" description of α-O_2 is also considered, but appears not to offer a satisfactory explanation of the unusual and imperfectly correlated properties of this phase.

I. INTRODUCTION

The magnetic,[1–20] structural,[21–38] thermodynamic[39–55] and spectroscopic[56–73] properties of the condensed phases of oxygen have been under study for nearly a century. Yet important aspects of their behavior remain poorly understood. Of particular interest are the properties of the lowest-temperature solid phase, alpha oxygen, the only known antiferromagnetic molecular crystal and the only known homogeneous insulating antiferromagnet. Experimental work, especially on magnetic and spectroscopic properties, has been hindered because an isolated single crystal of α-O_2 has never been obtained. For example, estimates of the strength of the exchange interaction in the antiferromagnetically ordered state have had to be based on susceptibility data from polycrystalline samples whose degree of preferred orientation was unknown, or from theoretical fits to other magnetic or spectroscopic data only partially complete. The easy axis of antiferromagnetic alignment has not been determined unambiguously, and the detailed magnetic structure remains uncertain. No small source of difficulty in completely characterizing the magnetic properties of α-O_2 resides in the fact that the Néel transition to the paramagnetic state is anticipated by the lower-temperature structural phase transition from alpha to beta oxygen. Previous experimental data have sometimes been inconsistent, as have been deductions from these data, for both α-O_2 and the higher-temperature solid phases. It will be part of the purpose of this paper to review these discrepancies, and to suggest resolutions where possible. However, the principal aim of this paper is the presentation and analysis of new magnetic susceptibility data in powder and in larger grained, preferentially oriented samples of α-O_2, in similar samples of β-O_2, and in polycrystalline and single-crystal samples of γ-O_2. The nature and degree of the preferred orientation in these samples, as well as some important features of the solid-state transformations in oxygen, have been described and analyzed in Ref. 36, and use will be made of these results.

Gamma oxygen is cubic, space group $Pm3n$ with eight molecules per unit cell,[23] and is stable between 54.4 and 43.8 K. Two kinds of rotational disorder characterize the molecules in the unit cell; the structure is shown in Fig. 1. The susceptibility of this phase has been measured previously and found to increase with decreasing temperature.[3–7] No evidence of long-range magnetic order is found in neutron diffraction patterns from γ-O_2, though some evidence for magnetic inequivalence of the two kinds of disordered molecules per unit cell has been inferred.[12]

Beta oxygen is rhombohedral, space group $R\bar{3}m$,[22,24,26] and is stable from 43.8 to 23.9 K. The structure is shown in Fig. 2. It has been suggested that the molecules precess about the threefold axis of this phase, with angle of tilt 30° by one estimate[24] and 75° by another.[28] Arguments have been presented, however, in favor of a flipping rather than a precessional motion, with tilt angle increasing from 41° at 26 K to 49° at 42 K.[66] The basal-plane lattice constant, a, of β-O_2 increases strongly with increasing temperature, while c, the lattice constant normal to the basal plane, exhibits a slight decrease with increasing temperature.[29] The susceptibility has been measured previously and generally found to decrease with decreasing temperature.[2–7] Despite this behavior, typical of ordered antiferromagnets, no long-range order is clearly apparent in neutron diffraction patterns from polycrystalline samples of β-O_2.[8,24] There is evidence in these patterns for short-range order at 27 K.

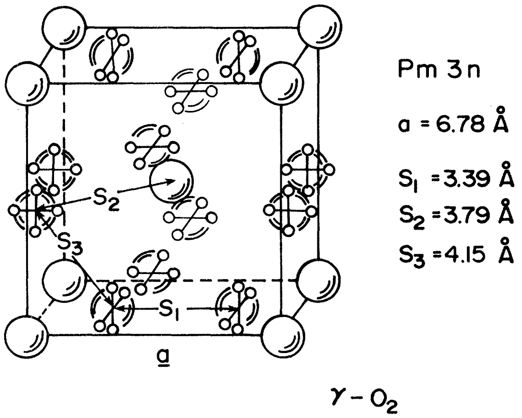

FIG. 1. Crystal structure of γ-O_2. Molecules at corners and center of unit cell are not freely rotating but rather statistically disordered in the 16(i) positions, with molecular axes along cubic threefold axes. Molecules in faces are statistically disordered in the 24(k) positions, with molecular axes along two of the three cubic axes at a given site.

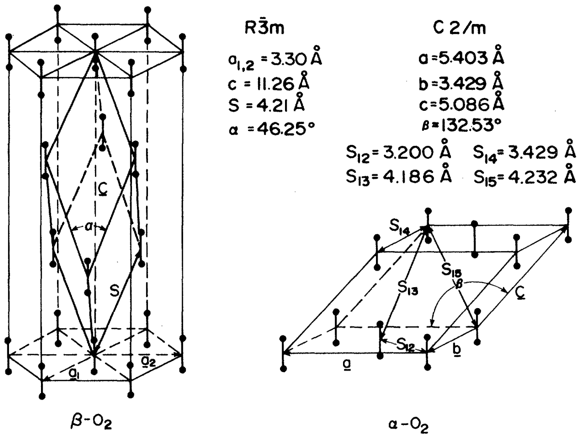

FIG. 2. Crystal structures of β-O_2 and α-O_2. Internuclear axes are drawn normal to a_1a_2 and ab planes in beta and alpha oxygen, respectively.

Alpha oxygen is monoclinic, space group $C2/m$,[25,27] and is stable below 23.9 K. The structure is shown in Fig. 2. There are two molecules in the conventional unit cell, though a chemical primitive cell containing only one molecule can be constructed. The susceptibility of this phase has been measured previously and found to decrease with decreasing temperature.[2–7] Neutron diffraction patterns from polycrystalline samples exhibit magnetic superlattice lines[8,25] whose probable identity and relative intensities suggest a two sublattice model for the antiferromagnetic structure, with moments directed along the twofold axis, $\pm\vec{b}_\alpha$.

The plan of this paper is as follows. A brief description of experimental methods is given in Sec. II. In Sec. III the experimental results of this work are presented and comparison is made with earlier susceptibility measurements. The essential findings concerning the distribution of crystallite orientations in our β-O_2 and α-O_2 samples are also summarized. In Sec. IV the magnetic susceptibility data from the α-O_2 samples are analyzed, assuming a two-sublattice model for the magnetic structure. The data are studied first independent of any assumptions concerning the crystallite orientations and then in conjunction with the results of x-ray orientation analyses. The two approaches lead to rather consistent results for the principal antiferromagnetic susceptibilities, $\chi_\perp$ and $\chi_\parallel(T)$, and a set of most probable values for these parameters is presented.

In Sec. V an attempt is made to provide as consistent a theoretical account for the magnetic properties of solid oxygen as the available data allow. We employ for this purpose not only our results but also magnetic, spectroscopic, thermal, and structural results of others. First the situation with regard to γ-O_2 and β-O_2 is surveyed. Then, in Secs. V C 1 through V C 8, the properties of α-O_2 are considered in detail. What is known concerning the magnetic structure of this phase is discussed in Sec. V C 1. Mean-field theory estimates for the Néel temperature and exchange interaction, from the observed value of $\chi_\perp$, are obtained in Sec. V C 2, and the crystal structure is discussed with a view to estimating the number of effective neighbor interactions. In Sec. V C 3 the perpendicular susceptibility is studied further, and the influences of single-molecule and crystalline anisotropy, and of zero-point spin deviations, are considered. In Sec. V C 4 the parallel susceptibility and its temperature dependence is analyzed, in order to obtain further information on the strength of the exchange interactions and the influence of the anisotropy. Antiferromagnetic resonance data are discussed in Sec. V C 5, and alternative theories for AFMR in an antiferromagnet with orthorhombic anisotropy are examined, again in order to estimate the relevant exchange and anisotropy parameters. In Sec. V C 6 the available heat-capacity data are studied. An approximate separation of lattice and magnetic contributions is effected, and the latter are analyzed employing alternative theoretical expressions. In Sec. V C 7 the question of the probable Néel temperature of α-O_2 is pursued, through the application of mean field and other theories of successively greater refinement. Finally, in Sec. V C 8 the information provided by other recent magnetic and spectroscopic studies is considered.

In the concluding Sec. VI we consider some possible explanations for the somewhat inconsistent picture that emerges from the analyses of Sec. V. The likelihood of rather important intrasublattice exchange interactions are considered, and their probable effect on the various properties is estimated. A very approximate calculation of relative exchange interactions between four distinguishable pairs of neighbors in α-O_2 is described. The results suggest that a resolution of the discrepancies uncovered in Sec. V may reside in a multisublattice model for the magnetic structure of α-O_2, and possibly one involving noncollinear sublattices. Lastly, the question of the effective lattice dimensionality of α-O_2 is considered, with a view to testing the notion that an effective dimensionality lower than three offers an alternative prospect of resolving the difficulties alluded to in previous sections.

II. EXPERIMENTAL

The methods employed in growing single crystals of γ-O_2 and effecting their transformation into polycrystalline but preferentially oriented samples of β-O_2 and α-O_2 have been described.[36] Magnetic susceptibilities were measured employing a mutual inductance bridge, operating at 155 Hz, similar to that described by Pillinger, Jastrum, and Daunt.[74] A pair of mutual-inductance coils was mounted on the oxygen cell, each coil consisting of an inner secondary winding and an outer primary winding. The two primaries were wound in the same sense, while the two secondaries were wound in opposite senses.[18] The coils could not be moved relative to the sample, necessitating corrections to the raw susceptibility data. The bridge and coils system were calibrated by equating a measurement of the susceptibility of liquid oxygen around 58 K to values from an empirical equation based on the only reliable absolute measurements of the susceptibility of liquid oxygen available.[1] The level of liquid oxygen in the cell at the time of calibration was approximately midway between the centers of the two coils sections. The exact position of the liquid level was determined by comparing the calibration bridge reading for each sample with bridge readings determined in a standard experiment where the liquid oxygen level was exactly midway between the two coils. Correction was made for small differences in temperature, molar volume, and susceptibility between the actual and standard experiments.[18] In transforming from liquid to γ-O_2, and thence to β-O_2 and α-O_2, the upper surface of the sample was observed to remain essentially plane and to move toward the lower coil. Solid-phase susceptibilities were corrected for the effects of sample contraction in the cell cross section and along the cell axis.[18]

Temperatures were determined using a copper-Constantan thermocouple[75] calibrated at the boiling points of liquids nitrogen, hydrogen, and helium. Corrections for differences between actual and standard atmospheric pressure and for the hydrostatic head effect in a liquid-nitrogen reference bath were made. The uncertainties in sample temperatures for the susceptibilities given in Sec. III are estimated to be approximately 0.5 K for γ-O_2 0.7 K for β-O_2 and 1.0 K for α-O_2.

III. RESULTS OF THE MEASUREMENTS

A. Susceptibilities

In Fig. 3 are shown the measured susceptibilities for five samples of γ-O_2 studied here. The samples

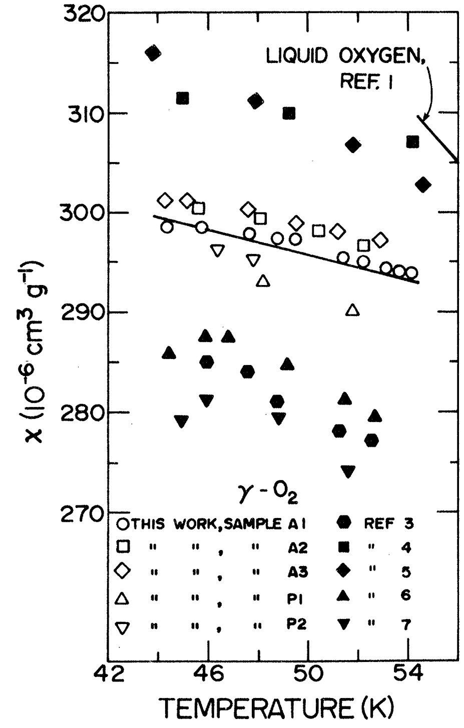

FIG. 3. Magnetic susceptibility of γ-O_2 in this and earlier work. A best line through the present data is shown.

are denoted P1, P2, A1, A2, and A3 and are the same ones discussed in Ref. 36. The letter "P" denotes a powder sample and the letter "A" denotes either a single-crystal sample of γ-O_2 or a preferentially oriented aggregate sample of β-O_2 or α-O_2.

Gamma oxygen is cubic and its susceptibility is therefore isotropic. The data from the five samples of this work span a range of 2.5% in susceptibility at constant temperature. It is probable that the differences arise from effects of sample contraction which have not been completely corrected for. It is evident that a straight line is a fair approximation to any of the five sets of data, and a mean line through all the data of the five sets, with each data point weighted equally, appears in Fig. 3. The rms deviation of the data from the line is 0.9%. An independent propagation of errors calculation of the relative uncertainty in a γ-O_2 susceptibility datum leads to an estimate of 1.0%.

The value of the susceptibility of γ-O_2 at the melting point, 54.4 K, is 293×10^{-6} $cm^3 g^{-1}$, estimated from the mean line through the data. The susceptibility of liquid oxygen at the melting point is, from the empirical equation of Ref. 1, 310×10^{-6} $cm^3 g^{-1}$. We observe, therefore, a drop in the susceptibility at the melting point of 17×10^{-6} $cm^3 g^{-1}$ or 5.5%. Kanda, Haseda, and Otsubo[4,5] observed no drop in susceptibility at the melting point, while Jamieson and Hollis Hallett[6,7] observed a considerably larger drop, about 13%. It is natural to attribute the drop in susceptibility to the decrease in molar volume on solidification and to the consequent increase in mean exchange interaction. The data of the earlier workers are also shown in Fig. 3. The differences between their results are much greater than the spread in our own data. Moreover, the data in different publications of the same authors do not agree, a fact which has hitherto gone unremarked. This applies to the liquid oxygen calibration data in these references as well (especially those of Kanda *et al.*). However, the calibration data differences do not explain (in fact, are in the opposite sense) the differences in the γ-O_2 data, nor in the β-O_2 and α-O_2 data. Jamieson and Hollis Hallett estimate their susceptibilities to be accurate to 5%. Kanda *et al.* do not give any uncertainties. We believe Kanda *et al.* may have overlooked a sample contraction effect, which when corrected for would reduce their solid phase susceptibilities relative to that of the liquid standard. This may apply also to the data of Borovik-Romanov, Orlova, and Strelkov[3(b)] shown in Fig. 3. These data, however, agree reasonably well with those of Jamieson and Hollis Hallett, though they exhibit more scatter than the selected (for clarity) examples in Fig. 3 suggest. The authors give 3% as the absolute uncertainty in these data. It is observed that our γ-O_2 susceptibilities exhibit a smaller variation with temperature, by about a factor of 2, than do those of earlier workers.

In Fig. 4 are shown the measured susceptibilities for five samples of β-O_2 studied here. These data span a range of 3.5% in susceptibility at constant temperature. In Table I appear values of the susceptibility at high and low temperatures in the range of this phase, and corresponding susceptibility difference, estimated from smooth curves (not all shown) through the data in Fig. 4. The differences vary only slightly from sample to sample, and bear no apparent relation to the magnitudes of the susceptibilities at either of the two temperatures. The magnitude order of the five sets of β-O_2 susceptibility data bears no apparent relation to that observed in α-O_2 daughter samples (to be discussed) nor in the magnitude order of the γ-O_2 parent sample susceptibilities. Nor does the magnitude order correlate with the average orientation of the trigonal axis of β-O_2, deduced from analysis of the Laue photographs of these samples. There is some slight correlation between the $\Delta\chi$ in Table I and the magnitude order of the α-O_2 susceptibilities, to be presented, but this is considered fortuitous. These observations are consistent with the fact that the relative uncertainties in the β-O_2 susceptibilities, about 1.2%, and in the susceptibility differences are as large or larger than the variation in the differences among the five samples.

Also shown in Fig. 4 are β-O_2 susceptibility data, from powder samples, measured by Borovik-

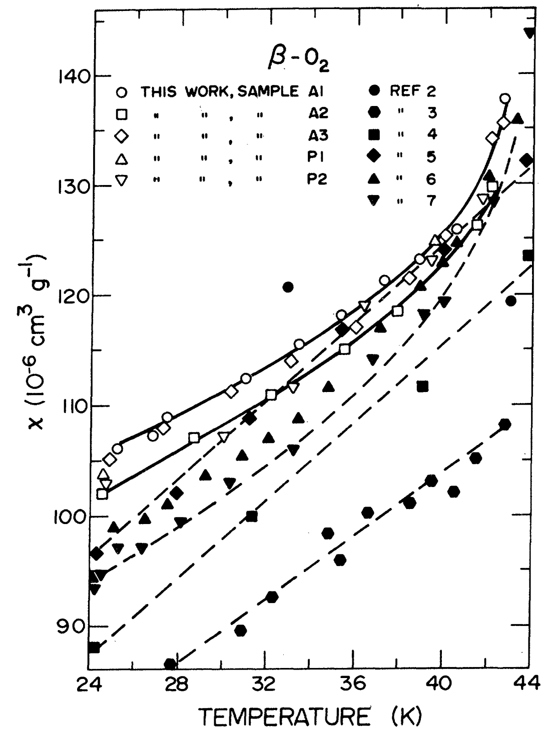

FIG. 4. Magnetic susceptibility of β-O_2 in this and earlier work. Solid and dashed curves are drawn through present and earlier data, respectively.

Romanov *et al.*,[3] by Kanda *et al.*,[4,5] and by Jamieson and Hollis Hallett,[6,7] as well as two data obtained by Perrier and Kamerlingh Onnes.[2] The data of Kanda *et al.* differ considerably depending on the reference and in either case exhibit a more nearly linear dependence on temperature than do the data of Jamieson and Hollis Hallett, or our own. The data of Borovik-Romanov *et al.* also exhibit a nearly linear temperature dependence and are the smallest β-O_2 susceptibility data ever observed. From smooth curves through these data we have estimated susceptibility values at the two temperatures and have entered these in Table I. The accuracy of these estimates is believed to be 0.3 K and 1.5×10^{-6} $cm^3 g^{-1}$. The high-temperature data from these references are sometimes similar to our own, though somewhat smaller generally. The low-temperature data are considerably smaller than our own. The earlier conjecture that Kanda *et al.* may have overlooked a sample contraction effect would suggest that their β-O_2 susceptibilities should be smaller than they appear.

In Fig. 5 are shown the measured susceptibilities for five samples of α-O_2 studied here. In Table II appear values of the susceptibility at various temperatures in the range of this phase, estimated from smooth curves through the data. Also given in Table II is the susceptibility difference, for each sample, between 22.5 and 5 K. This difference is observed to increase as the susceptibility decreases, except for samples P2 and A3 which are most similar in susceptibility. The three samples with smallest susceptibility are those consisting of preferentially oriented α-O_2 aggregates. The susceptibilities of the powder samples P1 and P2 are significantly different, so that not both and possibly neither sample is truly randomly oriented. The relative uncertainties in the α-O_2 susceptibility data among the various samples are estimated to be 1.1% at 5 K and 1.7% at 22.5 K. The correction for sample contraction effects[18] is the same for all data of a given sample, since the molar volume of α-O_2 is temperature independent.[29] Relative susceptibilities at different temperatures are therefore not uncertain from this source.

TABLE I. Temperature dependence of the susceptibility of beta oxygen in this and earlier work (table entries are read from best smooth curves through data).

Sample	χ(42 K)	χ(25 K)	$\Delta\chi$
	all times 10^{-6} $cm^3 g^{-1}$		
A1	132.1	106.2	25.9
A2	128.1	102.5	25.6
A3	131.4	105.3	26.1
P1	(131)	104.3	(26.7)
P2	129.6	103.1	26.5
Ref. 3	107	82	25
Ref. 4	119	89	30
Ref. 5	128	98	30
Ref. 6	129	98	31
Ref. 7	127	95	32

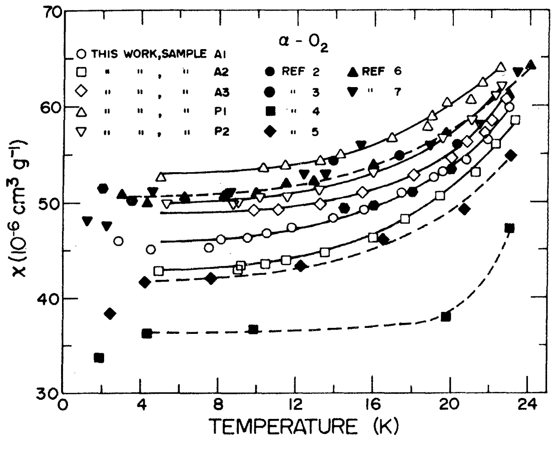

FIG. 5. Magnetic susceptibility of α-O_2 in this and earlier work. Solid and dashed curves are drawn through present and earlier data, respectively.

TABLE II. Temperature dependence of the susceptibility of alpha oxygen in this and earlier work (table entries are read from best smooth curves through data).

Sample	χ(22.5 K)	χ(20 K)	χ(15 K)	χ(10 K)	χ(5 K)	χ(22.5 K) $-$ χ(5 K)
			all times 10^{-6} cm^3 g^{-1}			
P1	63.9	60.1	55.3	53.5	53.0	10.9
P2	61.7	57.1	52.4	50.4	49.9	11.8
A3	60.3	55.0	50.8	49.2	(48.9)	(11.4)
A1	58.4	53.7	48.9	46.5	45.9	12.5
A2	56.4	51.4	45.6	43.5	42.8	13.6
Ref. 4	44	39	37	36	36	8
Ref. 5	54	49	44	43	42	12
Ref. 6	61	58	53	51	51	10
Ref. 7	60	57	54	52	51	9

Also shown in Fig. 5 are the α-O_2 susceptibility data, from powder samples, of Perrier and Kamerlingh Onnes,[2] of Borovik-Romanov *et al.*,[3] of Kanda *et al.*,[4,5] and of Jamieson and Hollis Hallett.[6,7] The increasing susceptibility at low temperatures in the data of Borovik-Romanov is probably due to a paramagnetic impurity. The data of Perrier and Kamerlingh Onnes have been corrected (increased by about 1.9%) for the varying density of their sample between liquid and alpha oxygen and for the poor value of the density of liquid oxygen they used. This correction was recommended by these authors as soon as more reliable densities became available. These data are similar to those of our sample A3 at about 20 K, but below that exhibit a smaller decrease with decreasing temperature. Unfortunately, they do not extend below 13.9 K, so that it is difficult to make further comparison. The data of Kanda *et al.* and of Jamieson and Hollis Hallett extend to lower temperatures. These authors do not appear to consider the sudden decrease in susceptibility sometimes observed between 4 and 2 K to be significant. From smooth curves through these data we have estimated the susceptibility at selected temperatures and have entered this information in Table II. The accuracy of these estimates is about 0.3 K and 1.5×10^{-6} cm^3 g^{-1}. The data of Kanda *et al.* are lower than those of Jamieson and Hollis Hallett and exhibit a larger difference between 22.5 and 5 K. This relation is similar to that observed in our data. But the data of previous workers are not fully consistent with our own, usually exhibiting a smaller or less uniform tempera-

TABLE III. Orientations, fractional weights and uncertainties, and resulting magnetic character in three α-O_2 samples.

	Sample A1				Sample A2				Sample A3		
Orientation	w_f	$\sigma(w_f)$	$\langle\cos^2\rho\rangle$[a]	Orientation	w_f	$\sigma(w_f)$	$\langle\cos^2\rho\rangle$[a]	Orientation	w_f	$\sigma(w_f)$	$\langle\cos^2\rho\rangle$[a]
I	0.097	0.032	0.474	IX	0.052	0.031	0.459	XVIII	0.133	0.126	0.469
II	0.039	0.018	0.357	X	0.135	0.069	0.354	XIX	0.073	0.028	0.485
III	0.172	0.076	0.469	XI	0.089	0.046	0.486	XX	0.026	0.016	0.340
IV	0.206	0.076	0.443	XII	0.086	0.037	0.466	XXI	0.079	0.034	0.315
V	0.257	0.157	0.476	XIII	0.158	0.070	0.387	XXII	0.385	0.159	0.349
VI	0.107	0.164	0.472	XIV	0.055	0.025	0.490	XXIII	0.126	0.053	0.431
VII	0.058	0.020	0.031	XV	0.051	0.028	0.454	XXIV	0.039	0.022	0.439
VIII	0.064	0.240	0.064	XVI	0.106	0.045	0.320	XXV	0.069	0.079	0.129
				XVII	0.267	0.114	0.464	XXVI	0.069	0.041	0.471
	$c_\perp = 0.590$ (0.095)[b]				$c_\perp = 0.576$ (0.009)[b]				$c_\perp = 0.622$ (0.028)[b]		

[a] $\langle\cos^2\rho\rangle_i = (\frac{1}{3})\sum_j \cos^2\rho_{ij}$ where ρ_{ij} is the angle between the applied magnetic field and the $\vec{b}_\alpha$ axis for the jth modification of the ith orientation

[b] $c_\perp$ is the coefficient of $\chi_\perp$, and $(1-c_\perp)$ that of $\chi_\parallel$, in the sample susceptibility if it is assumed that the magnetic moments are along $\pm\vec{b}_\alpha$. Numbers in parentheses are standard deviations in $c_\perp$ calculated from those in the fractional weights.

ture dependence. This is particularly apparent in the data of Ref. 4, where a considerably smaller susceptibility than that of even our most preferentially oriented sample was reported, but with only a small temperature variation between 20 and 4 K. If a sample contraction effect was indeed overlooked by Kanda *et al.*, then their α-O_2 susceptibilities should be smaller yet. It is evident that few, if any, of the earlier data are representative of randomly oriented powder samples, and the data of Ref. 4 seem especially questionable.

B. Orientation

Transmission Laue photographs of the solid oxygen samples under discussion and the method used in their analysis have been described in Ref. 36. Gamma oxygen samples A1, A2, and A3 were shown to be single crystals of differing orientation. The β-O_2 and α-O_2 samples derived from these γ-O_2 single crystals were shown to be composed of 8, 9, and 9 principal orientations, of varying weight, in samples A1, A2, and A3, respectively. Each orientation in α-O_2 was shown to consist of three "modifications" of essentially equal weight. These modifications share an approximately identical $[001]_\alpha$ direction but are otherwise rotated with respect to one another by approximately 120°; i.e., their [010] axes are related by a common axis which is almost threefold. This crystallographic "degeneracy" limits somewhat the conclusions that can be drawn from the susceptibility data. Some deductions are possible however, and will be made in Sec. IV. In Table III we summarize the essential findings regarding the identity and weight of the orientations making up the α-O_2 samples A1, A2, and A3. The remaining columns of Table III will be explained in Sec. IV.

IV. ANALYSIS OF SUSCEPTIBILITY DATA

In this section we will extract, first from the susceptibility data alone and then from these data in conjunction with the results of the orientation analyses, information concerning the magnitudes and temperature dependences of the principal crystal susceptibilities in α-O_2. To this end some simple assumptions will be made, the justification of which will eventually be examined.

The simplest initial assumption is that α-O_2 is a two-sublattice antiferromagnet. The evidence for this will be discussed in Sec. V. A second assumption is that of uniaxial symmetry. This is clearly not exact for a monoclinic crystal, but in Sec. V it will be shown that departures from uniaxial symmetry do not strongly affect the analysis of the susceptibility data. Given the above we may write[76]

$$\chi_\theta = \chi_\parallel \cos^2\theta + \chi_\perp \sin^2\theta \tag{1}$$

for the susceptibility of α-O_2 in the direction of a magnetic field applied at an angle θ from the antiferromagnetic easy axis along which the susceptibility takes the principal value $\chi_\parallel$. Here $\chi_\perp$ is the principal value of the susceptibility normal to the easy axis. A small temperature dependence in $\chi_\perp$ can result from quantum-mechanical effects[77] or from a temperature dependence of the exchange integral. The first effect is not large however, and there are reasons for thinking the second effect will be unimportant in α-O_2; therefore $\chi_\perp$ will be assumed to be independent of temperature. It will also be assumed that $\chi_\parallel$ at 0 K is zero. This is the case if Van Vleck T-independent contributions[78] to the susceptibility (from orbital excited states) are small. They are presumably small in oxygen in view of the large separation, 7918 cm^{-1}, between the $^3\Sigma_g^-$ ground state and the $^1\Delta_g$ first excited state.[79] An order of magnitude calculation will be made for this contribution in Sec. V. A final assumption will be made, that $\chi_\parallel$ at 5 K is also essentially zero. This is a safe assumption if 5 K is not much more than 10% of the true Néel temperature of α-O_2. The latter is not the same as $T_{\alpha\beta} = 23.9$ K but higher. This also will be discussed in Sec. V. The fact that the susceptibilities in Fig. 5 do not change very much between 10 and 5 K supports this assumption.

One may now write for the measured susceptibility of each of the five α-O_2 samples

$$\chi_i(T) = c_i\chi_\perp + (1-c_i)\chi_\parallel(T) \ , \tag{2}$$

where c_i is a sample dependent constant between 0 and 1, $\chi_\perp$ and $\chi_\parallel(T)$ are the principal crystal susceptibilities and where $i =$ A1, A2, A3, P1, or P2. With the approximations discussed above one has

$$\kappa_i = \chi_i(5\text{ K}) \approx c_i\chi_\perp \ , \tag{3}$$

$$\delta_i = \chi_i(22.5\text{ K}) - \kappa_i \approx (1-c_i)\chi_\parallel(22.5\text{ K}) \ , \tag{4}$$

where the reference temperature 22.5 K has been used since it is the highest temperature included within the range of each of the five sets of data. The most reliable values for $\chi_\perp$ and $\chi_\parallel$ (22.5 K) are obtained on using the data from the two most widely separated samples, A2 and P1, to solve for the c_i and principal susceptibilities. Using the $\chi_i(T)$ in Table II there results: $\chi_\perp = 94.2 \times 10^{-6}$ cm^{3}g^{-1}, $\chi_\parallel(22.5\text{ K}) = 24.9 \times 10^{-6}$ cm^{3}g^{-1}, $c_{A2} = 0.454$, and $c_{P1} = 0.563$. The three other c_i can be obtained by minimizing

$$\phi = \sum_i \phi_i = \sum_i \{(\kappa_i - c_i\chi_\perp)^2 + [\delta_i - (1-c_i)\chi_\parallel(22.5\text{ K})]^2\} \ . \tag{5}$$

On setting $\partial\phi/\partial c_i = 0$ there results: $c_{A1} = 0.486$, $c_{A3} = 0.516$, and $c_{P2} = 0.530$. The observed susceptibilities at 5 and 22.5 K are fitted to within 0.5% by these parameters. From the measured susceptibilities at 10, 15, and 20 K, the parallel susceptibility, and its standard deviation, is calculated to be: $\chi_{\parallel}(20\text{ K}) = 15.0 \pm 1.3$, $\chi_{\parallel}(15\text{ K}) = 5.1 \pm 0.6$, and $\chi_{\parallel}(10\text{ K}) = 1.1 \pm 0.2$, all $\times 10^{-6}\text{ cm}^3\text{ g}^{-1}$. All the measured susceptibilities at 10, 15, and 20 K are fitted to 1.5% or better by these parameters.

The standard deviations indicated above do not represent the real uncertainties in $\chi_{\parallel}$ or $\chi_{\perp}$. A propagation of errors calculation[18] shows that $\chi_{\parallel}$ and $\chi_{\perp}$ are characterized by relative uncertainties of about 30%, if one takes the uncertainties in the α-O_2 data as ranging from 1.1 to 1.7%. The c_i determined above are also uncertain by about 30%. For a randomly oriented polycrystalline sample c_i takes the value $\frac{2}{3}$ in Eq. (2). Each of the c_i obtained above is substantially less than $\frac{2}{3}$. But considering the uncertainty in the c_i, the susceptibilities of either sample P1 or P2 are not necessarily uncharacteristic of a randomly oriented powder sample. Were one to set, arbitrarily, $c_{\text{P1}} = 0.667$, then Eqs. (3) through (5) lead to the values: $\chi_{\perp} = 79.5 \times 10^{-6}\text{ cm}^3\text{ g}^{-1}$; $\chi_{\parallel}(22.5\text{ K}) = 30.5$, $\chi_{\parallel}(20\text{ K}) = 18.7$, $\chi_{\parallel}(15\text{ K}) = 6.3$, and $\chi_{\parallel}(10\text{ K}) = 1.3$, all $\times 10^{-6}\text{ cm}^3\text{ g}^{-1}$; and $c_{\text{A1}} = 0.576$, $c_{\text{A2}} = 0.538$, $c_{\text{A3}} = 0.611$, and $c_{\text{P2}} = 0.628$. The fit to the observed susceptibilities is only slightly inferior, using these parameters, to that obtained with the previous set.

The susceptibility data may also be analyzed in conjunction with the x-ray-determined distributions of orientations, with a view to confirming the hypothesis that the spin alignment in α-O_2 is along the twofold axis, $\vec{b}_{\alpha} = [010]_{\alpha}$. It is apparent that if three modifications of α-O_2, related to one another as described in Sec. III B, are present in equal amounts, then susceptibility measurements cannot determine the orientation of the easy axis, or its component, in the *ab* plane. It is easy to show[18] that the susceptibility measured in any direction in the *ab* plane is

$$\chi_{ab} = \tfrac{1}{2}\chi_{\parallel} + \tfrac{1}{2}\chi_{\perp} \ . \tag{6}$$

There is no angular dependence, due to the averaging effect of the three modifications. Suppose on the other hand that the susceptibility is measured out of the common *ab* plane, at an angle ϕ from the common $[001]_{\alpha}$ direction (normal to *ab* plane). The susceptibility in this case is[18]

$$\chi'_{\phi} = (\tfrac{1}{2}\sin^2\phi)\chi_{\parallel} + (1 - \tfrac{1}{2}\sin^2\phi)\chi_{\perp} \ , \tag{7}$$

where the prime distinguishes this from the more general formula, Eq. (1), already given. The coefficient of $\chi_{\parallel}$ cannot exceed 0.5.

In Table III are presented the calculated coefficients of $\chi_{\perp}$, called $c_{\perp}$, for α-O_2 samples A1, A2, and A3. It is assumed that the three modifications of α-O_2 per orientation are equally present, that the fractional weights for each orientation, from Ref. 36, apply and that $\vec{b}_{\alpha}$ is the easy axis of each modification. In obtaining these results, Eq. (7) was not actually applied, since the $[001]_{\alpha}$ directions differ somewhat among the three modifications per orientation. Instead $c_{\perp}$ has been calculated from

$$c_{\perp} = 1 - \sum_i w_{if}\langle\cos^2\rho\rangle_i \ , \tag{8}$$

where $\langle\cos^2\rho\rangle_i = \frac{1}{3}\sum_j \cos^2\rho_{ij}$ and where ρ_{ij} is the angle between the applied field and $\vec{b}_{\alpha}$ for the jth modification of the ith orientation. The standard deviations in the $c_{\perp}$ were determined by a propagation of errors calculation[18] from the standard deviations in the w_{if}, and are also given in Table III.

It is possible now to show that one previous suggestion for the magnetic structure in α-O_2 can be eliminated using the present results. It has been suggested[27] that the magnetic moments are along the $(001)_{\alpha}$ plane normal direction in α-O_2, i.e., parallel to the molecular axes. In this case the three modifications per orientation would give essentially the same susceptibility. With ϕ the angle between the $(001)_{\alpha}$ direction and the applied field, the coefficient of $\chi_{\perp}$ in the measured susceptibility would be

$$c_{\perp} = 1 - \sum_i w_{if}\langle\cos^2\phi\rangle_i \tag{9}$$

a quite different result from Eq. (8). If $c_{\perp}$ is calculated from Eq. (9) it is found to equal 0.821, 0.849, and 0.758 for samples A1, A2, and A3, respectively. These values are believed to be too much at variance with those determined from the susceptibility data alone. They are also inconsistent with the susceptibilities of the powder samples, P1 and P2, for which $c_{\perp}$ is presumably not very different from 0.667. In order for the susceptibilities of samples P1 and P2 to be larger than those of samples A1, A2, and A3, as observed, it would have to be assumed that $\chi_{\parallel} > \chi_{\perp}$. This is physically unreasonable.

It has been found that for the three preferentially oriented samples, $c_{\perp}(\text{A3}) > c_{\perp}(\text{A1}) > c_{\perp}(\text{A2})$, with each coefficient less than that expected for a randomly oriented polycrystalline sample, $c_{\perp} = 0.667$. The magnitude order of the observed susceptibilities is consistent with the familiar circumstance that $\chi_{\perp} > \chi_{\parallel}$ in the antiferromagnetic regime. To pursue this comparison, Eq. (2) may be rewritten in the form

$$\chi_i(T) = \chi_{\parallel}(T) + [\chi_{\perp}(T) - \chi_{\parallel}(T)]c_i \ , \tag{10}$$

where $\chi_{\perp}$ is now allowed a temperature dependence. A linear least-squares fitting of the parameters $\chi_{\parallel}(T)$ and $\chi_{\perp}(T)$ can be performed, using the susceptibility values from Table II and the x-ray-determined c_i (c_{P1} and c_{P2} taken to be 0.667). This analysis is performed at each of the temperatures 22.5, 20, 15, 10, and 5 K, and $\chi_{\parallel}(5\text{ K})$ is constrained to be zero. There results: $\chi_{\parallel} = 25.0$, 15.2, 5.9, and 1.6, all $\times 10^{-6}$

cm^3 g^{-1}, at 22.5, 20, 15, and 10 K, respectively; and $\chi_\perp = 81.2$, 79.6, 77.4, 76.9, and 77.0, all $\times 10^{-6}$ cm^3 g^{-1}, at 22.5, 20, 15, 10, and 5 K, respectively. The uncertainties in the $\chi_\parallel$ values are several times larger than in the preceding fitting attempts where the x-ray determined c_i were not employed. The uncertainties in the $\chi_\perp$ values are about 5%.

It is arguable that since the x-ray determined c_i are relatively more uncertain than the observed $\chi_i(T)$, Eq. (10) should be rewritten so that the $\chi_i(T)$ are the independent variables:

$$c_i = -\{\chi_\parallel(T)/[\chi_\perp(T) - \chi_\parallel(T)]\} + [\chi_\perp(T) - \chi_\parallel(T)]^{-1}\chi_i(T) \quad . \tag{11}$$

A linear least-squares fit based on this equation and with the other constraints the same yields: $\chi_\parallel = 28.8$, 16.8, 6.6, and 2.1, all $\times 10^{-6}$ cm^3 g^{-1}, at 22.5, 20, 15, and 10 K, respectively; and $\chi_\perp = 78.9$, 78.7, 77.0, 76.6, and 77.0, all $\times 10^{-6}$ cm^3 g^{-1}, at 22.5, 20, 15, 10, and 5 K, respectively. Uncertainties are similar to those in the preceding list.

Given the uncertainties, neither the difference between the $\chi_\perp$ values in the two fitting attempts nor the slight temperature dependence in $\chi_\perp$ are significant. The $\chi_\parallel$ values in the two fits also are rather similar. In either case the overall fit to the susceptibility data is less good than when the x-ray determined c_i were not used, though differences between observed and calculated susceptibilities do not exceed 3% in even the worst cases and are generally less than 2%.

A final approach is to calculate values of $\chi_\perp$ and $\chi_\parallel$ from the data of each sample separately, after that averaging to obtain a mean value over the five samples. The x-ray determined c_i, $\chi_\parallel(5\text{ K}) = 0$, and $\chi_\perp = \text{constant}$ are assumed. There results: $\chi_\perp = 77.0 \pm 2 \times 10^{-6}$ cm^3 g^{-1}; and $\chi_\parallel = 32.2 \pm 2.0$, 19.7 ± 2.0, 6.7 ± 0.9, and 1.4 ± 0.3, all $\times 10^{-6}$ cm^3 g^{-1}, at 22.5, 20, 15, and 10 K, respectively. In this list the uncertainties indicated are standard deviations in the mean values obtained. A propagation-of-errors calculation[18] based on the uncertainties in the observed $\chi_i(T)$ and in the x-ray determined c_i yields more realistic uncertainties of about 10% in $\chi_\perp$ and from 20 to 30% in $\chi_\parallel$.

Argument as to which set of principal susceptibilities is best is unfruitful in view of the uncertainties. It is believed that the first set presented in this section, with $\chi_\perp = 94.2 \times 10^{-6}$ cm^3 g^{-1}, is least reliable because no use is made of the x-ray results and because the value of $c_{\text{P1}} (= 0.563)$ is considerably smaller than the random powder value, 0.667. Averaging over all the other sets obtained in this section leads to the values: $\chi_\perp = 78 \pm 8 \times 10^{-6}$ cm^3 g^{-1}, with negligible temperature dependence; and $\chi_\parallel = 29.1 \pm 7$, 17.6 ± 4, 6.4 ± 1.5, and 1.6 ± 0.5, all $\times 10^{-6}$ cm^3 g^{-1}, at 22.5, 20, 15, and 10 K, respectively, with $\chi_\parallel(5\text{ K}) = 0$ assumed.

V. DISCUSSION

In this section an attempt will be made to provide as consistent a description of the magnetic properties of the solid phases of oxygen as the available data permit, with particular reference to α-O$_2$. It is our belief that recent discussions have sometimes underestimated the difficulties in the way of a really satisfactory understanding of the observed magnetic behavior, and that a critical review of our knowledge of the magnetic properties of solid oxygen would prove useful.

All susceptibility data presented in the foregoing include diamagnetic and Van Vleck temperature-independent paramagnetic contributions. An accepted value[80] for the diamagnetic susceptibility of the oxygen atom as a chemical substituent is -4.6×10^{-6} cm^3 mole^{-1}. We take as a sufficiently good approximation to the diamagnetic susceptibility of molecular oxygen the value -9.2×10^{-6} cm^3 mole^{-1}, or -0.29×10^{-6} cm^3 g^{-1}. The quadratic Zeeman term usually omitted from the Hamiltonian leads to a Van Vleck temperature-independent contribution to the susceptibility from unpopulated orbital excited states.[78]

$$\chi_{\text{VV}} = N\mu_B^2(2-g)/\lambda \quad , \tag{12}$$

where λ is the spin-orbit coupling constant and the other symbols have their usual meanings. For molecular oxygen,[81] $\lambda = -21$ cm^{-1} and $(2-g) \leq 0.01$. Therefore $\chi_{\text{VV}} \leq 1.24 \times 10^{-4}$ cm^3 mole^{-1} $= 3.9 \times 10^{-6}$ cm^3 g^{-1}. The total temperature-independent contribution is approximately 3.6×10^{-6} cm^3 g^{-1}, which is small relative to the observed susceptibilities of solid oxygen and probably an overestimate.

A. Gamma oxygen

Our data and those of previous workers reveal an increasing susceptibility with decreasing temperature throughout all (or most) of the stability range of γ-O$_2$. The susceptibility has been said previously[3–7] to follow a Curie-Weiss law, but we think such a statement requires considerable qualification. Reasonable looking fits to the data can be obtained with a very large Weiss constant ($\Theta \approx 150$ K) and a very large Curie constant ($C \approx 1.9$ cm^3 deg mole^{-1}). But the validity of the Curie-Weiss law depends upon Θ not being large compared to T, which is not fulfilled here. Equally important, the Curie constant

$$C = Ng^2\mu_B^2 S(S+1)/3k \tag{13}$$

equals 1.00 cm^3 deg mole^{-1} for $g = 2.00$ and $S = 1$. The value $g = 2.00$ is appropriate to the orbitally nondegenerate ground state of molecular oxygen, $^3\Sigma_g^-$. Spin-orbit interaction can mix orbital angular momentum into the ground state, leading to a value of g different from 2.00. But the nearest orbital excited state, $^1\Delta_g$, is 7918 cm^{-1} above $^3\Sigma_g^-$ and the effect of such mixing should be small. Microwave spectra[81] of gaseous oxygen support the value $g = 2.00$. In the condensed phases the ground to excited-state separations[56, 57] are essentially the same as in the free molecule, and no significant shift in g is expected. Any anisotropy induced in g by crystal fields of symmetry lower than cubic is probably also insignificant, though magnetic resonance experiments are wanting to test this.

Fixing the Curie constant at 1.00 $\mathrm{cm}^3\,\mathrm{deg\,mole}^{-1}$ leads to a Θ still not small compared to T, and one which exhibits a pronounced temperature dependence. Using our (mean) data there results $\Theta = 52.2$ K at $T = 54.2$ K and $\Theta = 60.4$ K at $T = 44.3$ K. Similar trends in Θ occur for the data of others. Correcting the observed susceptibilities for diamagnetic and Van Vleck temperature-independent contributions, shifts the values of Θ up about 1.5 K but leaves the temperature dependence unchanged. It is questionable whether any Curie-Weiss fit over such a limited temperature range (44 to 54 K) and with $\Theta > T$ has much significance. However, some plausibility attaches to the temperature dependence of Θ itself. Between 54 and 44 K the lattice parameter of γ-O_2 decreases[29] by 0.9%. This should presumably lead to an enhanced average exchange interaction and, therefore, to an increase in Θ with decreasing temperature.

The nearest orbital excited state is some $200kT$ above the $^3\Sigma_g^-$ ground state, while the zero-field splitting of the triplet ground state [$\delta/k = 5.70$ K (Ref. 81)] is small compared to kT in the γ-O_2 temperature range. These are the usual conditions for the validity of the Curie-Weiss law. Its apparent failure here may be due to the significant size of the rotational spacings relative to kT at these temperatures (the γ-O_2 crystal structure permits considerable if hindered rotation), or to the presence of short-range correlations which are neglected in any first-order mean-field theory.

It is worth mentioning in this connection that the susceptibility of liquid oxygen also fails to be fit completely satisfactorily by a Curie-Weiss law. With $C = 1.00$ $\mathrm{cm}^3\,\mathrm{deg\,mole}^{-1}$, Θ varies from 39.8 K at $T = 90.1$ K to 46.5 K at $T = 54.4$ K, using the results of Ref. 1. The structural similarities between liquid and gamma oxygen have been noted before.[65, 70] It has to be considered that both rotational effects and short-range correlations in the liquid[21] may influence the susceptibility in this phase as well.

B. Beta oxygen

From the very similar differences in susceptibility, between 42 and 25 K, observed for several different samples of β-O_2 studied here, it seems likely that any anisotropy in the susceptibility of this phase is quite small. The question arises however, do the differences between the 25-K susceptibility values observed here and those observed in earlier work argue for substantial anisotropy in the susceptibility of this phase? Consideration suggests not. Among the five samples studied by us there is a range of only 3.5% in the 25 K susceptibilities. The same samples, after transformation to α-O_2, exhibit a range of 24% in susceptibility at 5 K. If the anisotropy in the susceptibility of β-O_2 is only about one-seventh as large as that in α-O_2, then the differences between our 25 K susceptibilities and those of previous workers would suggest that their samples were almost completely aligned. But this is disproved by their α-O_2 data, which exhibit no evidence of such extreme preferred orientation. We believe that other factors than anisotropy are responsible for the differences between our own and earlier data.

An interesting feature of the magnetism in β-O_2 is that the susceptibility decreases with decreasing temperature. Such behavior is typically seen in the case of ordered antiferromagnets below their Néel temperature. Yet neutron diffraction data[8, 24] on polycrystalline samples of β-O_2 fail to exhibit distinct magnetic diffraction lines, though there is some evidence for enhanced intensity in nuclear lines that may be due to magnetic contributions. The simplest kind of antiferromagnetic structure for β-O_2 would consist of antiferromagnetically aligned (00.1) layers, within which the moments would be aligned ferromagnetically. However, no higher order (00.3) magnetic reflection (as is observed in $CoCl_2$, also $R\bar{3}m$, for example)[82] appears in the pattern. Such a magnetic structure would require a radical realignment of magnetic moments on transforming to α-O_2, where there is evidence that the (001) layers [which are slightly distorted daughters of (00.1) β-O_2 layers] are antiferromagnetically ordered. Difficulties also arise in the case of a pseudohelical arrangement of three ferromagnetic (00.1) layers per unit cell, with the net ferromagnetic moment per layer rotated 120° and 240° from layer to layer. This possibility may deserve further consideration perhaps, since it would not double the chemical unit cell and so would not lead to (unobserved) superlattice lines.

In a given (00.1) layer in β-O_2 each molecule has six equivalent near neighbors; therefore an antiferromagnetic structure within the layer cannot be sustained in the absence of crystallographic distortions. These distortions would be necessary so that a given molecule will not have two ferromagnetically coupled and four antiferromagnetically coupled crystallographically equivalent neighbors. Such distortions might not be resolvable by the available diffraction data. Given such distortions, it may be possible to construct antiferromagnetically ordered arrangements which do not produce either separate magnetic lines or contribute additional magnetic intensity to nuclear lines.

We suspect then that the absence of magnetic structure in β-O_2 has not been decided unequivocally by the available neutron diffraction data. These data are, it should be noted, from polycrystalline and not single-crystal samples. In at least one set of data there appear two weak, unidentified lines which cannot be accounted for on the basis of the assumed crystal structure.[8] On the other hand, there is evident in the neutron diffraction patterns diffuse scattering intensity, presumably indicative of short-range magnetic order, appearing at $\sin\theta/\lambda$ values where resolved magnetic peaks in α-O_2 appear.[8] The absence of a lambda-type anomaly in the heat capacity at the γ-β transition may not be an objection to the idea of a magnetically ordered β-O_2 structure, since a major structural change and a pronounced change in the temperature dependence of the heat capacity occurs at this transition.[39,51] There is also a sizeable latent heat (1.776 cal mole^{-1}) associated with the transition,[39,51] in which an entropy change associated with magnetic ordering might be contained. On the other hand, it can be argued that the observed anisotropy in the susceptibility of β-O_2 is too small to be consistent with either three-dimensional or two-dimensional magnetic ordering.

A qualitative explanation for the temperature dependence of the susceptibility of β-O_2, without invoking an ordered antiferromagnetic structure, can also be suggested. The drop in susceptibility on transforming from γ to β-O_2 is due at least partly to an enhancement in the mean antiferromagnetic exchange interaction in the denser (by 5%) lower-temperature phase. Yet considerable orientational disorder persists in β-O_2, as neutron diffraction and, especially, Raman spectra[65,66] indicate. Whether the disorder is described as due to precession or flipping, the exchange interaction will be strongly modulated by the molecular motion. This might be sufficient to prevent the development of long-range magnetic order. Moreover, the interactions between neighboring molecules in β-O_2 can be expected to be strongly temperature dependent, since the thermal expansion parameters of β-O_2 are large and unusual. In the (00.1) basal plane layer the lattice constant decreases by 2% between 42 and 26 K. Normal to the (00.1) layer the variation in lattice constant is much less, but is of opposite sign.[29] The only observed Raman frequency[65] in β-O_2 increases from 46 cm^{-1} at 42 K to 51 cm^{-1} at 26 K. This frequency measures the strength of the Lennard-Jones interaction, which has been the basis for successful structural predictions in the case of several diatomic solids.[34] Raman data suggest a definite temperature dependence for the angle of tilt of the molecular axes with respect to the c axis of β-O_2, tilt angle decreasing with decreasing temperature.[66] Exchange interactions are very sensitive to both the orientation and the separation of interacting units.[83] It is possible that orientational effects lead to an enhancement of the perpendicular (out-of-plane) exchange interactions at the expense of the parallel (in-plane) exchange interactions, as the temperature decreases. Beta oxygen may then become progressively more three-dimensional as the $\beta \rightarrow \alpha$ transition temperature is approached. This effect, together with the presence of short-range magnetic order, may provide a qualitative explanation for the temperature dependence of the susceptibility of β-O_2.

C. Alpha oxygen

1. *Magnetic structure*

In analyzing the α-O_2 susceptibility data in Sec. IV it was assumed that two sublattices were present with spin magnetic moments parallel and antiparallel to the $\vec{b}_\alpha = [010]$ axis. The evidence for this is from the available neutron diffraction data on polycrystalline samples.[8,25] Although nuclear reflections obey the selection rule in α-O_2, $h+k=2n$, magnetic reflections need not, and two purely magnetic lines are observed, $(\bar{1}01)$ and (100). The relative intensities of these lines are probably best accounted for if the molecular moment is parallel or antiparallel to $\vec{b}_\alpha$. Our examination of the relative intensities of the nuclear lines in the data of Collins and Alikhanov suggests that this judgment is not called seriously into question by any small preferred orientation that may have been present in these samples, though small enhancement of the nuclear (020) line seems apparent. Most conclusive seems the complete absence of an (010) magnetic line in any of the available diffraction patterns. Magnetically scattered intensity is proportional to $\sin^2\delta$ where δ is the angle between the scattering vector and the magnetic moment. Only a small angle between the scattering vector [010], parallel to $\vec{b}_\alpha$, and the magnetic moment can account for the absence of the (010) reflection, since neither the variation in magnetic form factor,[11] Lorentz-polarization factor[84] nor the temperature factor[11] sufficiently diminishes the expected intensity of (010) relative to the other two magnetic lines. It is interesting to note that neutron scattering from samples believed to be monolayers of oxygen absorbed on Grafoil[15] suggests a magnetic ordering with moments parallel and antiparallel to an axis analogous to $\vec{b}_\alpha$ in bulk α-O_2. The assumed magnetic structure can be visualized by considering moments directed along $+\vec{b}_\alpha$ in the case of the eight corner sites of the unit cell in Fig. 2, and moments directed along $-\vec{b}_\alpha$ in the case of the two base-center sites of the same unit cell.

It is not possible to rule out on symmetry grounds a magnetic structure exhibiting a slight canting of the magnetic moments from the $\vec{b}_\alpha$ axis. But no evidence for such canting (leading to a weak ferromagnetic moment) is apparent in any susceptibility data. Neither of the usual mechanisms leading to weak ferromagnetism,[85] large anisotropy in the g value and consequent nontrivial antisymmetric exchange interaction, or differently oriented crystal fields at inequivalent sites, is operative in the case of α-O_2. It would be surprising, therefore, if a canted magnetic structure did develop.

2. Mean-field theory considerations

It is useful to begin by applying a few simple mean-field theory relations to the results of the susceptibility analysis given in Sec. IV. For a two-sublattice antiferromagnet with intrasublattice exchange negligible compared to intersublattice exchange

$$\chi = C/2T_N \tag{14}$$

is the expected value of the susceptibility at the Néel temperature.[76] This is also the value of the perpendicular susceptibility below T_N in the same theoretical approximation. One can then estimate T_N from $\chi_\perp$ or vice versa. The agreement is typically good to 20% or better, the principal source of discrepancy being the statistical mechanical deficiencies of the mean-field theory. As a rule, mean-field theory overestimates the ordering temperature. In Sec. IV the result $\chi_\perp = 78 \times 10^{-6}\ \mathrm{cm^3\,g^{-1}}$ was obtained for α-O_2. Of this $3.6 \times 10^{-6}\ \mathrm{cm^3\,g^{-1}}$ is from diamagnetic and paramagnetic contributions unrelated to the exchange interactions or the anisotropy. Using the value $\chi_\perp = 74 \times 10^{-6}\ \mathrm{cm^3\,g^{-1}} = 2.37 \times 10^{-3}\ \mathrm{cm^3\,mole^{-1}}$ in Eq. (14), one finds that $T_N = 211$ K. This is a surprisingly large value, and is in fact inconsistent with the temperature dependence and relative magnitude of $\chi_\parallel$, also determined in Sec. IV. In Fig. 6 are plotted $\chi_\perp$ and $\chi_\parallel$ vs T. The behavior of $\chi_\parallel$ is qualitatively reasonable. At low temperatures the dependence on T is at least as strong as T^2 (in the absence of anisotropy) and more generally exponential.[77] At higher temperatures $\chi_\parallel$ is almost linear in T. In the simplest mean-field theory approximation, $\chi_\parallel = \chi_\perp$ at T_N. Although the extrapolation of $\chi_\parallel$ in Fig. 6 entails some uncertainty, the estimate $T_N = 30.5 \pm 3$ K appears reasonable. This comparison reveals one of the signal characteristics of the magnetism in solid oxygen: an apparent failure of mean-field theory by nearly an order of magnitude, reflected principally in the small size of the observed susceptibility. The extent to which this failure can or cannot be corrected by more refined considerations will be examined in the following.

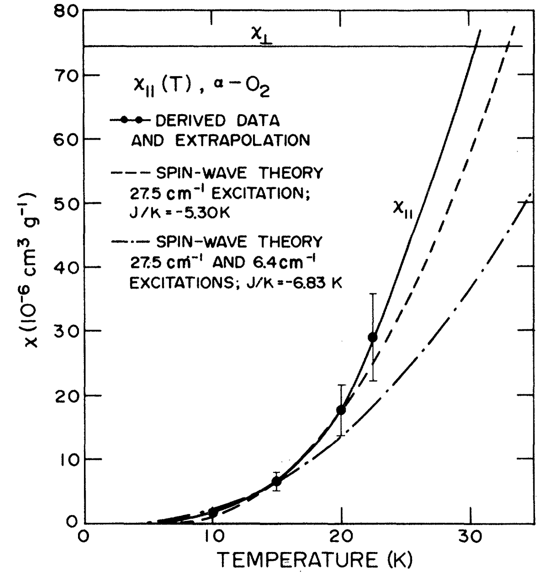

FIG. 6. Temperature dependence of the magnetic susceptibility parallel to the easy axis in α-O_2. The solid curve is an extrapolation through the derived (see text) data. The dashed curves are theoretical fits to same. The susceptibility perpendicular to the easy axis is also shown.

At this point it is useful to obtain an estimate for the effective exchange interaction in α-O_2, in the same theoretical approximation as the foregoing. A mean-field theory prediction is[77]

$$\chi_\perp = N g^2 \mu_B^2 / 4 z_2 |J_2| \ , \tag{15}$$

where z_2 is the number of nearest-neighbor magnetic sites on the opposite sublattice from a given site and where J_2 is the exchange interaction between nearest-neighbor sites on opposite sublattices. The exchange Hamiltonian from which the above result is derived, and which will be generally adopted in this paper, is

$$\mathcal{H}_{\mathrm{ex}} = -2 \sum_{i>j} J_{ij} \vec{S}_i \cdot \vec{S}_j \ . \tag{16}$$

The molecular-field theory approximation consists in replacing $\vec{S}_i \cdot \vec{S}_j$ by $\vec{S}_i \cdot \langle \vec{S}_j \rangle$, where $\langle \vec{S}_j \rangle$ is a thermally averaged expectation value. In the case of antiferromagnetic exchange, $J_{ij} < 0$. Equation (15) may be corrected for anisotropy by the addition of a term, small compared to $4z_2|J_2|$, to the denominator. It will be shown that such a correction does not affect the value of $\chi_\perp$ for α-O_2 very much. Employing the value $\chi_\perp = 2.37 \times 10^{-3}\ \mathrm{cm^3\,mole^{-1}}$ and assuming $g = 2$, there results: $z_2|J_2| = 2.18 \times 10^{-14}$ erg or $z_2|J_2|/hc = 110\ \mathrm{cm^{-1}}$ or $z_2|J_2|/k = 158$ K. This estimate will be revised downward slightly when the effects of anisotropy and zero-point spin deviations are considered.

Barrett, Meyer, and Wasserman[27] interpreted the crystal structure of α-O_2 in terms of a molecular contact criterion given by Bader, Henneker, and Cade.[86]

They concluded that in α-O_2 a given molecule, at say $\{\frac{1}{2},\frac{1}{2},0\}$, is in "contact" with four molecules in the same *ab* layer, at $\{0,0,0\}$, $\{0,1,0\}$, $\{1,0,0\}$, and $\{1,1,0\}$, and with four molecules in neighboring *ab* layers, at $\{1,0,1\}$, $\{1,1,1\}$, $\{0,0,\bar{1}\}$, and $\{0,1,\bar{1}\}$. These relationships are illustrated in Fig. 7, adopted from Ref. 28. The numbering of the molecules in this figure will be made use of later. For the four neighbors in the same *ab* layer, the separation of both nearest-neighbor molecular centers and nearest-neighbor nuclei are the same, 3.200 Å. For the four neighbors in adjoining *ab* layers the separations are 4.186 and 3.153 Å between molecular centers and nearest nuclei, respectively. Here an internuclear separation of 1.207 Å, the same as that for the free molecule,[79] has been assumed. Both sets of four neighbors, are, on the basis of the assumed magnetic structure (Sec. V C 1), on the opposite magnetic sublattice. Two other in-plane neighbors to a given molecule, at $\{\frac{1}{2},1\frac{1}{2},0\}$ and $\{\frac{1}{2},\frac{\bar{1}}{2},0\}$, that is at $\pm b_\alpha$ with respect to it, are not in contact with it according to the Bader-Henneker-Cade criterion. The nearest nuclear separation of molecules separated by $\pm b_\alpha$ is 3.429 Å, substantially greater than in the case of the other eight neighbors. The translation $\pm b_\alpha$ remains within a given magnetic sublattice. It has therefore been frequently assumed that *intra*sublattice exchange, J_1, is weak compared to *inter*sublattice exchange, J_2, all the more so in that the relevant quantity is not J but zJ, and that $z_1=2$ while $z_2=8$. The difference between the two kinds of opposite sublattice neighbors has also frequently been neglected, and for the present we shall do the same.

Employing the result $z_2|J_2|=2.18\times10^{-14}$ erg and assuming $z_2=8$, one obtains $|J_2|/hc=13.8$ cm^{-1} or $|J_2|/k=19.8$ K. Blocker, Simmons, and West[9] have studied the hcp and fcc phases of solid solutions of oxygen and argon. In such solutions nearest-neighbor distances vary from 3.43 to 3.77 Å, and considerable orientational disorder exists.[87] From susceptibility data Blocker *et al.* deduced a mean exchange interaction equal to $|J|/hc=2.6$ cm^{-1} or $|J|/k=3.7$ K. The relative orientations of interacting O_2 molecules are no less important than their separations in determining overlap integrals and exchange interactions. But from this comparison one suspects, at least, that a value $|J|/k=19.8$ K, and corresponding mean-field $T_N=211$ K, is too high for α-O_2. However, in the case of α-O_2 a somewhat larger value of exchange interaction is expected than for the O_2-Ar mixtures, which remain merely paramagnetic down to 1 K.

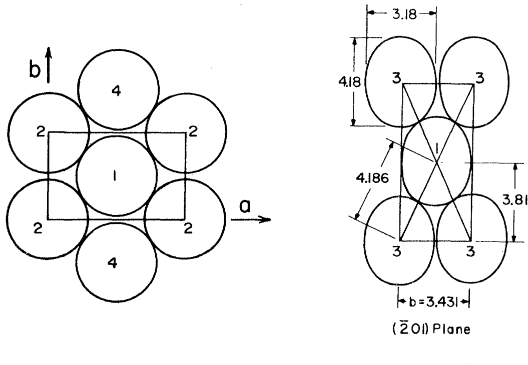

FIG. 7. Packing characteristics in α-O_2, adopted from Ref. 28. Molecules 2 and 3 are inequivalent neighbors of molecule 1, and are presumed to be on the opposite magnetic sublattice from it. They are in "contact" with molecule 1 at their 0.002 electron density contours (see Refs. 28 and 86). Molecule 4 is presumed to be on the same magnetic sublattice as molecule 1, but is not in "contact" with it at the 0.002 contour. All distances in the figure are in angstroms.

3. Perpendicular susceptibility

We now wish to estimate the effects of, first, single molecule and/or crystalline anisotropy, and second, zero-point spin deviations, on the magnitude of the perpendicular susceptibility. In the case of uniaxial anisotropy the Hamiltonian is expressible in the form

$$\mathcal{H}=\sum_i [g\mu_B\vec{H}\cdot\vec{S}_i-D(S_i)_z^2]-2\sum_{i>j}J_{ij}\vec{S}_i\cdot\vec{S}_j\ , \tag{17}$$

i.e., as a Zeeman term, an anisotropy term, and an exchange term. Here $D>0$ and $\pm z$ is the axis of spin alignment. It has been shown by Kubo[77] that, neglecting zero-point spin deviations, the perpendicular susceptibility at 0 K is given by

$$\chi_\perp=Ng^2\mu_B^2/(4z_2|J_2|+2D)\ . \tag{18}$$

The above Hamiltonian is not appropriate for α-O_2. Here the axis of spin alignment is believed to be along $\pm b_\alpha$, while the dominant anisotropy is probably that of the free molecule,[81] $\mathcal{H}_{\text{anis}}=AS_x^2$ where x is the internuclear axis and $A/hc=3.96$ cm^{-1} or $A/k=5.70$ K. This intramolecular anisotropy results from both spin-spin and spin-orbit interaction.[88] In the case of crystalline α-O_2 at least one additional term, of the form BS_y^2, will be necessary to account for crystal-field effects and to stabilize a preferred spin structure. The anisotropy is then effectively orthorhombic.

Keffer and Kittel[89] have treated the semiclassical theory of antiferromagnet resonance in the case of orthorhombic symmetry, and have also given expressions for the perpendicular susceptibilities,

$$\begin{aligned}\chi_x&=-2\gamma M(a-b)/(\omega^2-\omega_1^2)\ ,\\ \chi_y&=-2\gamma M(c-d)/(\omega^2-\omega_3^2)\ ,\end{aligned} \tag{19}$$

where $\gamma=g\mu_B/\hbar$, $M=\frac{1}{2}Ng\mu_BS$ is the magnitude of the sublattice magnetization at 0 K, ω is the frequency of the applied field, ω_1 and ω_3 are the AFMR frequencies, and where a, b, c, and d are exchange/anisotropy parameters defined by

$$a=\gamma(H_E+K_2/M),\quad b=\gamma(H_E+K_4/M)\ ,$$
$$c=\gamma(H_E+K_1/M),\quad d=\gamma(H_E+K_3/M)\ . \tag{20}$$

Here H_E is an exchange field and K_1, K_2, K_3, and K_4 are macroscopic anisotropy constants in terms of which the anisotropy energy may be expressed

$$E_{\text{anis}}=(K_1/2)(\alpha_1^2+\alpha_2^2)+(K_2/2)(\beta_1^2+\beta_2^2)$$
$$+K_3\alpha_1\alpha_2+K_4\beta_1\beta_2\ , \tag{21}$$

where α_i and β_i are the direction cosines of the ith sublattice magnetization vector with respect to the x and y axes, respectively. Keffer and Kittel show that $K_3<K_1$ and $K_4<K_2$, and we shall neglect K_3 and K_4 in the following. The expression for the anisotropy energy is the counterpart of the microscopic Hamiltonian $\mathcal{H}_{\text{anis}}=AS_x^2+BS_y^2$. In the limit that $\omega\rightarrow 0$ (static applied field), ${}^0\chi_x=2\gamma M/(c+d)$ and ${}^0\chi_y=2\gamma M/(a+b)$, where use has been made of expressions for ω_1 and ω_3 which will be given later. Using the above definitions and the familiar mean-field theory expression[90] for the exchange field, $H_E=2z_2|J_2|S/g\mu_B$, one obtains

$${}^0\chi_x=Ng^2\mu_B^2/(4z_2|J_2|+2K_1/NS^2)\ ,$$
$${}^0\chi_y=Ng^2\mu_B^2/(4z_2|J_2|+2K_2/NS^2)\ . \tag{22}$$

The K_i are macroscopic anisotropy constants per mole of spins of magnitude $S(S+1)\approx S^2$, and the K_i/NS^2 are the corresponding microscopic anisotropy parameters. With this identification, the perpendicular susceptibilities take the same form as in the uniaxial case, Eq. (18). One frequently sees Eq. (18) written in the form $\chi_\perp(\alpha)=\chi_\perp(0)/(1+\alpha/2)$, where α is an anisotropy parameter defined by $\alpha=H_A/H_E$, where H_A is an anisotropy field expressible in mean-field theory[90] as $2DS/g\mu_B$, and where $\chi_\perp(0)$ is given by Eq. (15). Similar expressions can be written in the nonuniaxial case on identifying A and B with K_1/NS^2 and K_2/NS^2, respectively, and with the definition of two anisotropy fields, $H_A=2AS/g\mu_B$ and $H_B=2BS/g\mu_B$.

Assuming now that $|J_2|/hc=13.8$ cm^{-1} and that $z_2=8$, it is evident that the effect of a microscopic anisotropy constant $A/hc=3.96$ cm^{-1} is very small: $\chi_\perp(\alpha)/\chi_\perp(0)=0.98$. Moreover, the difference between ${}^0\chi_x$ and ${}^0\chi_y$, that is the anisotropy in the perpendicular susceptibility, will be less than 2%. This would justify the neglect of such anisotropy in the data analysis of Sec. IV. If on the other hand a value of $|J_2|/hc\approx 3$ cm^{-1} is more appropriate for α-O_2 (i.e., similar to that observed in O_2-Ar mixtures), then a larger anisotropy effect is expected, $\chi_\perp(\alpha)/\chi_\perp(0)=0.92$. Even so, the anisotropy in the perpendicular susceptibility would not exceed 8%, and the exchange interaction deduced from Eq. (15) would be only about 8% too large. The assumption of no anisotropy in $\chi_\perp$ made in the data analysis remains acceptable. However, as already indicated, the magnitude of $\chi_\perp$ cannot be accounted for by so small an exchange interaction.

The effect of zero-point spin deviations on the perpendicular susceptibility will now be considered. This is a quantum-mechanical effect which arises because, as first shown by Anderson,[91] the true ground state for a two-sublattice antiferromagnet is not the perfectly antiparallel Néel state, even at 0 K. The effective magnitude of the spin is reduced with respect to the Néel value and the ground-state energy is lowered. Spin-wave theory[92] yields the following expression for the perpendicular susceptibility when zero-point deviations are taken into account,

$${}^c\chi_\perp(\alpha)=\chi_\perp(\alpha)[1-\Delta S(\alpha)/S-e(\alpha)/(2+\alpha)zS]\ , \tag{23}$$

where $\chi_\perp(\alpha)$ is the susceptibility in the absence of zero-point deviations but including the effect of anisotropy, and where $\Delta S(\alpha)$ and $e(\alpha)$ are anisotropy-dependent parameters reflecting the effect of zero-point deviations on the length of the spin and the ground-state energy, respectively.

$\Delta S(\alpha)$ is a slowly varying function of α, and depends only weakly on lattice type for a given dimensionality. Lines[93] has tabulated values of $\Delta S(\alpha)$ for the simple cubic lattice. For α-O_2, taking $A/hc=3.96$ cm^{-1}, $S=1$, and $g=2$ gives $H_A=2AS/g\mu_B=8.48\times 10^4$ Oe. Also, taking $|J_2|/hc=13.8$ cm^{-1} gives $H_E=2z_2|J_2|S/g\mu_B=2.37\times 10^6$ Oe. Hence, $\alpha=0.036$, and from Line's results we estimate that $\Delta S(\alpha)\approx 0.064$. The parameter $e(\alpha)$ is essentially independent of anisotropy up to $\alpha\approx 0.01$ and decreases only weakly for larger α. In three dimensions its value is very nearly independent of lattice type, and we will adopt the (adjusted) simple cubic result,[92] $e(0.036)\approx 0.56$. It follows from Eq. (23) that ${}^c\chi_\perp(\alpha)=\chi_\perp(\alpha)\times 0.90=\chi_\perp(0)\times 0.98\times 0.90=0.89\chi_\perp(0)$. If $|J_2|/hc$ is taken to be of the order 3 cm^{-1}, the estimated correction for zero-point spin deviations is, with $\alpha\approx 0.167$ now, about 0.93. In this case $\chi_\perp(\alpha)=\chi_\perp(0)\times 0.92$ and therefore ${}^c\chi_\perp(\alpha)=0.86\chi_\perp(0)$. The foregoing suggests that a diminution of from 11 to 14% in the perpendicular susceptibility of α-O_2 may be present due to the combined effects of anisotropy and zero-point spin deviations. Such an adjustment is obviously insufficient to remove the basic anomaly, that the observed perpendicular susceptibility implies an unreasonably large T_N and a much larger exchange interaction than is suggested (as will be seen) by other data.

4. *Parallel susceptibility*

We consider now the temperature dependence of the parallel susceptibility of α-O_2 deduced from the present data, and its relation to theory. Kubo has shown[77] that for an isotropic two-sublattice antiferromagnet, spin-wave theory yields a T^2 dependence for the parallel susceptibility at temperatures low compared to T_N. The presence of anisotropy, which introduces an energy gap into the spin-wave spectrum, makes the temperature dependence exponential. Eisele and Keffer[94] have treated the case of a two-sublattice antiferromagnet with uniaxial anisotropy and have derived an expression for the parallel susceptibility

$$\chi_{\parallel} = [Ng^2\mu_B^2/(z|J|S)^3] \times (\pi^2 A_1/24)(kT)^2\chi(T/T_{AE}) \;, \qquad (24)$$

where A_1 is a constant characteristic of the lattice and where $\chi(T/T_{AE})$ is a function which accounts for the anisotropy. T_{AE} is k^{-1} times the energy gap introduced into the spin-wave spectrum. In writing this expression we have adopted the convention for the exchange integral given by Eq. (16). In obtaining this result Eisele and Keffer assumed the anisotropy to be of the crystal-field form, that is not dependent on mutual orientation of spins as would be the case, for example, for anisotropic exchange or magnetic dipole-dipole interactions. Such effects are probably not important in α-O_2 although the anisotropy responsible for the 6.4-cm^{-1} magnetic excitation could be dipolar in origin. The theoretical approximation employed in obtaining the above result, essentially that the spin-wave dispersion goes as $\vec{k}$, renders it somewhat less reliable for higher temperatures, where spin-wave states not following this form of dispersion are being populated. Nevertheless, this result has been employed in some recent studies.[95,96]

For vanishing anisotropy ($T_{AE} \to 0$), $\chi(T/T_{AE}) \to 1$ and Kubo's T^2 law results. Eisele and Keffer present a plot of $\chi(T/T_{AE})$ from which it is possible to estimate the value of this function to an accuracy of a few percent. If the anisotropy is orthorhombic two different spin-wave modes can arise, with energies $kT_{AE}(1)$ and $kT_{AE}(2)$ for zero wave vector. If the applied magnetic field is small compared with the anisotropy-exchange fields $(H_E H_A)^{1/2}$ and $(H_E H_B)^{1/2}$, then $\chi_{\parallel}$ should again be given by Eq. (24) but with $\chi(T/T_{AE})$ replaced by $\frac{1}{2}[\chi(T/T_{AE}(1)) + \chi(T/T_{AE}(2))]$.

The behavior of $\chi_{\parallel}(T)$ for α-O_2 can be analyzed using the theory of Eisele and Keffer. The value of A_1 is not known for this lattice. By comparison with values of A_1 for the simple cubic and face-centered cubic lattices,[77] we estimate that for α-O_2, $A_1 \approx 0.5$, to within 30% or so. An uncertainty of this magnitude in A_1 will lead to only about a 10% uncertainty in any value of $|J|$ derived from Eq. (24). In order to obtain the observed order of magnitude for $\chi_{\parallel}$ at 5, 10, 15, 20, and 22.5 K, it is necessary to use in Eq. (24) a much smaller value of $|J|$ than was employed in accounting for the magnitude of $\chi_{\perp}$, in both cases taking $z=8$. In Eq. (24), $z|J|$ can include the effects of intrasublattice exchange, i.e., $zJ = z_2J_2 - z_1J_1$. The relative importance of a z_1J_1 term will be discussed in Sec. VI.

In Fig. 6 we show the temperature dependence of the parallel susceptibility of α-O_2 as derived from our data and two prospective theoretical fits. In one case we consider only the 27.5 cm^{-1}, $\vec{k}=0$ spin-wave excitation ($T_{AE}=39.6$ K) in evaluating $\chi(T/T_{AE})$. In the other case we consider the 6.4 cm^{-1}, $\vec{k}=0$ excitation as well [$T_{AE}(2)=9.2$ K] and employ the average value of $\chi(T/T_{AE})$ indicated above. In each case $z=8$ is assumed and $|J|$ is chosen so that $\chi_{\parallel}$ (calculated) equals the observed value of $\chi_{\parallel}$ at 15 K, that is 6.4×10^{-6} $cm^3\,g^{-1}$. The 15-K point was chosen in order to make comparison with a reasonably large value of $\chi_{\parallel}$ yet to avoid temperatures very near $T_{\alpha\beta}$. When only the higher energy excitation is assumed, $|J|/k=5.30$ K or $|J|/hc=3.68$ cm^{-1}. When both excitations are assumed, $|J|/k=6.83$ K or $|J|/hc=4.75$ cm^{-1}.

The parallel susceptibility calculated on the basis of a single spin-wave excitation fits the data well. The small calculated value of $\chi_{\parallel}(5\text{ K})$ is consistent with the earlier assumption that $\chi_{\parallel}(5\text{ K}) \approx \chi_{\parallel}(0\text{ K}) = 0$. At each of the higher temperatures the calculated value of $\chi_{\parallel}$ agrees with the observed value to well within the experimental uncertainty of the latter. A slightly better overall agreement might be achieved through a least-squares fit of $|J|$ to all of the data, but this is not worthwhile. A rough estimate of the Néel temperature can be obtained from setting $\chi_{\parallel}(T) = \chi_{\perp}$ at T_N, and the resulting value is about 33 K. The parallel susceptibility calculated on the basis of two spin-wave excitations fits the data less well, though probably not so much so that it must be completely dismissed. A somewhat larger value of $|J|$ obtains in this case, though one still small compared with that deduced from the value of $\chi_{\perp}$. For T_N one might estimate, on setting $\chi_{\parallel}(T_N) = \chi_{\perp}$, a value of about 41 K.

In accounting for $\chi_{\parallel}$ (observed) up to at least 20 K, we have employed a spin-wave theory up to some 60% or more of T_N. This is considerably in excess of the usual fraction of T_N (about 10%) for which such a theory is normally valid. It is arguable[95] that the very large energy gap, $T_{AE}=39.6$ K, leads to a suppression of spin-wave excitations (and their interaction) until T is quite close to T_N. This argument ignores the lower-energy excitation at 9.2 K. The better agreement obtained above on neglecting this lower excitation may be significant. It has even been suggested[97] that the 6.4-cm^{-1} observation is an experimental artifact. This question will be pursued in the discussion of the AFMR observations in Sec. V C 5 and of the magnetic heat capacity in Sec. V C 6.

The observations of Blocker *et al.*[63] show that the AFMR frequency decreases with increasing temperature. Allowing for a temperature dependence in $T_{AE}(1)$ suggested by these data, and assuming a similar temperature dependence in $T_{AE}(2)$, leads to no significant changes in the calculated $\chi_{\parallel}$ up to about 20 K. Even at 20 K the differences from the previous analysis [$\chi(T/T_{AE}(1))$ now 14% larger, $\chi(T/T_{AE}(2))$ now 4% larger] are not major. The differences become much more significant at 22.5 K [$\chi(T/T_{AE}(1))$ now 63% larger, $\chi(T/T_{AE}(2))$ now 11% larger]. This does not, however, greatly worsen the fit at 22.5 K when only one spin-wave excitation is assumed, and improves the fit at 22.5 K when two spin-wave excitations are assumed. It is arguable that so close to $T_{\alpha\beta}$, where the observed AFMR frequency falls to zero, the theoretical assumptions are increasingly questionable and the comparison should not be pressed.

5. *Antiferromagnetic resonance*

The theory of Keffer and Kittel[89] for the AFMR frequencies in the case of orthorhombic anisotropy was introduced in Sec. V C 3. In terms of the exchange-anisotropy parameters defined there, the resonance frequencies can be expressed

$$\begin{aligned} \omega_1 &= [(a-b)(c+d)]^{1/2} \ , \\ \omega_3 &= [(c-d)(a+b)]^{1/2} \ , \end{aligned} \tag{25}$$

for the two nondegenerate modes. Adopting now the same approximations made in Sec. V C 3 these equations become

$$\begin{aligned} \omega_1 &= \gamma(2H_E H_B + H_A H_B)^{1/2} \ , \\ \omega_3 &= \gamma(2H_E H_A + H_A H_B)^{1/2} \ , \end{aligned} \tag{26}$$

where $H_A = K_1/M$ and $H_B = K_2/M$, the usual definition for the anisotropy field in terms of the macroscopic anisotropy constant. When $H_A = H_B$ the two frequencies are degenerate and the expressions reduce to that for the case of uniaxial anisotropy. We now express the AFMR frequencies in terms of microscopic exchange and anisotropy constants, employing the expressions for H_E, H_A, and H_B given in Sec. V C 3,

$$\begin{aligned} \hbar\omega_1 &= 2(2z_2|J_2|B + AB)^{1/2} S \ , \\ \hbar\omega_3 &= 2(2z_2|J_2|A + AB)^{1/2} \ . \end{aligned} \tag{27}$$

If it is assumed that the 6.4- and 27.5-cm^{-1} excitations in α-O_2 both correspond to zero-field AFMR modes, Eqs. (27) may be used to obtain the exchange interaction and the anisotropy parameters. An additional condition is, however, required, since there are three parameters to be determined. It will be assumed that A has the same value in α-O_2 as in the free molecule, where it determines the strength of the coupling between the spin and the internuclear axis. Hence, we take $A/hc = 3.96$ cm^{-1}, or $A/k = 5.70$ K. With this assumption, and taking $z_2 = 8$, Eqs. (27) yields the values $|J_2|/hc = 2.97$ cm^{-1} or $|J_2|/k = 4.28$ K and $B/hc = 0.20$ cm^{-1} or $B/k = 0.29$ K. The corresponding exchange and anisotropy fields are $H_E = 5.09 \times 10^5$ Oe, $H_A = 8.48 \times 10^4$ Oe, and $H_B = 4.3 \times 10^3$ Oe, where $g = 2$ has also been assumed. These fields reproduce the observed frequencies when substituted into Eqs. (26).

Wachtel and Wheeler[10] have derived expressions for the AFMR frequencies in α-O_2 starting from the microscopic Hamiltonian

$$\mathcal{H} = \sum_i [A(S_i)_x^2 + B(S_i)_y^2] - \sum_{i>j} J'_{ij} \vec{S}_i \cdot \vec{S}_j \ , \tag{28}$$

where x is the internuclear axis, where y is normal to both x and the preferred axis of spin alignment z, and where $J'_{ij} = 2J_{ij}$. The Hamiltonian was rewritten as a sum of single-molecule terms and interaction terms. The single-molecule exchange interaction was approximated by $-J'z\langle S_z\rangle (S_i)_z$, where $\langle S_z \rangle$ is the expectation value of S_z in the single-molecule ground state and where zJ' is due to neighboring molecules on the opposite sublattice. The single-molecule energies and eigenstates were deduced. The separation between the first excited state and the ground state is significant, since it corresponds to the spin-wave energy at the Brillouin zone edge for certain directions in $\vec{k}$ space. This energy separation is $\epsilon_a = (A+B)/2 + z|J'|$ when $(zJ')^2 > [(A-B)/2]^2$, as is the case in α-O_2 for any reasonable choice of parameters. Wachtel and Wheeler treated the interaction terms in a second quantization formalism and derived expressions for the spin-wave frequencies. It is readily confirmed from these equations that $\hbar\omega_k = \epsilon_a$ for the zone boundary wave vectors π/a, π/b, and $\pi/c \sin\beta$. The expressions for $\omega_{k=0}$ given by Wachtel and Wheeler are easily reduced to the following forms ($S = 1$):

$$\begin{aligned} \hbar\omega_1 &= (2z|J'|B + B^2)^{1/2} \ , \\ \hbar\omega_2 &= (2z|J'|A + A^2)^{1/2} \ . \end{aligned} \tag{29}$$

Two differences between these equations and those obtained from the theory of Keffer and Kittel are apparent. First, the terms quadratic in the anisotropy are pure rather than mixed. This will have only a small effect on the resonance frequencies, since $2z|J'| >> A$ or B. Second and more significant, a factor of 2 is missing from the first term in brackets (remembering that $J' = 2J$) and a factor of 4 is missing from the second term in comparison with Eqs. (27). Therefore, A and B determined through the use of these equations will be twice too large. That this discrepancy is present may be confirmed by considering the situation, $A=B$. The single-molecule anisotropy terms in the Hamiltonian can then be rewritten as

$$A(S_x^2+S_y^2)=A(\vec{S}^2-S_z^2)=-AS_z^2+AS(S+1)\ , \quad (30)$$

that is, the anisotropy is uniaxial with z the preferred axis. Kubo[77] has treated this case from the microscopic point of view and obtained the result

$$\hbar\omega=2(z|J'|A+A^2)^{1/2}S\ . \quad (31)$$

Equations (29) do not reduce to this form on setting $A=B$; it is necessary to substitute $2A$ for A and $2B$ for B as well.

Wachtel and Wheeler employed their equations and the two observed AFMR frequencies to solve for A, B, and J'. The necessary third condition for a solution was obtained by adopting a particular interpretation of some spectroscopic observations[59–62] of the bimolecular transitions in α-O_2. These are transitions in which a single photon excites two O_2 molecules, either to the same or to different orbital excited states. Wachtel and Wheeler assumed that a value $\epsilon_a=37.5$ cm^{-1} could be inferred from the shifts of these and other bands in α-O_2 relative to their positions in γ-O_2 and β-O_2, and also from the positions of magnon sidebands relative to the main lines. If this interpretation is accepted then the following set of parameters results: $|J'|/hc=4.01$ cm^{-1}, $A/hc=10.1$ cm^{-1}, and $B/hc=0.7$ cm^{-1} (which fits the data better than the value $B/hc=0.5$ cm^{-1} given in Ref. 10). The values of A and B are much larger than in the solution following from Eqs. (27), discussed earlier, and the value of A seems unreasonably large. These differences are largely ascribable to the factor-of-2 discrepancy already mentioned; i.e., A/hc and B/hc should be 5.05 and 0.35 cm^{-1}, respectively. This still represents an enhancement in A over the free molecule value, but may not be unreasonable in view of the compression of the electron cloud in the solid. More disconcerting is the small value of J', corresponding in our convention to $|J_2|/hc=2.00$ cm^{-1} or $|J_2|/k=2.88$ K. This is an even *smaller* value than that found in O_2-Ar mixtures which exhibit no signs of magnetic order down to 1 K, and in which the average intermolecular distances are larger than in α-O_2.

Burakhovich, Krupskii, Prokhvatilov, Freiman, and Erenburg[19(a)] have attempted to interpret the AFMR frequencies, certain features in the single and bimolecular optical-absorption spectra, and the heat capacity of α-O_2 in terms of a "quasi-two-dimensional" model for the magnetic structure of this phase. Their treatment is similar to that given by Wachtel and Wheeler, one principal difference being that the intersublattice exchange interactions are assumed to take different values depending on whether the interacting molecules are in the same *ab* layer or in adjacent *ab* layers. A second important difference is that in the analysis of Burakhovich *et al.*, the Brillouin-zone boundary frequencies for the two spin-wave modes are taken to be degenerate and equal to 75 cm^{-1} for $\vec{k}=\pi/a$ and π/b, and nondegenerate and centered on 37.5 cm^{-1}, with 8.5 cm^{-1} splitting, for $\vec{k}=\pi/c\sin\beta$. On this basis the following exchange interactions and anisotropy parameters are said to follow: $|J'_{\parallel}|/hc=17.2$ cm^{-1}, $|J'_{\perp}|/hc=0.94$ cm^{-1}, $A/hc=5.71$ cm^{-1}, and $B/hc=0.99$ cm^{-1}. Here A and B have the same significance as in the theory of Wachtel and Wheeler. $J'_{\parallel}$ is the intersublattice exchange interaction between molecules (four neighbors) in the same *ab* layer and $J'_{\perp}$ is the intersublattice exchange interaction between molecules (four neighbors) in adjacent *ab* layers; the prime again indicates that these J are twice those of our convention. The spin-wave dispersion was calculated and plotted on the basis of these results; see Fig. 8 adopted from Ref. 19(a).

It seems to use that the results of Burakhovich *et al.*[19(a)] are open to question. The same missing factor of 2 that was noted in the theory of Wachtel and Wheeler occurs here, and the final equations[19(b)] of Burakhovich *et al.* do not, on setting $A=B$ and taking $\vec{k}=0$, reduce to that given by Kubo. Apart from this, the reasonableness of the derived parameters seems questionable. The enhancement in A over the free molecule value is much less than in the analysis of Wachtel and Wheeler. However, if it is assumed that A (and B) should be reduced by a factor of 2, then a diminution in the value of this parameter relative to that of the free molecule is implied. Compression of the electron cloud is expected to lead to an enhancement of a zero-field splitting parameter,[98] and such compression should presum-

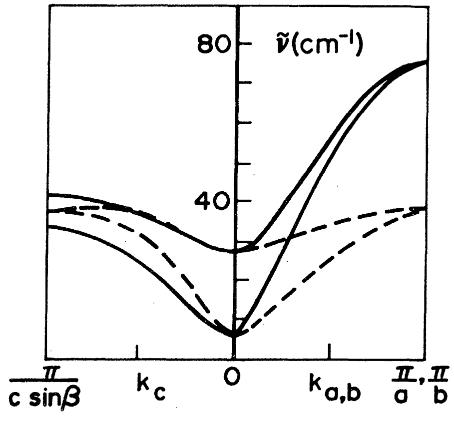

FIG. 8. Spin-wave dispersion in α-O_2 suggested in Ref. 10 (dashed curves) and Ref. 19 (solid curves), adopted from Ref. 19(a). See Ref. 69 for a contrary view.

ably occur in a close-packed structure like α-O_2. On the other hand, if hindered rotation were the dominant effect in the closed-packed lattice, a diminution in A might result, since a minimum in the potential energy of rotation reduces the coupling of the spin to the rest of the molecule.[98] It is interesting to observe that heat capacity[99] and EPR measurements[100] on solid α-N_2 containing from a few tenths to a few percent of O_2 impurity suggest a reduction in A for O_2 by about 10%. There may, however, be evidence (less clear) for an enhancement in A of O_2 as impurity in Ar-O_2 and CO-O_2 mixtures.[101] It seems to us that the value of B obtained by Burakhovich *et al.* is probably too large; certainly it is difficult to see how such a value could arise from intermolecular dipole-dipole interactions. A reduction in B by a factor of 2 makes this problem somewhat less severe of course, though the value remains surprisingly large. More puzzling, however, is the fact that the dispersion curves given by Burakhovich *et al.* do not conform to their parameters. We find that these curves are consistent with the indicated values of $J'_{\parallel}$ and $J'_{\perp}$ only in conjunction with somewhat different values of A and B, $A/hc = 3.96$ cm^{-1} and $B/hc = 1.24$ cm^{-1}. There appears to be some flexibility in the choice of A and B, but their sum must be much nearer to 5 cm^{-1} than to 7 cm^{-1}. At any rate, it is clear that the free molecule value for A is consistent with the indicated dispersion.

Perhaps the most remarkable result that emerges from the analysis of Burakhovich *et al.*[19(a)] is the very large difference between $J'_{\parallel}$ and $J'_{\perp}$. This difference is essential only in order to produce a pair of nondegenerate frequencies centered about 37.5 cm^{-1} at the $\vec{k} = \pi/c \sin\beta$ zone boundary. Were $J'_{\parallel} = J'_{\perp}$ (but with $|J'_{\parallel}| + |J'_{\perp}|$ the same), the two $\vec{k} = 0$ frequencies, 6.4 and 27.5 cm^{-1}, and the set of degenerate frequencies at the $\vec{k} = \pi/a$ and π/b zone boundaries, with value 75 cm^{-1}, could still be reproduced. But the frequencies at the $\vec{k} = \pi/c \sin\beta$ boundary would then assume the degenerate value of 75 cm^{-1} also. Burakhovich *et al.* have argued that the 8.5 cm^{-1} gap in the spin-wave dispersion, centered about 37.5 cm^{-1} for $\vec{k} = \pi/c \sin\beta$, is suggested by spectroscopic data, and that a large anisotropy in J' accounts better for the available low-temperature heat capacity data. However, the spectroscopic data are difficult to interpret, not least of all because of the lack of single-crystal data, and the theories that have been developed to explain them are quite complicated, and conflicting.[62,64,69,71,72] Regarding the heat capacity data, a detailed theoretical treatment of the phonon and libron dispersion in α-O_2 has only recently appeared,[38] and should influence conclusions regarding the lattice contribution to the heat capacity. This contribution accounts for more than 90% of the total heat capacity, and would need to be accurately separated from the magnetic contribution before any far-reaching conclusions on anisotropy in J could be formed. In Sec. V C 6 it will be argued that the magnetic heat capacity, in so far as it can be separated, can be accounted for without assuming drastically different intersublattice exchange interactions.

The very different values of J' deduced by Wachtel and Wheeler and by Burakhovich *et al.* arise from the quite different assumptions made about the magnitude of ϵ_a, the separation between the ground and first excited single molecule states. The value of ϵ_a is largely determined by the magnitude of zJ' and is essentially the exchange splitting of the original ground state. The parameters derived by us on the basis of the Keffer and Kittel theory of AFMR lead to a value, $\epsilon_a = 50$ cm^{-1}. This result is, we think, not clearly less consistent with the available spectroscopic data than the values 37.5 and 75 cm^{-1} assumed elsewhere.

6. *Heat capacity*

Under favorable circumstances important magnetic information can be extracted from heat capacity data. Unfortunately, several factors combine to make this difficult in the case of solid oxygen. Principal among these is the coincidence of magnetic and structural phase transitions at $T_{\alpha\beta}$. This, along with a second solid-state transformation at 43.8 K, prevents an accurate separation of magnetic and nonmagnetic contributions to the heat capacity. This kind of analysis is desirable in order to verify the expected total magnetic contribution to the entropy [generally $R \ln(2S+1)$ where the ground state is orbitally nondegenerate] and to estimate the fraction of magnetic entropy and energy acquired above and below the ordering transition. Such information is useful in appraising the extent of short-range magnetic order above the transition, the effective lattice dimensionality of the system and the character of the magnetic interactions.

Certain difficulties would arise even in the absence of crystallographic phase transitions. The Debye temperature for α-O_2 is estimated[51] to be 104.5 K at 0 K, and therefore the simple T^3 law for the phonon contribution to the total heat capacity can be expected to apply up to about 10 K at most. Well below $T_{\alpha\beta}$ the simple approximation, $C(\text{lat}) = AT^3$, ceases to be valid. Yet it is between 10 K and $T_{\alpha\beta}$ that the magnetic contributions to the heat capacity become very important. Another obstacle arises due to possible libronic contributions to the lattice heat capacity. One study[51] has invoked a libronic contribution in order to improve the fit to the observed data in the 10 to 20 K region, ignoring, however, the magnetic contributions. Here the libronic heat capacity was approximated by an Einstein (i.e., single-frequency) function. Libronic modes have been observed[65] in Raman spectra of α-O_2, at 44 and 79 cm^{-1} in a sample at 10 K. Recent theoretical calculations[38] suggest that the higher frequency is due to two librons, with two nearly degenerate modes contributing to the lower frequency. Another difficulty that arises for higher temperatures in the α-O_2 stability range, is that the difference $C_p - C_v$ may no longer be negligible. The observations consist of C_p values, while theoretical expressions predict values of C_v. The difference, $C_p - C_v$, depends on the isothermal compressibility and coefficient of thermal expansion. These quantities are probably not very well determined for α-O_2, though the available data[47,50] suggest an appreciable difference between C_p and C_v only above about 20 K.

At the $\alpha \rightarrow \beta$ transition there is observed, superimposed on an already rapidly increasing heat capacity, a sharp lambda-type anomaly, characteristic of many magnetic transitions. Fagerstroem and Hollis Hallet[51] have estimated that within this anomaly in their data, centered at 23.8 K, there is a quantity of magnetic entropy equal to $R\ \ln(1.65^{+0.25}_{-0.15})$. This is only 46% of the total entropy, $R\ \ln 3$, expected in the case of an orbitally nondegenerate triplet ground state, ${}^3\Sigma_g^-$. For the reasons discussed above, it is not possible to determine accurately the distribution of the remaining magnetic entropy above and below the transition. Nor are the data in the immediate neighborhood of the anomaly sufficiently precise to permit a critical law analysis. We believe, however, that the sharpness and magnitude of the observed anomaly argue against the "quasi-2D" magnetic ordering suggested for α-O_2 by one group.[19]

By focusing on only very low-temperature heat capacity data, many of the difficulties discussed in the preceding paragraphs are avoided, though at the price of dealing with less accurate experimental values. Between 2 and 8 K, the phonon heat capacity can be approximated by $C(\text{lat}) = aT^3$, where $a = 12\pi^4 R/5\Theta_D^3$. This contribution can be evaluated assuming for Θ_D a value, 104.5 ± 1.0 K at 0 K, based on data between 2 and 4 K where only a T^3 contribution seems indicated. If one subtracts the lattice contribution from the observed heat capacity, the remainder may be identified with that due to the spin waves. At temperatures well below that of magnetic ordering at T^3 form for the spin-wave contribution to the heat capacity of an antiferromagnet often obtains. Were this so here, the lattice and magnetic contributions between 2 and 8 K might not be separable. The T^3 spin-wave form depends,[102] however, on kT being considerably greater than $h\nu_0$, the "energy gap" in the spin-wave dispersion at $\vec{k} = 0$. Between 2 and 8 K, $kT < h\nu_0$ for either of the two $\vec{k} = 0$ spin-wave frequencies already discussed. One expects under these conditions an essentially exponential dependence of magnetic heat capacity on temperature given approximately by

$$C(\text{mag}) = AT^{-1/2} \exp(-E_0/kT) \ , \tag{32}$$

where A is a constant and where E_0 is the energy gap in the spin-wave spectrum.[103] Analyzing the available low-temperature heat capacity data in α-O_2 from this point of view, we find that a plot of $\ln\{[C(\text{obs}) - C(\text{lat})]T^{1/2}\}$ vs $1/T$ yields a straight line in the 2.6- to 4.8-K range, with $|\text{slope}|$ equal to $|-22.9\ \text{K}|$; see Fig. 9. This is less than the value 39.6 K expected assuming a gap frequency $\bar{\nu}_0 = 27.5$ cm^{-1} and greater than the value 9.3 K expected assuming $\bar{\nu}_0 = 6.4$ cm^{-1}. The temperature range considered here is very restricted and the derived values of $C(\text{mag})$ are rather uncertain. We do not, therefore, attach much significance to the apparent fit in this region.

Alternatively, one may extend the analysis to higher-temperature data, where $C(\text{obs}) - C(\text{lat})$ is numerically much larger. For this purpose $C(\text{lat})$ was obtained from a table of the Debye heat-capacity function,[104] assuming $\Theta_D = 104.5$ K. Below 12 K both the contribution of libronic modes to the lattice heat capacity and the difference $C_p - C_v$ can be assumed to be negligible. Data between 4.80 and 11.86 K are well accounted for by a straight line (see Fig. 9) of slope equal to -38.5 K. This is quite close to the value expected (-39.6 K) if only the 27.5 cm^{-1}, $\vec{k} = 0$ excitation is considered. Data at temperatures above 11.86 K deviate away from the line in the expected direction.

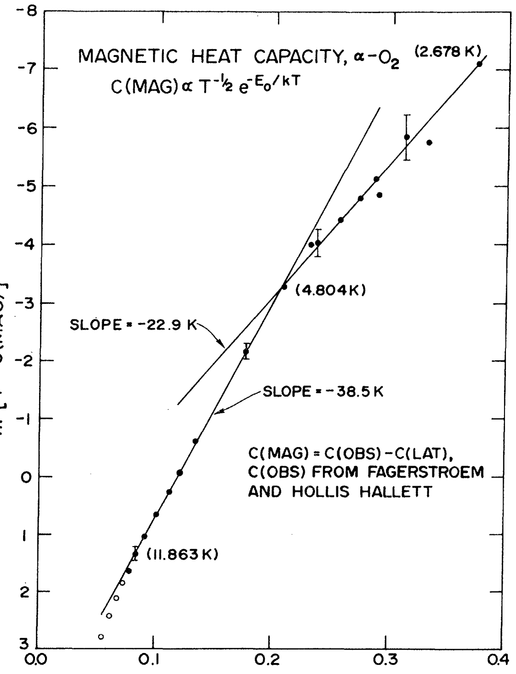

FIG. 9. Analysis of the (derived) magnetic heat capacity in α-O_2. Open circles near the bottom are for temperatures too high to make a reliable separation of lattice and magnetic contributions.

A more exact method of analysis is to apply the theory of Eisele and Keffer,[94] who treated not only the (parallel) magnetic susceptibility but also the magnetic heat capacity. Their expression for the latter is

$$C(\text{mag}) = R\,(4\pi^4 A_1/120)(kT/z|J|S)^3 C(T/T_{AE}) \;, \tag{33}$$

where A_1 is the same lattice-dependent constant already mentioned in Sec. V C 4, and where $C(T/T_{AE})$ is a function which accounts for the anisotropy. Again, J is according to the convention of Eq. (16). For vanishing anisotropy $(T_{AE} \rightarrow 0)$, $C(T/T_{AE}) \rightarrow 1$ and Kubo's T^3 law for the magnetic heat-capacity results. $C(T/T_{AE})$ can be estimated from a plot given by Eisele and Keffer. In the case of orthorhombic anisotropy, and two different spin-wave excitations, $C(T/T_{AE})$ is to be replaced by $\frac{1}{2}[C(T/T_{AE}(1)) + C(T/T_{AE}(2))]$.

As in the analysis of the $\chi_{\parallel}$ results earlier, we adopt the value $A_1 = 0.5$ and take $z = 8$. The value of $|J|$ is obtained by requiring exact agreement for the 12 K datum, about the highest temperature for which one can feel safe in neglecting those complicating effects already discussed. The results of the fitting procedure are shown in Fig. 10. One needs to assume the existence of both the 27.5- and the 6.4-cm^{-1} excitations in order to account for the observed magnetic heat capacity. This appears to be at variance with the conclusion emerging from the analysis of the $\chi_{\parallel}(T)$ results in Sec. V C 4, though there the difference between assuming one spin-wave mode or two was somewhat less pronounced. It is apparent that a considerably smaller value of $|J|$ is required to account for the magnetic heat capacity than for the parallel susceptibility. The value obtained, $|J|/k = 3.05$ K, is similar to that suggested by the analysis of Wachtel and Wheeler.[10]

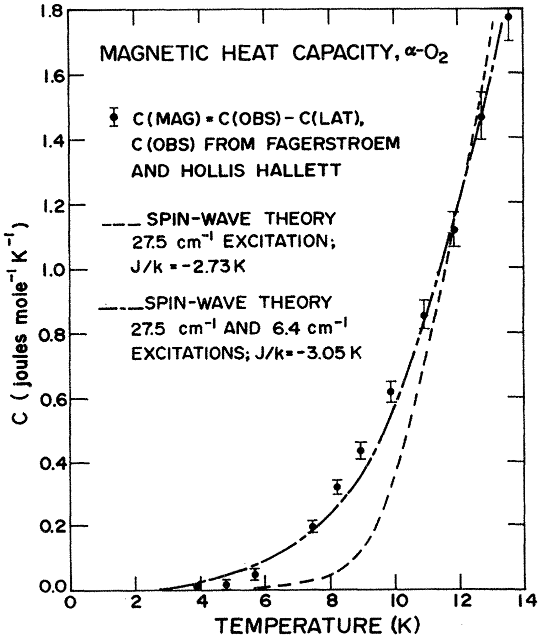

FIG. 10. Temperature dependence of the (derived) magnetic heat capacity in α-O_2. The dashed curves are fits to the data, based on Eq. (33).

7. Néel temperature

In Sec. V C 2 it was observed that from the magnitude of the perpendicular susceptibility one could estimate, using the simplest form of mean-field theory, a value $T_N = 211$ K. This is much in excess of what might be considered reasonable for α-O_2, and constitutes a considerably greater overestimate than even mean-field theory generally produces. The temperature dependence of the parallel susceptibility, together with the assumption that $\chi_{\parallel} = \chi_{\perp}$ at T_N, suggests a value for T_N between 30 and 35 K, which is much more reasonable.

It is also possible to infer a rough value of T_N from the temperature dependence of the 27.5 cm^{-1} (at 2.5 K) AFMR resonance frequency,[63] alluded to in Sec. V C 4. The observed frequency remains relatively high until T closely approaches $T_{\alpha\beta}$ $[\nu(T)/\nu(2.5\text{ K}) = 0.84$ at 21 K], and rapidly falls to zero as $T \rightarrow 23.9$ K. The data lie well above a simple mean-field theory prediction[105] for the temperature dependence, assuming $S = 1$ and $T_N = 23.9$ K. This does not mean that T_N is necessarily much greater than $T_{\alpha\beta}$ however, since several mechanisms have been shown[106] to lead to this type of anomalous temperature dependence. At least one of these mechanisms, involving the presence of more than one important exchange interaction, may operate in α-O_2. Even so, it seems clear from these data that the true Néel temperature of α-O_2 cannot be an order of magnitude greater than $T_{\alpha\beta}$. Employing frequency data only up to $T = 17.5$ K, and comparing with the mean-field behavior referred to, it appears that T_N is around 35 K.

Some other estimates for the Néel temperature of α-O_2 can be made using values of the exchange interaction estimated in previous sections. The mean-field theory expression for T_N in the case of a two-sublattice antiferromagnet is[92]

$$T_N = [2S(S+1)/3k](-z_2 J_2 + z_1 J_1) \;, \tag{34}$$

where J_2 (negative) is the exchange interaction between near neighbors on opposite sublattices, J_1 is the exchange interaction between near neighbors on the same sublattice, and z_i is the number of each kind of neighbor. $J_1 < 0$ lowers, and $J_1 > 0$ raises, the Néel temperature relative to that calculated ignoring intrasublattice interactions. For the present we neglect J_1, assume $z_2=8$, and take $S=1$. Then, employing values of J_2 obtained in previous sections, one calculates: $T_N=211$ K for $J_2/k=-19.8$ K (from $\chi_\perp$), $T_N=56.6$ K for $J_2/k=-5.30$ K (from $\chi_\parallel$), $T_N=45.7$ K for $J_2/k=-4.28$ K (from AFMR), and $T_N=32.5$ K for $J_2/k=-3.05$ K [from $C(\mathrm{mag})$]. The value of J_2 deduced by Wachtel and Wheeler,[10] $J_2/k=-2.88$ K, yields $T_N=30.7$ K. The mean value of J_2/k deduced by Burakhovich *et al.*,[19] -6.54 K, yields $T_N=69.8$ K. Evidently, a value of $|J_2/k|$ between 3 and 4 K is most consistent with the probable value of T_N.

A more refined calculation of the Néel temperature, considering the effect of anisotropy, may be obtained following the procedure of Moriya.[107] The latter has shown, first of all, that with a spin singlet ground state magnetic ordering at a nonzero temperature will occur only if a certain relation exists between the exchange and anisotropy parameters. In terms of the parameters employed in Eq. (28), the criterion for a nonzero Néel temperature is that

$$|J'|/(A-B) > \frac{1}{2z} , \qquad (35)$$

where z is the number of near neighbors on the opposite sublattice. It is evident that this criterion is easily satisfied by any of the sets of parameters which have been mentioned so far as possibly appropriate to α-O_2. The source of this criterion is the requirement that below the Néel temperature the expectation value of S_z at a given magnetic site not vanish. This expectation value is, at 0 K,

$$\langle S_z\rangle = \{1-[(A-B)/2zJ']^2\}^{1/2} . \qquad (36)$$

There will therefore be a "spin-shortening" effect due to the anisotropy. It is readily confirmed that this effect is negligible in α-O_2. Using the parameters deduced by Wachtel and Wheeler leads to a value $\langle S_z\rangle=0.989$. Using the parameters derived here, starting from the theory of Keffer and Kittel for the AFMR frequencies, leads to a value $\langle S_z\rangle=0.999$. It is clear that the anomalously high Néel temperature predicted from Eq. (14), or from Eq. (34), using the value of J_2 derived from the observed value of $\chi_\perp$, cannot be avoided by invoking a reduction in magnitude of the spin due to an anisotropy induced spin shortening. It has already been observed, in Sec. V C 3, that neither does the effect of zero-point spin deviations lead to an effective reduction in S by more than 10%.

The Néel temperature can be evaluated by considering the general expression for $\langle S_z\rangle$ in the case of arbitrary temperature. This involves the partition function over the single-molecule eigenstates, the eigenvalues for which have been given by Wachtel and Wheeler.[10] It is possible to obtain from these a relation between T_N, $|J'|$, A and B,

$$\exp[-(A+B)/2kT_N]+2\cosh[(A-B)/2kT_N] = [4z|J'|/(A-B)]\sinh[(A-B)/2kT_N] , \qquad (37)$$

which follows on assuming that $\langle S_z\rangle$ and the consequent exchange fields experienced by each sublattice vanish at T_N. Wachtel and Wheeler have observed that with their derived parameters the value of T_N following from the above is about 35 K. This represents only a slight enhancement over the value obtained earlier from Eq. (34). Using the set of parameters derived by us on the basis of the Keffer-Kittel theory of the AFMR frequencies, there follows $T_N\approx 46$ K. Again, this is only slightly larger than the result obtained, ignoring the anisotropy, from Eq. (34).

More sophisticated theories of the anisotropy dependence of the Néel temperature lead to conclusions little different from those above. Lines,[108] Devlin,[109] and others have investigated this dependence using Green's-function methods. The general conclusion is that while mean-field theory underestimates the influence of anisotropy on T_N, Green's-function treatments overestimate this effect. Using the parameters from our analysis of AFMR in α-O_2, $D/hc=3.96$ cm^{-1} and $|J_2|/k=2.97$ cm^{-1}, and for $S=1$ in the case of a body-centered cubic lattice (the lattice dependence is slight), Lines's treatment leads to an enhancement in T_N over its value according to Eq. (34) by 5% in a mean-field treatment and by 17% in a Green's-function treatment. Devlin's results are essentially identical with those of Lines in this exchange versus anisotropy regime.

8. *Other experimental results*

Dundon[17] has studied the magnetic susceptibility and the heat capacity of solid oxygen as a function of pressure and magnetic field, to 170 atm and 5 kG. Neither property is changed in magnitude by these external influences, though $T_{\alpha\beta}$ increases by about 0.0035 K atm^{-1} judging from the temperature of the apparent discontinuity in susceptibility between beta and alpha oxygen and the temperature of the heat-capacity maximum. It appears from these results that the crystallographic and magnetic transitions are inseparable up to 170 atm and corresponding $T'_{\alpha\beta}$, and that the crystallographic transition is not induced by incipient antiferromagnetism, but rather the reverse.

English, Venables, and Salahub[35] have reached somewhat different conclusions from a theoretical study of the relative stabilities of the β-O_2 and α-O_2 crystal structures. They conclude that but for the effect of exchange interactions between oxygen molecules, β-O_2 would continue to be stable below 23.9 K, and that the transition to α-O_2 occurs because the latter structure maximizes the energy-lowering exchange interactions. The crystallographic phase transition can, therefore, be viewed as a consequence of the magnetic ordering. It seems to us that these calculations, though interesting, cannot be accepted as definitive in view of the limitations of the models employed in estimating the dispersion and exchange forces. The conclusion reached seems contrary to the available experimental evidence.

Dundon and Reaves[20] have measured the nuclear heat capacity of samples of α-O_2 enriched to 40 at.% ^{17}O, in the range 0.05 to 0.20 K. They conclude that the internal field at an oxygen nucleus, which is the dipole field due to the electronic moments, is 49.7 ± 2 kG. A corresponding ^{17}O NMR frequency should be seen at about 28.7 MHz, but has not been observed as yet. It is, however, questionable whether this result sheds any light on, for example, the question of the magnitude of the exchange field and corresponding exchange interactions.

Important information concerning the magnetic properties of solid oxygen can be sought from spectroscopic observations. But the conclusions to be drawn from the available data are not completely clear. Of greatest experimental and theoretical interest recently have been the bimolecular transitions in solid oxygen, $2^3\Sigma_g^- \rightarrow 2^1\Delta_g$ or $2^1\Sigma_g^+$ or $^1\Delta_g + {}^1\Sigma_g^+$, occurring via single-photon excitation. A number of authors have proposed theories of varying complexity in an effort to explain the detailed structure and intensities of the pure electronic and electronic-vibrational bands of these systems.[62,64,69,71,72] An outstanding question here is what combination of quasiparticle excitations (excitons, magnons, phonons, etc.) is required to account for all the complicated features of the spectra. Of most interest to us are estimates of spin-wave energies or exchange interactions which can be extracted from the data and the theories. The conflicting interpretations of Wachtel and Wheeler[10] and of Burakhovich *et al.*[19] have been mentioned in Sec. V C 5. From their examination of the spectra of both single-molecule and bimolecular transitions, Bhandari and Falicov[69] have estimated a value for the spin-wave energy at the Brillouin-zone boundary even larger than those already cited, namely, some 160 cm^{-1}. Estimates of the exchange interaction have also been somewhat various. Gaididei *et al.*[72(c)] conclude nothing definite about the principal antiferromagnetic exchange, J_2, between opposite sublattices, but make an estimate for that between neighbors on the same sublattice separated by $\pm\vec{b}_\alpha$, $|J_1'/hc| \approx 2.75\ \text{cm}^{-1}$. This is a perhaps surprisingly large value for these neighbors, and is conceded by these authors to be very uncertain. Fujiwara[71] is also rather noncommittal, but considers a value $|J_2'/hc| \approx 10\ \text{cm}^{-1}$ reasonable within the context of his theory. Bhandari and Falicov have estimated extremely large values for the exchange integrals, $J_2'/hc = -40\ \text{cm}^{-1}$ (with $z_2 = 4$, that is considering only the opposite sublattice neighbors 3.200 Å away in the *ab* plane) and $J_1'/hc = -25\ \text{cm}^{-1}$ (with $z_1 = 2$, for same sublattice neighbors at $\pm\vec{b}_\alpha$), and suggest that these magnitudes may be underestimates. These very large values are consistent with the very large zone boundary spin-wave energy inferred by the same authors, 160 cm^{-1}. Although Bhandari and Falicov believed that these exchange integrals were also consistent with a probable Néel temperature of 40 K, we believe this is not so. Substituting these parameters into Eq. (34) yields a value, $T_N = 106$ K. Assuming $J_1 > 0$ yields an even larger value for T_N. The theory of Bhandari and Falicov considers only the interactions between neighbors in a given *ab* plane. Were one to assume $z_2 = 8$ and accept the 160-cm^{-1} estimate for the zone boundary spin-wave energy (essentially equal to $z_2|J_2'|$), then a value $J_2'/hc = -20\ \text{cm}^{-1}$ results, that is $-10\ \text{cm}^{-1}$ in our convention. This value is approximately that obtained from the value of $\chi_\perp$ in Sec. V C 2. Lastly, one group[68] has observed repeated intervals of 60 cm^{-1} in the sideband of the 0-0 line of the single-molecule transition $^3\Sigma_g^- \rightarrow {}^1\Sigma_g^+$, and has suggested that this may be connected with a spin-wave excitation. It seems only fair to say that a consensus does not exist on what can be concluded precisely from the optical spectra.

VI. CONCLUSION

From the foregoing analyses a somewhat disparate set of estimates for the exchange interaction in α-O_2 has emerged. Values obtained by us range from $|J_2/hc| \approx 12\ \text{cm}^{-1}$ or $|J_2/k| \approx 17$ K, from the (corrected) value of $\chi_\perp$, to $|J/hc| = 2.1\ \text{cm}^{-1}$ or $|J/k| = 3.0$ K, from the magnetic heat capacity. Estimates from $\chi_\parallel(T)$ and AFMR frequencies lie between these extremes. Values as high as 20 cm^{-1} have been inferred by others. These differences, and especially the fact that the value of $\chi_\perp$ leads to an unacceptably high Néel temperature, suggest that the situation in solid α-O_2 is perhaps more complicated than assumed. The supposition underlying most of the preceding analysis has been that a two-sublattice model involving only one important exchange interaction is correct. The identification of more than one significant exchange interaction is, in general, not easy to establish experimentally. The lack of single-crystal data for α-O_2 accentuates this difficulty. It has been suggested, however, that the self-consistency of a set of exchange constants for a given material, determined from as many different physical properties as possible, is perhaps the best test of this question.[110] The present analysis has evidently revealed some inconsistencies. It should therefore be of interest to consider some lines along which an eventual resolution of these discrepancies might proceed.

The assumed magnetic structure has been described in Sec. V C 1. Eight neighbors of a given molecule make "contact" with the latter at their 0.002 electron density contours. These neighbors divide into two nonequivalent sets of four equivalent neighbors each. Denoting the given molecule 1, the neighbors in question are those labeled 2 and 3 in Fig. 7. the corresponding intermolecular separations are indicated in Fig. 2 as S_{12} and S_{13}. Terms involving $z_2J_2=8J_2$ have been employed to account for exchange between molecule 1 and these two types of neighbors. The interactions J_{12} and J_{13} may be rather different. An important question is, therefore, to what extent can the substitution of $8J_2$ for $4J_{12}+4J_{13}$ be expected to be adequate? If the eight neighbors in question are indeed on the opposite magnetic sublattice from molecule 1, and if J_{12} and J_{13} are not so different in magnitude that a two-dimensional rather than a three-dimensional theory is needed (as implied by Burakhovich *et al.*,[19] whose $J_{\parallel}'=2J_{12}$ and $J_{\perp}'=2J_{13}$), then the simplification in question should be adequate; i.e., the thermodynamic, if not the spectroscopic, properties should be the same. In particular, $\chi_{\perp}$ should be given by the theoretical expressions which have been employed earlier.

It was mentioned in Sec. V C 2 that intrasublattice exchange, J_1, has generally been neglected in discussion of the magnetic properties of α-O_2. The same sublattice neighbors to a given molecule 1 are the two molecules labeled 4 in Fig. 7 and two others (not shown in Fig. 7) which are at lattice translations $\pm(\vec{a}_\alpha+\vec{c}_\alpha)$ from the given molecule, and which we call molecules 5. The corresponding intermolecular separations are indicated in Fig. 2 as S_{14} and S_{15}. The justification for the neglect of exchange between these neighbors and molecule 1 is, at the least, uncertain. Although the separation S_{14} is significantly greater than S_{12}, and although the distance between nearest nuclei of molecules 1 and 4 is greater than between molecules 1 and 3 (see Sec. V C 2), molecule 4, like molecule 2, may be ideally situated for exchange with molecule 1. Molecule 5 is, moreover, only slightly more distant from molecule 1 than is molecule 3, with $S_{15}/S_{13}=1.011$ and the corresponding ratio of nearest nuclear separations equal to 1.019. If the exchange interactions within a sublattice are comparable to those between sublattices, then the parallel susceptibility should be affected. A net antiferromagnetic intrasublattice exchange interaction will lead to a reduction in the apparent value of $|J|$ extracted from susceptibility data [cf. Eq. (24)], since $zJ=z_2J_2-z_1J_1$. However, in order to account for the much smaller value of $|J|$ deduced from $\chi_{\parallel}(T)$ compared to that deduced from $\chi_{\perp}$, one would have to assume that the effective magnitude of J_1 was several times larger than that of J_2. This is physically unreasonable.

It is somewhat less clear whether the AFMR frequencies should reflect intrasublattice exchange. In a semiclassical treatment they do not, since a torque term involving $\vec{M}_i\times\vec{M}_i$ for sublattice i vanishes. This appears to be not necessarily the case in a quantum-mechanical treatment of corresponding $\vec{k}=0$ spin-wave frequencies.[111] However, the value of $|J|$ determined from the AFMR data is significantly smaller than that deduced from $\chi_{\parallel}(T)$. And the value of $|J|$ deduced from the magnetic heat capacity, which property reflects the spin-wave energies rather directly, is smaller yet. It is far from clear then that a consistent interpretation of the effects of intrasublattice exchange for all the properties under consideration can be put forward, at least on the basis of the assumed two-sublattice model, or indeed that any of the properties can be satisfactorily explained simply by introducing intrasublattice exchange.

Not withstanding the above considerations, it would obviously be desirable to have some notion of the relative strengths, even if not the actual magnitudes, of the exchange interactions between different pairs of neighbors in α-O_2. Such information might suggest the direction which a satisfactory theory of the magnetic properties should take. Unfortunately, exchange interactions in solids are extremely difficult to calculate from first principles.[112] The essential problem is that not only is detailed information about the localized wave functions, in this case the outer molecular orbitals of the oxygen molecule, required, but knowledge of how these functions are perturbed by the crystalline environment is also needed. Solid oxygen also presents, at first glance, a small problem of principle, in that the dominant exchange is evidently antiferromagnetic yet the material is homogeneous. The usual definition of the exchange integral leads necessarily to a positive, or ferromagnetic, interaction between electrons in perfectly orthogonal orbitals. The predominance of antiferromagnetic ordering in insulating systems is usually ascribed to the presence of suitable intervening diamagnetic species between the magnetic sites and the associated mechanism of superexchange, which yields a large negative contribution to the total exchange integral. In solid oxygen there are no intervening diamagnetic species. This, however, is only an apparent dilemma. It is necessary to recognize that even in a homogeneous material there can be two contributions to the total exchange integral, so-called "potential" exchange, which is always positive, and so-called "kinetic" exchange, which is always negative.[112] The potential exchange term is the true Heisenberg-Dirac exchange. The kinetic exchange term involves an admixture of virtual ionized states into the wave functions, and can be expressed in terms of a "hopping integral," b, and ionization potential, U, for a given exchange pair. The total exchange integral is

$$J_{ij} = J_{ij}^0 - (b^2/U)_{ij} \quad , \tag{38}$$

where J_{ij}^0 is the potential exchange between sites i and j. If the kinetic term predominates, the net interaction is antiferromagnetic.

To a reasonable degree of approximation, both the potential and kinetic terms in Eq. (38) depend on the square of the overlap integral for the magnetic orbitals of the interacting pair.[113] Without making any pretense of quantitative calculation, it nevertheless seems useful to estimate the relative overlap integrals between the various pairs of interacting molecules in α-O_2. To this end we have approximated the antibonding molecular orbitals of the oxygen molecule, π_x^* and π_y^*, by simple linear combinations of atomic orbitals: $\pi_{x,y}^* = N_a[2p_{x,y}(1) - 2p_{x,y}(2)]$, where (1) and (2) refer to the atoms of the molecule and where N_a is a normalization factor. For the atomic wave functions we have employed a Slater-type orbital (STO) approximated by a sum of six Gaussian functions (STO-6 G), each of the form $g_{2p}(\alpha, \vec{r}) = (128\alpha^5/\pi^3)^{1/4} r \exp(-\alpha r^2)\cos\theta$. The different Gaussian exponents, α_{2k}, for the six functions of the set and the coefficients, $d_{2p,k}$, of each function in the sum,

$$\phi_{2p}(1, \vec{r}) = \sum_{k=1}^{6} d_{2p,k}\, g_{2p}(\alpha_{2k}, \vec{r}) \quad ,$$

were taken from a standard reference.[114] The α_{2k} were multiplied by $\xi^2 = 2.25^2$, the square of the recommended Slater exponent for the $n = 2$ shell of atomic oxygen, since $\phi_{2p}(1, \vec{r})$ is constructed on an $\xi = 1$ basis. Formulas for overlap integrals between arbitrarily oriented Gaussian functions were taken from an unpublished set of calculations by Huzinaga.[115] The quantities $\langle \pi_x^*(i) + \pi_y^*(i) | \pi_x^*(j) + \pi_y^*(j) \rangle$, where i and j refer to the two neighboring molecules in α-O_2, were evaluated. The resulting relative overlap integrals for the four molecular pairs of interest were found to be

$$|\langle 1|2\rangle| = 1, \quad |\langle 1|3\rangle| = 0.282,$$

$$|\langle 1|4\rangle| = 0.269, \quad |\langle 1|5\rangle| = 0.176 \quad ,$$

where the bra and ket notations identify the molecules numbered 1 through 5, already described. If one now takes each of the terms in Eq. (38) to be proportional to $|\langle i|j\rangle|^2$, and if no important and unforeseen cancellation effect occurs for any particular pair, then one expects very roughly that

$$J_{12} \approx 13J_{13} \approx 14J_{14} \approx 32J_{15} \quad .$$

Consistent with physical intuition, J_{12} (intersublattice) is predicted to be largest and J_{15} (intrasublattice) smallest. But J_{15} differs by only about a factor of 2 from J_{14} (intrasublattice) and J_{13} (intersublattice). Therefore, in the case of four of eight intersublattice neighbors the exchange interaction is by no means clearly stronger than for the four intrasublattice neighbors. The comparison also suggests, because of the much larger J_{12}, that exchange interactions are considerably stronger within a given *ab* plane than between adjacent planes. This is more or less as suggested in Ref. 19, but still does not seem to us sufficient justification for calling α-O_2 a "quasi-two-dimensional" antiferromagnet. Nevertheless, taken together these results, if correct, obviously constitute an unusual situation. Whether or not a satisfactory theory of the magnetic properties of α-O_2 can be constructed on the basis of such a model, it is up to theorists to decide.

It must be emphasized that the reliability of the above results is very uncertain. The perturbing influence of the crystalline environment has been entirely ignored. A combination of STO's, and certainly a single STO, is a poor approximation to a Hartree-Fock wave function, particularly with regard to representing the electron density accurately.[115] The sum-of-Gaussians approximation to the STO constitutes another source of possible error, especially in as much as the Gaussian function is more localized than the Slater orbital, a potentially important consideration in the present application. Even more important perhaps, the linear combination of atomic orbitals used here to approximate the π^* orbitals is naive, and considerably underestimates the radial extent of the electron density for a true Hartree-Fock antibonding *pi* orbital.[115] Finally, the assumption has been made that for all the molecular pairs considered, J_{ij}^0 and b^2 are both proportional to the square of the overlap integral and that unexpected cancellation effects are not important. It is very difficult to judge the size of the errors that might arise as a result of these approximations. Our suspicion is that little can be safely concluded other than that at least three of the relevant exchange interactions may be of comparable magnitude, and that it is certainly possible that the largest of the four interactions, J_{12}, is not really an order of magnitude greater than the others.

If the exchange interactions in α-O_2 are all of comparable magnitude, the situation can be much more complex than assumed. It is known from work on magnetic ordering in body-centered and face-centered cubic structures that different types of order can result, depending on the relative magnitudes of nearest- and next-nearest-neighbor interactions.[116] Even where a single antiferromagnetic axis is preserved, the magnetic structure may have to be described in terms of more than two sublattices. Such a situation might be occurring in α-O_2. The available neutron diffraction data, from powder samples, probably imply no more than that the moments are aligned parallel and antiparallel to $\vec{b}_\alpha$. A multisublattice structure with $\vec{b}_\alpha$ the antiferromagnetic axis is therefore possible. Unfortunately, one of the best indirect tests of multisublattice arrangements, the ratio of the Weiss constant Θ to the Néel temperature, cannot be invoked here. The true Néel temperature of α-O_2 is in some doubt, and the Weiss Θ values which some have suggested as appropriate to γ-O_2 are, as indicated in Sec. V A, both dubious and inapplicable to the α-O_2 structure.

One attraction of the multisublattice hypothesis is that it might help in explaining the anomalously low value of $\chi_\perp$ for α-O_2. We take our cue from Smart's analysis[116] of the body-centered cubic lattice, since the structure of α-O_2 can be equally well described on the basis of a body-centered monoclinic cell (in which the center molecule is our number 1 and the corner molecules are four each of numbers 2 and 3). For a four sublattice arrangement analogous to the second type of order in the bcc lattice, we find that

$$\chi_\perp = Ng^2\mu_B^2/[-8(J_{12}+J_{13}+J_{14}+J_{15})] \ . \qquad (39)$$

This expression seems capable, however, of leading only to somewhat larger values of $\chi_\perp$ than Eq. (15), assuming $J_2=(J_{12}+J_{13})/2$, so long as J_{12} is largest in magnitude and negative. This appers to be a rather general result for more complicated sublattice structures, that $\chi_\perp$ is somewhat larger than for a simpler model. However, this is not necessarily the case if more than one antiferromagnetic axis is involved. If the sublattice arrangement is noncollinear, the quantities $\chi_\perp$ and $\chi_\parallel$ lose much of their former significance, and rather unusual susceptibility behavior can result.[117,118] It seems to us at least possible, despite the (rather incomplete) neutron diffraction data, that this kind of situation could occur in α-O_2, and that it might be shown to provide a resolution of the various discrepancies which have been remarked in this paper. Apart from this, one would be inclined to invoke, for reasons at least somewhat obscure, a gross failure of mean-field theory or even the Heisenberg-Dirac Hamiltonian to describe adequately as unusual a magnetic system as α-O_2.

We conclude by making a few observations concerning the "quasi-two-dimensional" description of α-O_2 advanced by Burakhovich *et al.*[19] In the case of solid oxygen one feels safe in assuming that one is dealing with a Heisenberg system, in view of the well isolated $^3\Sigma_g^-$ ground state, its structure and the relative exchange and anisotropy energies. The Heisenberg model does not order in two dimensions. Real systems that are approximately two dimensional always reveal, at temperatures sufficiently low that interlayer interactions become important, three-dimensional effects, e.g., magnetic ordering. One may ask, is this what is happening in α-O_2? The idea appears attractive at first as a way of explaining the fact that the true value of T_N is very much lower than that following from mean-field theory and the observed value of the perpendicular susceptibility. That is, one accepts the value of J deduced from $\chi_\perp$ as correct and asks why T_N is much less than the value implied by this interaction. It should be observed that whether the number of neighbors on the opposite sublattice is assumed to be eight or four (two dimensional) is not important, since zJ is what matters. Although it commonly occurs that two-dimensional Heisenberg antiferromagnets order (three dimensionally) at T_N values substantially less than those predicted by mean-field theory, in only a very few cases is $T_N(\text{obs})/T_N(\text{MFT})$ less than 0.5, and in only one case cited in a recent review[119] is it as low as 0.28. Moreover, when the ratio of interplanar-to-intraplanar exchange is relatively large ($\geq 10^{-2}$) the above ratio tends not to be small. Even accepting the result of Burakhovich *et al.*, $J_\perp/J_\parallel = 0.055$, one does not expect the ordering temperature to be diminished by a factor as large as 5. Indeed, only two examples in the review cited are characterized by an interlayer-to-intralayer interaction ratio larger than 10^{-2}, so that the value suggested by Burakhovich *et al.* for α-O_2 does not seem sufficiently extreme to argue strongly for two dimensionality.

The alpha-to-beta and higher-temperature phase transitions spoil any chance for observing certain other typical two-dimensional properties. For example, a rounded maximum in the susceptibility of two-dimensional antiferromagnets is usually observed at a temperature about twice that of three-dimensional ordering and slightly less than that predicted for T_N by mean-field theory.[119] In solid oxygen this temperature is presumably above the melting point, so that the effect is unobservable. Another indication of two-dimensional behavior is an enhancement in the amount of magnetic entropy above the transition to three-dimensional order, and a corresponding diminution in magnetic entropy below the transition. But above 23.9 K the stable phase of solid oxygen is beta, and no conclusions about α-O_2 can be drawn. We believe then that the available evidence cannot be interpreted as proving that α-O_2 is "quasi-two dimensional," nor even that this hypothesis is clearly helpful in explaining the unusual properties of this phase.

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