Magnetisation of condensed oxygen under high pressures and in strong magnetic fields

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Abstract. The variation of the magnetic susceptibility of condensed oxygen with temperature and hydrostatic pressure up to 0.6 GPa has been investigated. The results yield an empirical relation between the exchange parameter and the intermolecular distance. High-field magnetisation data on α-oxygen indicate a spin-flop; the corresponding anisotropy agrees fairly well with results of magnetic dipole calculations, which also include a prediction for the direction of the magnetisation axis. Evidence is presented for magnetic long-range order in β-oxygen.

1. Introduction

Condensed oxygen has been the subject of several investigations since the beginning of this century and as a result the crystallographic structure of the three solid phases is known well (Krupskii *et al* 1979). Some details, however, are still not clear, of which the nature and order of the α and β phase transition has received the most attention. As the oxygen molecule possesses a magnetic moment, many studies have focussed on the magnetic properties. Magnetic susceptibility measurements and neutron diffraction data indicated that α-oxygen is antiferromagnetically ordered and the γ phase and the liquid are paramagnetic. As to the β phase there is little information and much speculation (Slyusarev *et al* 1979, 1980, Loktev 1979).

  In this paper we present absolute values of the magnetic susceptibility as a function of temperature and pressure. Our analysis provides an empirical relation between the exchange parameter and the intermolecular distance; evidence is presented for anti-ferromagnetic ordering in the β phase. Magnetisation measurements in very strong fields serve to obtain values for the perpendicular susceptibility, and a spin-flop phenomenon in α-oxygen yields the anisotropy field.

2. Experimental

The samples were prepared by condensing gaseous oxygen (Matheson Gas Products, 99.998% pure) at a pressure of 1–2 bar into the liquid phase. When an appropriate amount of liquid was condensed the sample holder was isolated from the gas supply. Freezing of the samples occurred in less than five minutes.

The susceptibilities were derived from the magnetisation in a 1 T field using a conventional induction-coil system. The sample holder for pressures of 1 bar or less was made of epibond and could contain about 5 g of solid oxygen. For higher pressures a copper–beryllium vessel (sample weight about 0.8 g) and helium as a pressure transmitting medium was used. At the lower temperatures and the higher pressures the helium solidifies, but then it is still accepted to be a hydrostatic medium. The pressure vessel, capillary, high-pressure valve etc were cleaned thoroughly in an ultrasonic freon bath to remove all traces of grease in order to avoid (explosive) burning of the material in a concentrated atmosphere of oxygen.

In a high-field magnetometer (Roeland *et al* 1967) the sample holder could contain about 0.3 g. The magnetic field was kept constant within 1:1000 for 50 ms, and to minimise magneto-caloric effects the sampel holder was immersed in liquid helium, hydrogen or neon.

3. Experimental results

The susceptibility as a function of temperature is shown in figure 1. The sum of diamagnetic and van Vleck-type paramagnetic contributions is estimated to be as small as $-2 \times 10^{-9}\ \text{m}^3\ \text{kg}^{-1}$ and can therefore be neglected. Data were obtained with increasing temperature and care was taken to go very slowly through the phase transitions. For instance the region of the β–γ transition was traversed in two hours, resulting in a significally different result compared with a period of half an hour (open circles in figure 1). Different runs could give a small difference in results, less than 2% in the β and γ phases and less than 4% in the α phase. The overall difference might be due to a condensation of a minor fraction of the sample in the 1 mm diameter capillary, whereas
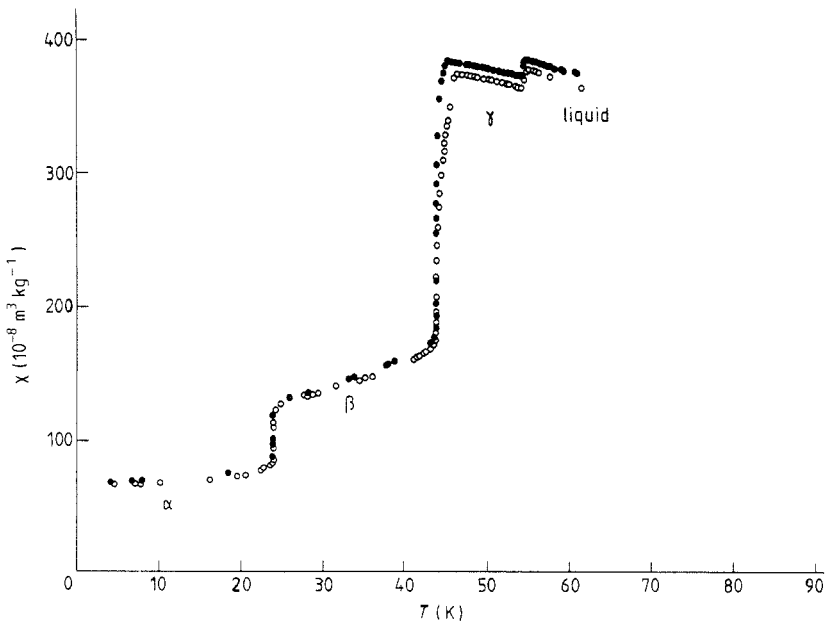

Figure 1. Susceptibility of condensed oxygen at zero pressure. Full circles represent a slow β–γ transformation (2 hours), open circles a faster one ($\frac{1}{2}$ hour).

the residual irreproducibility for the α phase has its origin in some irreproducible amount of preferred orientation (DeFotis 1977, 1981). The results presented in figure 1 were obtained in one run and represent the exact values within 2% for α-oxygen and 1% for β- and γ-oxygen, respectively.

The liquid presents more serious problems. The jump in the susceptibility accompanying melting is very reproducible (+3.5%) although other investigators obtained different values (Kanda *et al* 1954, 1955, Jamieson and Hollis Hallett 1966, DeFotis 1981) and freezing showed a different behaviour. The origin of these differences may lie in the large irreproducibilities we observed in the liquid phase, amounting to 10%. After a number of experiments, including varying the sample volume, thermal cycling and time effects, we had to conclude that at least part of the effects are intrinsic and not simply due to varying sample size or varying position in the magnetometer. However, at the moment we have no satisfactory explanation. It is worth noting that only a few of the published susceptibility data are explicitly quoted to represent absolute values (Kamerlingh Onnes and Perrier 1910, Kamerlingh Onnes and Oosterhuis 1913, Perrier and Kamerlingh Onnes 1914a, b). Some authors (Jamieson 1966, DeFotis 1977, 1981) fit their data to the value obtained by Kamerlingh Onnes at a temperature in the liquid phase, which, according to our findings, might introduce substantial systematic errors.
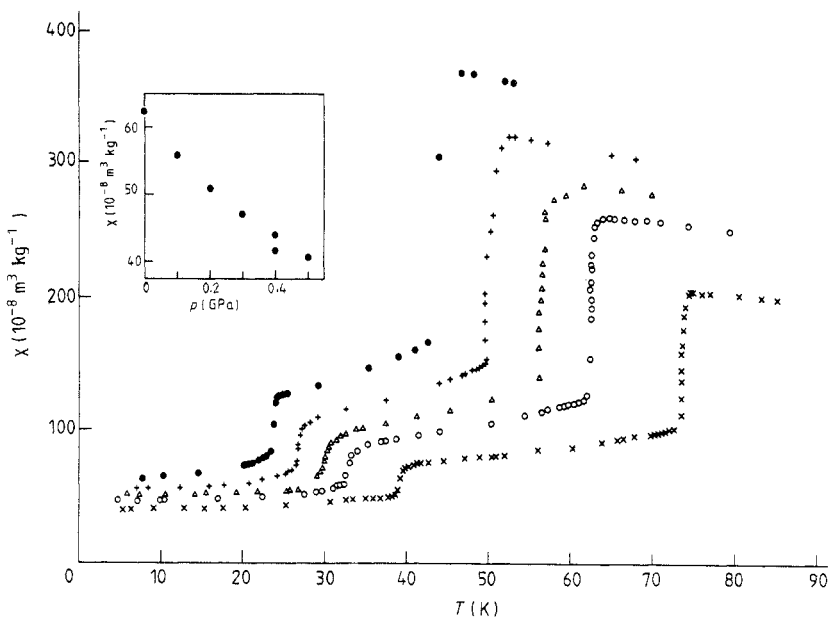

Figure 2. Pressure dependence of the susceptibility of solid oxygen. The insert shows the variation of the α-phase susceptibility at 4.2 K as a function of pressure.

The effect of applying hydrostatic pressure is very large as can be seen from figure 2. It must be noted that in the solid helium regime the uncertainty in the pressure values can be as 5%, which implies that the pressure dependence of the low-temperature susceptibility of α-oxygen, which is relatively inaccurate as mentioned before, cannot be extracted accurately from the data (see inset in figure 2). The shift of the transition temperatures with pressure is depicted in figure 3 and compared with data in the literature (Stevenson 1957, Stewart 1959).
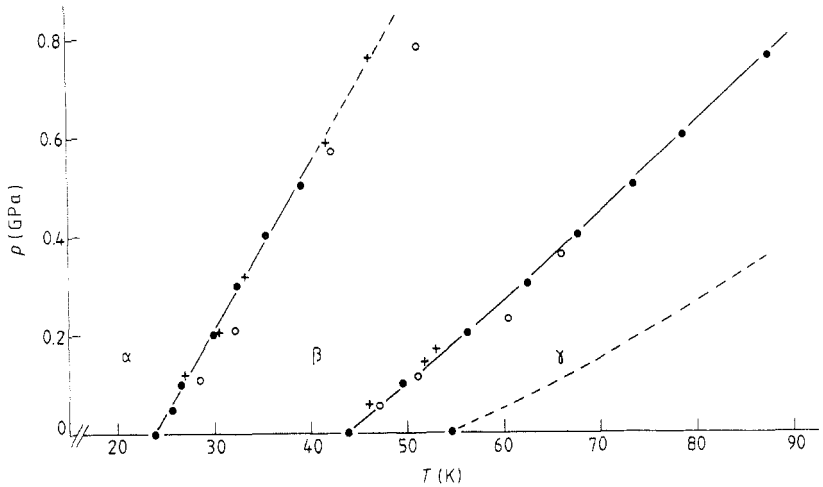
Figure 3. Phase diagram of oxygen. Full circles: present work; open circles: Stewart (1959); crosses: Stevenson (1957). The melting curve is taken from Mills and Grilly (1955).

Magnetisation curves in magnetic fields up to 35 T have been measured on α-oxygen at 1.4, 4.2 and 20.3 K and on β-oxygen at 27.1 K. The relative accuracy of the data is $\pm 0.5\%$, but as a consequence of the rather small sample quantity absolute accuracies are not better than $\pm 3\%$. The β-oxygen magnetisation curve is a straight line, while the α-phase shows a spin-flop, characterised by an inflexion point in the magnetisation curve at 7.2 ± 0.2 T, independent of temperature within the limits of accuracy. Figure 4 shows the approximate differential susceptibility at 4.2 K. The ratio between low-field and high-field susceptibility, 0.68, is in good agreement with the theoretical mean-field value,
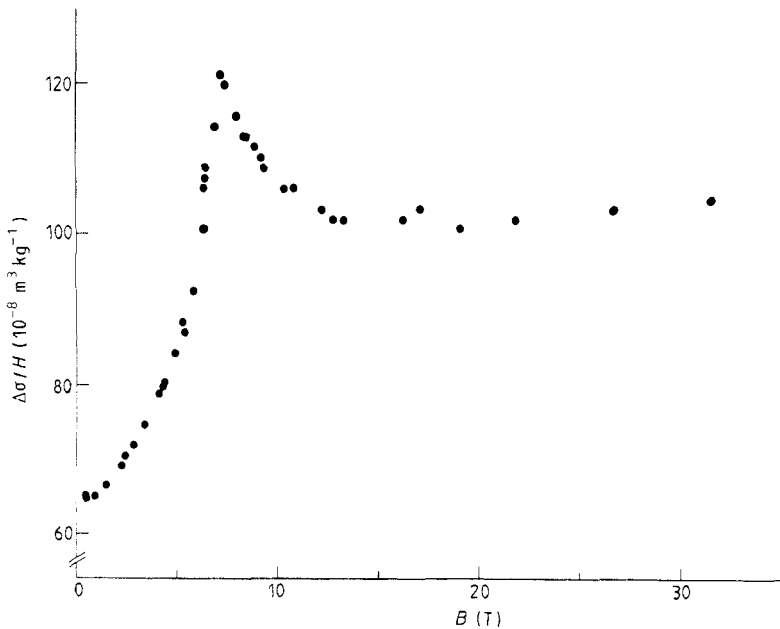

Figure 4. Approximate differential susceptibility ($\Delta B = 1$ T) as a function of field strength of α-oxygen at $T = 4.2$ K.

0.67, for a powdered uniaxial antiferromagnet. The slight increase of the differential susceptibility in the stronger fields is a real effect, for which we have no explanation at the moment.

4. Discussion

For an analysis of the experimental results we adopt the molecular-field approximation on the basis of an exchange Hamiltonian

$$H_{exch} = -2J_{12}S_1 \cdot S_2. \tag{1}$$

It is well established that α-oxygen is a two-sublattice antiferromagnet (Collins 1966, Alikhanov 1967). Our high-field magnetisation data provide the perpendicular susceptibility ($\chi_\perp = 9.64 \times 10^{-7}\,\mathrm{m^3\,kg^{-1}}$) which in a first approximation is given by

$$\chi_\perp = C(T_N + \theta)^{-1} = 3k_B C[4zJS(S + 1)]^{-1}. \tag{2}$$

C is the Curie constant, z the number of interacting neighbours of a molecule on the other sublattice, T_N the Néel temperature, θ the paramagnetic Curie temperature, k_B Boltzmann's constant and J the corresponding exchange parameter. Then, inserting the appropriate values for $\chi_\perp$ and C, $T_N + \theta = 408\,\mathrm{K}$ and the exchange field $B_{exch} = 2zJ(g\mu_B S)^{-1}$ equals 227 T.

The applied magnetic field forces the magnetisation axis of each of the crystallites in the powder specimen into a direction perpendicular to the applied field. We suppose that the rotation is in the *ab* plane, that is the plane perpendicular to the molecular axis. Then the spin-flop field is determined by the maximum anisotropy in the *ab* plane:

$$B_{sf}^2 = 2B_{anis}B_{exch}. \tag{3}$$

As our sample is a polycrystal, the inflexion point in the magnetisation curve, that is the maximum in the differential susceptibility, will be situated at lower field than the flop-field for a single crystal at 0 K (Néel 1936). The difference is about 30%, thus $B_{sf} \simeq 11\,\mathrm{T}$, and with $B_{exch} = 227\,\mathrm{T}$: $B_{anis} \simeq 0.26\,\mathrm{T}$.

In order to estimate the contribution of magnetic dipole–dipole interactions to the anisotropy, we have performed dipole field calculations for α-oxygen at 7 K, the lowest temperature for which Krupskii *et al* (1979) report accurate lattice parameters, and at 23 K. It has been noted in extenso by Colpa (1971) that one has to be very careful in calculating these fields because of problems of convergence. For antiferromagnets the dipole field is given by an alternating series, and thus might be free of these troubles. In our calculations convergence did occur, as was checked numerically. The ground state magnetisation axis was found to be parallel to the *b* axis, that is along the short edge of the rectangular centred face of the monoclinic cell, in agreement with the detailed (though not conclusive) analysis of Wachtel (1970) and DeFotis (1981) of the neutron diffraction data of Collins (1966) and Alikhanov (1967) as well as of susceptibility data (DeFotis 1981). In mono-molecular oxygen layers at low temperatures, having the same crystallographic structure as the *ab* plane in bulk α-oxygen, the magnetisation axis is also directed along the *b* axis as was shown by means of neutron diffraction (McTague and Nielsen 1976). The calculated anisotropy field corresponding to a rotation of the magnetisation axis from the *b* axis to the *a* axis equals 0.37 T (both at 7 and 23 K). Thus there is a good quantitative agreement with the experimental value and it seems that the magnetocrystalline anisotropy is determined by the dipole field.

At this point we want to compare our results with the literature data on spin-waves. In optical experiments two spin-wave modes have been observed at 4.2 K (Blocker *et al* 1969, Mathai and Alin 1971, Wachtel 1970, Wachtel and Wheeler 1970) at 6.5 and 27.3 cm^{-1}, respectively. Using the free-molecule value for the intramolecular anisotropy (that is, the difference between a moment in the *ab* plane and perpendicular to it) of 5.66 K (Meyer *et al* 1957) and 0.26 T for the in-plane anisotropy, the spin-wave frequencies follow from the formulae given by Lebesque (1979) (only major terms retained)

$$\omega_1^2 = g\mu_B B_{anis} 4z|J|S$$
$$\omega_2^2 = \omega_1^2 + 8z|J|SD(S - \tfrac{1}{2}). \tag{4}$$

Whereas in the molecular-field theory the perpendicular susceptibility contains the nearest-neighbour exchange only, (equation (2)), *J* in equation (4) represents the total exchange. We calculated this using an empirical relation between *J* and *R* (the intermolecular distance), to be established at the end of the discussion. With $2zJ_{total} = 248$ K the calculated frequencies equal 9.1 and 38.4 cm^{-1}, respectively, in poor agreement with experiment. Slyusarev *et al* (1980) propose to include a term $S_x^2 - S_y^2$, which can improve the situation. However, as one of the resulting frequencies is imaginary (due to the small anisotropy in the *ab* plane), the applicability of their expressions is questionable.

If the β phase were a paramagnet, its susceptibility would indicate a paramagnetic Curie temperature ranging from 287 K at 24 K to 180 K and 44 K. These values are so much larger than the temperatures at which the β phase exists that magnetic ordering should be expected. However, neutron diffraction patterns contain but few and weak indications of long-range magnetic order (Collins 1966, Stephens *et al* 1980), leading to the suggestion that only short-range order exists, without defining the type of the latter. Short-range order like that found in antiferromagnets just above the Néel temperature is not very likely in this case. Suppose T_N were close to 24 K, then at 44 K, roughly 2 T_N, the system should behave more or less as a normal paramagnet. A second kind of short-range order can be characterised by a high density of defects in the magnetic lattice, for instance because two possible magnetic structures differ only slightly in energy. It can be expected that the number of such defects will be the larger the more lattice defects are present. Now if we take into account the rough way in which the samples used in the neutron experiments were prepared, we doubt whether the absence of evidence for long-range order is an intrinsic property of β-oxygen, but rather is connected with samples containing a large number of lattice imperfections. One can argue why all this does not apply to α-oxygen. A reason may be that the α-oxygen crystal lattice and consequently the magnetic lattice differs from the β lattice and the magnetic interactions are roughly 50% stronger, thus the defect energies might be much higher. Anyhow, we adopt the viewpoint that β-oxygen is a long-range ordered antiferromagnet. Unfortunately we can give no substantial evidence for any particular type of order. Presumably the magnetisation axis will be perpendicular to the molecular axis, that is in the hexagonal plane. Then because of the six-fold symmetry there are a large number of identical directions and consequently the observation of a spin-flop is very unlikely in case of a two-sublattice antiferromagnet. In a three-sublattice structure (Loktev 1979) a spin-flop within the hexagonal plane will definitely be absent.

The γ phase has a susceptibility that can roughly be expected for a paramagnet with $\theta \simeq 60$ K. If it were an antiferromagnet, χ would increase with temperature, not in the least as a consequence of the lattice expansion, in contradiction to experiment.

Now, having described the gross features of the solid phases of oxygen, it remains to

Table 1. Calculated and experimental values of the exchange parameter fitted with $n = 14$ on the β-phase data point at 30 K.

Phase	Temperature (K)	Jk_B^{-1} (K) calc	exp
α	4.2	40.4	38.3
α	20	39.3	36.3 ± 2.5†
β	24	27.9	27.8
β	30	26.3	26.3
β	36	24.4	24.8
β	42	22.4	22.3
γ	44	19.0	16.0

† Large uncertainty due to large uncertainty in $\chi_\perp$.

Table 2. Calculated and experimental ratios of the exchange parameters in β-oxygen at atmospheric pressure (at $T = T_0$) and elevated pressures (at $T = T_p$).

T_0 (K)	T_p (K)	p (GPa)	J_0/J_p calc	exp
26.0	26.0	0.05	0.92	0.94
30.0	30.0	0.1	0.84	0.84
26.9	33.1	0.2	0.76	0.77
26.9	35.8	0.3	0.69	0.70
26.9	38.5	0.4	0.64	0.60
26.9	40.6	0.5	0.54	0.58
43.0	43.0	0.6	0.48	0.47

Table 3. Calculated and experimental ratios of the paramagnetic Curie temperatures of γ-oxygen at atmospheric pressure (at $T = 44$ K) and elevated pressure (at $T = T_p$).

T_p (K)	p (GPa)	θ_0/θ_p calc $n = 11$	$n = 12$	$n = 13$	$n = 14$	exp
52	0.1	0.88	0.87	0.85	0.84	0.84
62	0.2	0.77	0.75	0.74	0.72	0.79
64	0.3	0.71	0.69	0.67	0.65	0.71
70	0.4	0.65	0.62	0.60	0.57	0.67
74	0.5	0.61	0.58	0.56	0.53	0.53
79	0.6	0.57	0.54	0.52	0.49	0.57

account for the temperature and pressure dependence of the susceptibility χ in each of the phases and for the change in χ at the phase transitions. We will first consider the β phase. The variation with temperature of χ due to spin-wave excitations will be very small for two reasons: the relevant temperatures are small compared with the Néel temperature (116–156 K) as estimated from equation (2) taking $\theta = T_N$ (see also Lines 1970) and moreover, as discussed above, the measured susceptibility equals $\chi_\perp$ and thus will be hardly temperature dependent. Another, more important, cause for a variation of χ with temperature is connected with a change of the exchange field due to the large thermal expansion of the lattice of β-oxygen (Krupskii *et al* 1979).

Because we do not know the magnetic structure, we try an empirical description using equation (2). If we assume J to be proportional to R^{-n}, R being the nearest-neighbour distance, and use the literature data for the lattice parameters, a very good fit of the temperature dependence of χ is obtained with $n = 14.4 \pm 1.2$.

Encouraged by this success we have extended the calculations to the α and γ phases including the transitions and to the pressure dependence, making the following assumptions:

(i) R is given by the distance between the centres of the molecules, i.e. the non-spherical shape of the molecule is neglected;

(ii) J is an isotropic function of R only;

(iii) in the α and β phases only nearest-neighbour interactions are taken into account, because for a two-sublattice antiferromagnet in the molecular-field approximation the next-nearest-neighbour interactions cancel in the term $T_N + \theta$;

(iv) in γ oxygen, which is paramagnetic and has two different crystallographic sites and consequently constitutes a somewhat more complex system, only neighbours with a significant contribution to the exchange field (estimated from R^{-n}) are included;

(v) thermal variation of the lattice parameters, anisotropic in α- and β-oxygen, are taken from Krupskii *et al* (1979), while the volume compression data as given by Stevenson (1957), corrected for anisotropic compression of the lattice parameters (d'Amour *et al* 1981), are used.

With these assumptions and with $n = 14$ straightforward calculations can be made, the results of which are given in tables 1 and 2, starting from the experimental value of χ at 30 K and zero pressure. In view of the crude model the agreement between theory and experiment is quite good. The R-dependence in γ-oxygen can be fitted somewhat better with $n = 11$ (table 3), but it should be noted that the pressure dependence of the lattice parameters can only be extracted from the data of Stevenson (1957) with a large uncertainty. The temperature dependence of χ at atmospheric pressure yields $n = 14$.

5. Summary and conclusions

Essentially this paper consists of two parts. The first part comprises the report of new experimental data:

(i) the high-field magnetisation of α-oxygen, yielding the perpendicular susceptibility and a spin-flop field;

(ii) the high-field magnetisation of β-oxygen;

(iii) the pressure dependence of the susceptibilities of all three solid phases.

The second part consists of an analysis in the molecular-field approximation of both the temperature and the pressure dependence of the susceptibility using a simple empirical relation between the exchange parameter and the intermolecular distance, which gives surprisingly good results in view of the simplifications.

The starting point of the analysis was the assumption that β-oxygen is an ordered antiferromagnet. Although we have given reasons to believe this assumption is valid, one still might think it is a poor basis because direct experimental evidence is missing However one must bear in mind the following. First, whatever the magnetic structure (long-range or short-range order) of β-oxygen might be, if this structure does not vary

within the β-phase region, the susceptibility will be governed by the exchange interactions. And obviously the latter vary with R^{-14}. Secondly, the susceptibilities of the α and the γ phases can be linked through the same R^{-14} dependence of the exchange interactions; in other words the assumption about the β magnetic structure is not crucial. Actually one can now carry out the analysis the other way around and extract from the variation with temperature and pressure and the absolute value of the β-phase susceptibility strong evidence for long-range magnetic order. Of course it remains to be established directly by experiment and for that purpose neutron diffraction experiments as well as a careful search for magnon excitations in optical spectra are in progress.

It is surprising that the results presented in the paper allow for the validity of a simple power law $J \propto R^{-14}$ over a relatively large range of R (3.1 Å to about 3.7 Å) and for the applicability of an isotropic magnetic exchange. As to the former point, it can be mentioned that a similar behaviour is found in molecular hydrogen (de Boer 1942). The latter point is in fact the most surprising in view of the non-sphericity of the oxygen molecule and more experimental and theoretical evidence is necessary.

Acknowledgments

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