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Structure of Liquid Oxygen by Neutron Diffraction

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The angular distribution of 1.04 A neutrons scattered by specimens of liquid oxygen at 90.7°K, 69.0°K, 62.4°K, and 54.7°K has been measured over the angular range 3° to 78°. Pronounced excess scattering at low angles is taken to be magnetic in origin and its form suggests the possible existence of short range magnetic order in the liquid. The measured distributions corrected for magnetic scattering were transformed to the radial distribution functions $4\pi r^2[\rho(r)-\rho_0]$. An analysis of these gives 1.2_6 atoms and 1.26 A as the number of neighbors in, and the spacing of the diatomic shell, 2.7 A as the nearest distance of approach of 2 atoms in adjacent molecules in the liquid and about 3.9 A as the spacing of the main density maximum. The total number of atoms in the main density maximum increases from about 16 to 21 atoms for temperature change from 90.7°K to 54.7°K. The possible existence of the O_4 molecule is discussed.

INTRODUCTION

Both x rays[1] and neutrons[2] have been used to investigate the structure of liquid oxygen. The neutron diffraction measurements[2] contained excess scattering at low angles which was taken to be magnetic in origin. The form of this scattering was not known and was not subtracted from the measurements before transformation to the radial distribution functions.

This paper reports measurements of the angular distribution of neutrons scattered from specimens of liquid oxygen at four temperatures in the range 90.7°K to 54.7°K. The form of the low angle neutron scattering is compared with that theoretically calculated for magnetic scattering from oxygen with uncoupled magnetic moments. The distributions corrected for magnetic scattering were transformed to the density distribution in the liquid and were analyzed in terms of the spacings and number of neighbors under the coordinate shells. The accuracy of the measurements is discussed in terms of the effective resolution of the transforms. The possible existence of the O_4 molecule in the liquid is considered.

APPARATUS

The angular distributions of scattered neutrons were measured using one of the Chalk River Neutron Spectrometers[3] adjusted to monochromate 1.04 A neutrons. Measurements were made in the antiparallel rocking position. The specimens of liquid oxygen were held in a 0.970-cm diameter cassette having walls 0.010 in. thick for a height of $2\frac{1}{2}$ in. at the level of the neutron beam. The cassette was soldered to the base of the modified liquid helium chamber of the cryostat[4] in an arrangement similar to that used previously.[3] The cassette was filled with specimens of oxygen from a cylinder of oxygen gas.[5] The temperature of the cassette was measured, controlled and recorded by means of the vapor pressure[6] over the liquid oxygen used as the refrigerant in the liquid helium chamber.

MEASUREMENTS

The angular distributions of 1.04 A neutrons have been measured at about 137 equally spaced points in the angular range 3° to 78° for the specimens of liquid oxygen at 90.7°K, 69.0°K, 62.4°K, and 54.7°K. The background from the evacuated cassette at 80°K was measured at each of the angular points. At large angles, the background was essentially constant between the lines associated with the fcc structure of copper. Below 10°, it rose rapidly and became excessive for angles at and less than 3°. The background was corrected for the attenuation through the liquid oxygen using the known cross section for oxygen[7] before applying it as a correction to the measured curves.

The results of the measurements of the angular dependance of the scattered neutrons for each temperature are shown by the closed circles of Fig. 1. These intensities have been corrected for background, multiple scattering, and for counter resolution in the region of the main diffraction peak. The accuracy of the measurements may be estimated from the scatter of the experimental points. The large deviation of the points measured at the scattering angle of 3° is due to the excessive background at this point. The forms of all the curves are similar showing moderate scattering at low angles with a broad maximum in the region of 9°, a principal maximum in the region of 19°, and at large angles a series of oscillations about a broad maximum in the region of 62°. With decreasing temperature, the main maximum increases in height and shifts to larger

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[1] N. S. Gingrich, Revs. Modern Phys. **15**, 90 (1943).

[2] D. G. Henshaw, D. G. Hurst, and N. K. Pope, Phys. Rev. **92**, 1229 (1953).

[3] D. G. Henshaw, Phys. Rev. **111**, 1470 (1958).

[4] D. G. Hurst and D. G. Henshaw, Phys. Rev. **100**, 994 (1955).

[5] The oxygen was supplied by the Dominion Oxygen Company Ltd., and was stated to have a purity better than 99.6%. Before filling the cassette, the gas was purified by passing it through a commercial type hydrogen purifier to convert the hydrogen to water, which was removed on passage through a trap at liquid nitrogen temperatures. It is believed that little if any of the scattering is due to impurities.

[6] The temperature of the liquid oxygen was deduced from the vapor pressure using the tables given in the Westinghouse Research Report R-94433-2-A, Westinghouse Research Laboratories, East Pittsburgh, Pennsylvania.

[7] *Neutron Cross Sections*, Atomic Energy Commission Report, AECU-2040 (Technical Information Division, Department of Commerce, Washington, D. C., 1952).

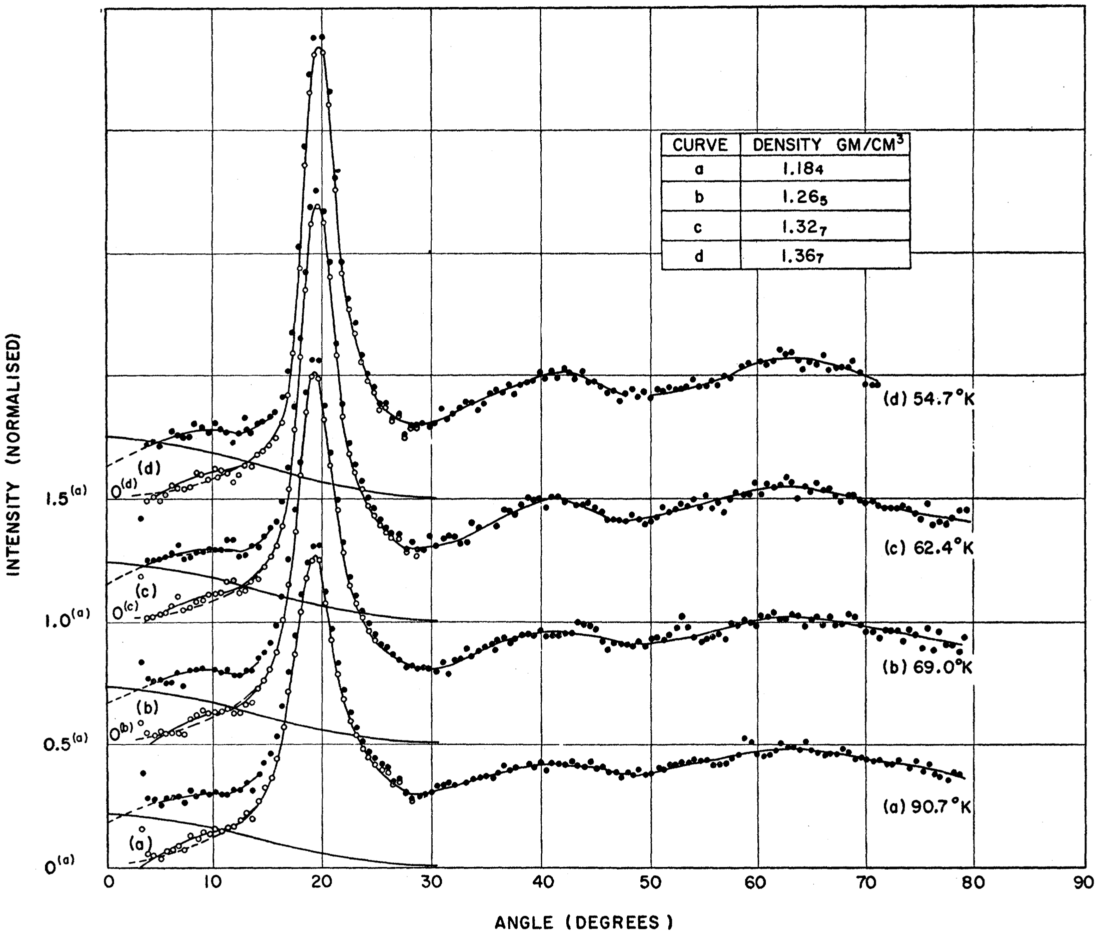

FIG. 1. The angular distribution of 1.04 A neutrons scattered from liquid oxygen at the temperatures indicated on the curves. The curves are shifted vertically, the zero for each curve being marked. The closed circles are the measured intensities corrected for background, counter resolution in the region of the main peak, and for multiple scattering. The smooth solid curve out to 30° gives the theoretically calculated magnetic scattering for oxygen with uncoupled magnetic moments. The open circles represent the scattered intensities corrected for magnetic scattering. The broken curve through these points at angles in the range 2° to 12° represents the intensity expected on the basis of similar x-ray diffraction measurements.

angles while the level of the scattering at large angles increases.

MAGNETIC SCATTERING

The scattering at low angles observed in the present and earlier[1] neutron diffraction measurements is in excess of that observed in corresponding x-ray diffraction measurements[1,8] where the extrapolated zero angle scattering is consistent with that calculated by the formula $L_0=nkT\chi_T$ where L_0=zero angle structure factor, n=particle number density, T=temperature, and χ_T=isothermal compressibility. Because isotope and spin incoherence are known to be small, this excess neutron scattering at low angles is taken to be magnetic in origin and must be subtracted before the curves may be analyzed in terms of the radial distribution function.

The smooth solid curves out to 30° of Fig. 1 show the calculated intensity of magnetic scattering assuming no ordering of the magnetic moments of the oxygen molecule. These curves were calculated using the theoretically calculated form factor due to Kleiner,[9] the known measured nuclear scattering cross section[7] of 8.4±0.4 barns per molecule, the known measured zero angle magnetic scattering cross section[10] of 4.58 barns per molecule, and the intensities[11] corresponding to the

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[8] D. G. Henshaw (unpublished).

[9] W. Kleiner, Phys. Rev. **97**, 411 (1955).

[10] H. Palevsky and R. M. Eisberg, Phys. Rev. **98**, 492 (1955).

[11] For a monatomic liquid, the scattering at large angles for neutrons of these wavelengths exhibits a series of oscillations which decrease in amplitude with increasing angle about a scattering level which is to a good approximation proportional to σ_{fa}, the free atom cross section. Thus the average scattering at large angles is proportional to σ_{fa}. For a diatomic liquid it is expected that the average large angle scattering should vary as $\sigma_{fa}(1+\sin\chi/\chi)$ where $\chi=(4\pi d/\lambda)\sin(\varphi/2)$, λ=neutron wavelength, φ=angle of scattering, and d=diatomic spacing. To check this hypothesis, the scattering intensities at large angles were calculated using the above formula and fitted to the experimental curve normalized to the intensity at the angle where $\sin\chi=0$ corresponding to $\chi=2\pi$ for values of d=1.20 A, 1.25 A, and 1.30 A, the separation of the expected diatomic spacing in liquid oxygen. A good fit to the aver-

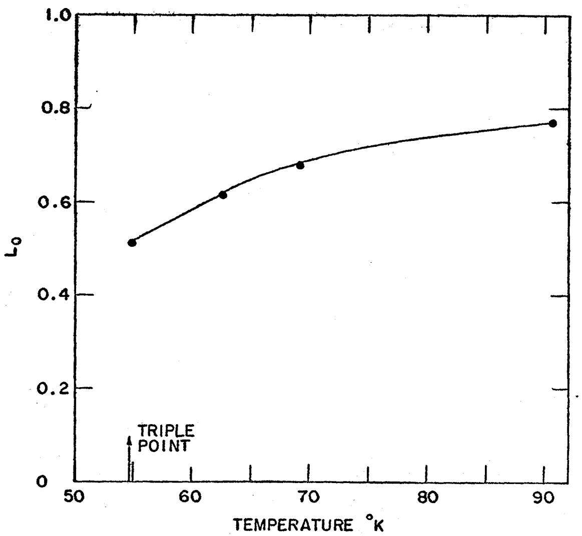

FIG. 2. The ratio of the extrapolated measured zero angle scattering to the calculated zero-angle magnetic scattering from oxygen with no ordering of the magnetic moments. This ratio is related to the short-range magnetic order in the liquid.

free atom cross section deduced from each of the curves.

The magnetic scattering calculated in this way was subtracted from the total scattering at each angle (the closed circles of Fig. 1) for angles out to 30°, beyond which the magnetic scattering is small. The results of these subtractions are shown by the open circles of Fig. 1. A smooth curve has been drawn through each set of points. In drawing this curve the point at 3° has been neglected because of the excessive background at that angle. The dotted curve at low angles through the points represents the form of the intensity expected on the basis of the x-ray diffraction measurements. The curves through the open circles tend to fall below and above the dotted curves at angles less than 5° and between 5° and 12°, respectively. The possibility that the broad maximum in the region of 9° may be due to $\lambda_0/2$ radiation is small because such a maximum has not been observed in the scattering from other liquids and the second order contamination is known to be small. This suggests that the actual magnetic scattering is different from that calculated on the basis of uncoupled magnetic moments. Assuming the validity of the calculated form factor,[9] these results then suggest deviations which may mean magnetic ordering in the liquid similar to that found for solid MnO at temperatures above its Curie temperature.[12] A measure of this ordering is given by L_0, the ratio of the measured zero angle scattering to that for a system of uncoupled magnetic moments. This ratio was determined for each of the curves by extrapolating the total scattering to zero angle (dotted curves of Fig. 1). The ratio of the zero angle scattering found thus to that calculated above gives L_0. The results are shown plotted as a function of temperature in Fig. 2 and indicate that the ordering increases with decreasing temperature. These measurements are consistent with the observed[13] behavior of the solid at temperatures above 23.8°K. Below this temperature, it is found that solid oxygen becomes antiferromagnetic.[13]

ATOMIC DENSITY DISTRIBUTION

The relation connecting the atomic distribution about an atom taken as center and the angular distribution of coherent nuclear scattered neutrons is given by:

$$4\pi r^2\{\rho(r)-\rho_0\}=\frac{2r}{\pi}\int_0^{\infty} si(s)\sin(rs)ds, \qquad (1)$$

where r = distance from an atom chosen as center, $\rho(r)$ = atomic density at a distance r, ρ_0 = mean atomic density of the liquid, $s=(4\pi/\lambda)\sin(\varphi/2)$, λ = neutron wavelength, φ = angle of scattering, $i(s)=(I_s-I_\infty)/I_\infty$, I_s = intensity of coherent nuclear scattering for the value s of the variable, I_∞ = value of I_s for $s=\infty$.

For measurements made over a finite range of s, the value of I_∞ cannot be determined directly. In this analysis, the value of I_∞ was chosen to satisfy

$$-2\pi^2\rho_0=\int^{\infty} s^2 i(s)ds,$$

which ensures that $\rho(r)\rightarrow 0$ for $r\rightarrow 0$. Since the intensity was measured out to a finite value of s, it was assumed that $i(s)=0$ at values of s greater than this.

In the present analysis, the angular distributions of scattered neutrons corrected for magnetic scattering of Fig. 1 are taken as the dotted curve through the open circles for angles up to 12°, the solid curve through the open circles up to 28° and the closed circles at larger angles.

Each of the diffraction patterns of Fig. 1 was transformed[14] to the atomic distribution function $4\pi r^2[\rho(r)-\rho_0]$ using Eq. (1) in steps of 0.2 A for spacings in the range 0 to 20.0 A. The value of I_∞ obtained using Eq. (2) was used to deduce the function $i(s)$ for each of the curves. The result of the computations are shown in Fig. 3 for each of the curves. The parabolic curves represent $-4\pi r^2\rho_0$ the negative of the mean atomic density. Each of the curves shows a peak in the region of 1.2 A, then an oscillation about $-4\pi r^2\rho_0$, a rapid increase at 2.7 A to a broad maximum at 3.8 A

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age experimental intensities was obtained using $d=1.25$ A while the calculated curves for $d=1.20$ A and $d=1.30$ A deviated considerably from the average scattering at large angles. It was therefore taken that the average scattering varied as $\sigma_{fa}(1+\sin\chi/\chi)$ at large angles. The average value of the intensities at the angles where $\sin\chi=0$ for $d=1.25$ A was taken as the intensity corresponding to the free atom cross section and used in determining the level of the magnetic scattering. At this angle the calculated magnetic scattering is small and may be neglected.

[12] C. G. Shull, W. A. Strauser, and E. O. Wollan, Phys. Rev. 83, 333 (1951).

[13] D. G. Henshaw (unpublished).

[14] The Fourier transforms were calculated on FERUT by the Computation Center, University of Toronto.

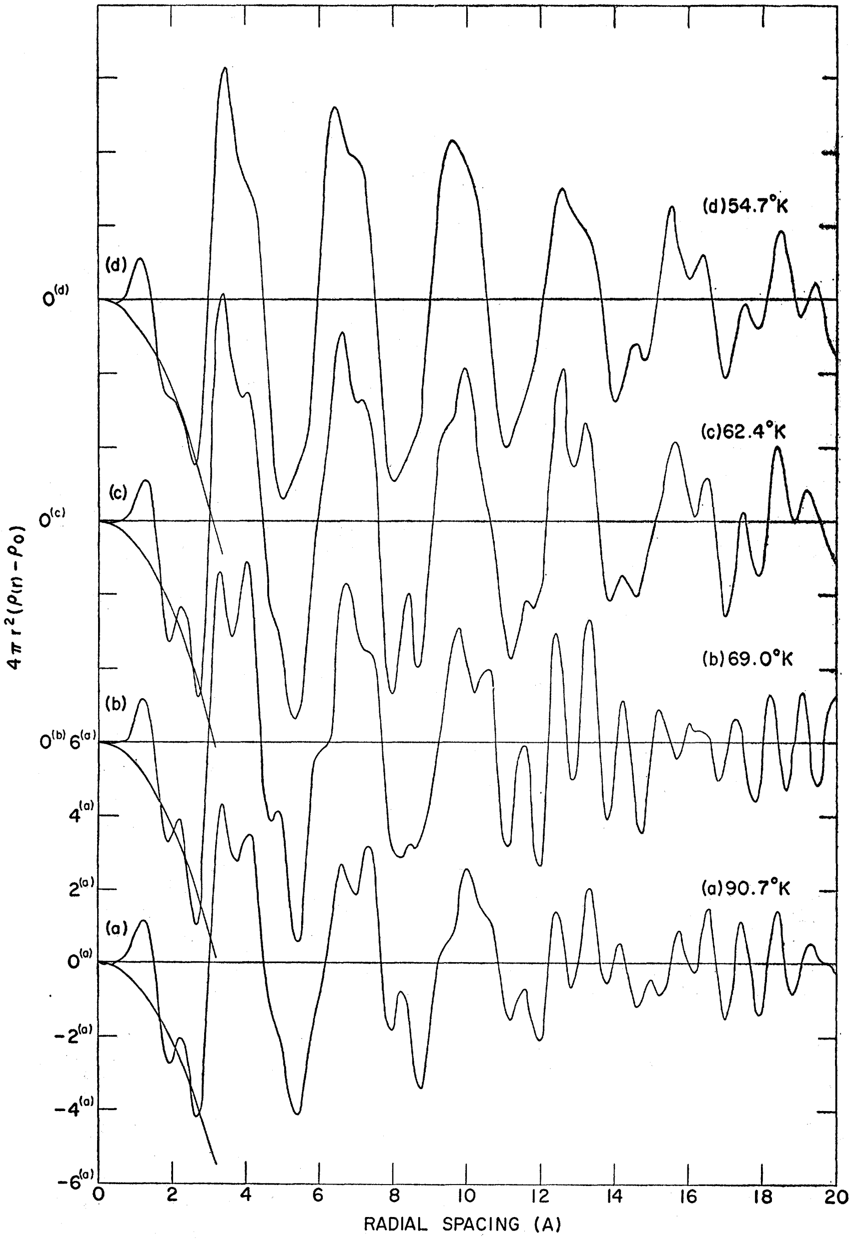

FIG. 3. The transforms $4\pi r^2 \times[\rho(r)-\rho_0]$. The curves are shifted vertically, the zero of each curve being marked. The parabolic curves are $-4\pi r^2\rho_0$.

beyond which there are oscillations about zero with an amplitude which decreases with increasing radial spacing. The oscillations about $-4\pi r^2\rho_0$ at 2.2 A are almost certainly spurious arising from experimental error and the finite range ($s_{\max}=7.6$ A^{-1}) over which the measurements were made which limits the resolution of these transforms[15] to $(2\pi/s_{\max})=0.78$ A and which produces nonrealistic oscillations on the transform. These oscillations extend to larger radial spacings and may cause the splitting of the main density maximum.

The radial distribution function $4\pi r^2\rho(r)$ together with the mean atomic density $4\pi r^2\rho_0$ is shown for each temperature in Fig. 4. Table I lists the analysis of these curves in terms of the radial spacing and the number of neighbors under each coordinate shell.[16] Analysis of these curves gives 1.26 A and 1.2_6 atoms as the average separation and average number of atoms at the diatomic spacing. Owing to the fact that the effective resolution of the transforms was 0.8 A, it cannot be said whether the value 1.26 atoms is significantly different from 1.0

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[15] J. Waser and V. Schomaker, Revs. Modern Phys. **25**, 671 (1953).

[16] The number of neighbors at the diatomic spacing was determined from the area under the peak centered about 1.26 A while for the main density maximum the peaks were assumed symmetrical in $4\pi r^2\rho(r)$ about the maximum in $4\pi r^2\rho(r)$.

TABLE I. Liquid oxygen.

		Diatomic peak		Main density maximum			Number of neighbors		
Liquid temperature (°K)	Liquid density (g/cc)	Position (A)	Number of neighbor atoms	Spacing where density rises from zero (A)	First maximum in $4\pi r^2\rho(r)$ (A)	Second maximum in $4\pi r^2\rho(r)$ (A)	First maximum symmetrical in $4\pi r^2\rho(r)$ atoms	Second maximum symmetrical in $4\pi r^2\rho(r)$ atoms	Total first and second atoms
90.7	1.184	1.28	1.29	2.6	3.42	4.14	7.6	8.3	15.$_9$
69.0	1.265	1.25	1.26	2.8	3.44	4.07	7.3	10.0	17.$_3$
62.4	1.327	1.30	1.27	2.7$_5$	3.42	4.14	9.6	8.7	18.$_3$
54.7	1.367	1.20	1.21	2.8	3.50	4.20	12.5	8.7	21.$_2$
	Average	1.26	1.26	2.7					

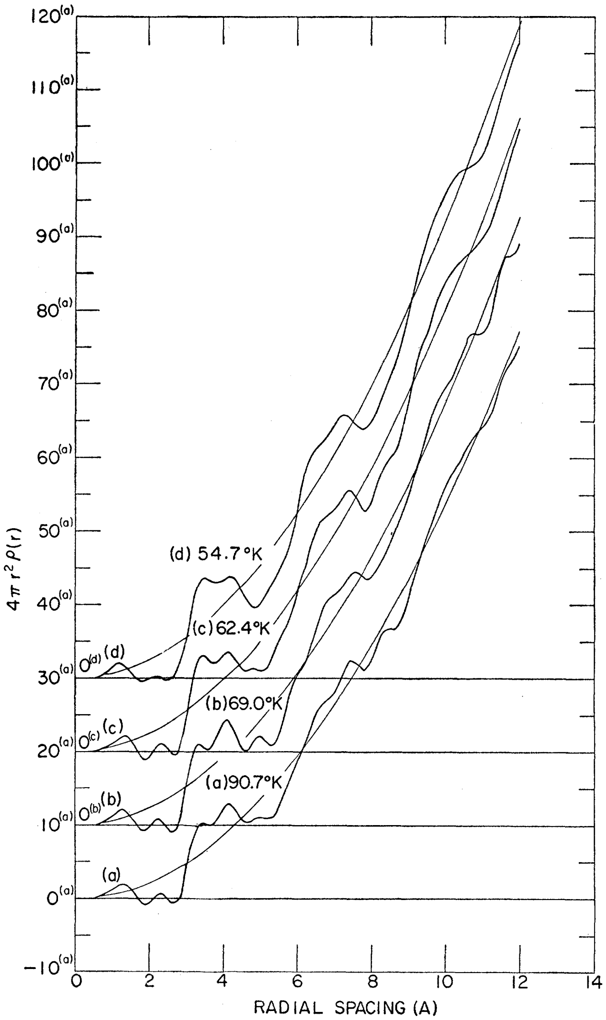

FIG. 4. The quantities $4\pi r^2\rho(r)$ and $4\pi r^2\rho_0$ (parabolic curve). The zeros for each curve are indicated.

atoms, the number expected for a diatomic molecule. The separation 1.26 A agrees with the spacing 1.25 A found above from the analysis of the large angle scattering. This value is not inconsistent with 1.21 A the separation of the diatomic molecule in the ground state.[17] The nearest distance of approach of two atoms in adjacent molecules is 2.7 A while the total number of atoms under the shells at 3.4 A and 4.1 A increases from 16 atoms to 21 atoms for temperature change from 90.7°K to 54.7°K, respectively. These curves have been analyzed on the basis of two distinct peaks at about 3.4 A and 4.1 A, respectively. The justification for this is not certain since the effective resolution of the transforms is 0.8 A.

DISCUSSION

The existence of O_4 has been suggested from the results of both spectroscopic and magnetic measurements on mixtures of liquid oxygen and nitrogen.[18] Lewis,[19] from the magnetic susceptibility of such mixtures, calculated that oxygen at 77.4°K should contain 40% by weight of O_4. Assuming that the molecule O_4 is tetrahedral with a spacing between atoms equal to that of the O_2 molecule, a simple calculation on the basis of 1.26 atoms under the diatomic shell would indicate the existence of 12% by weight of O_4. This number is considerably less than that required to explain the susceptibility measurements and these results cannot be used to confirm the existence of the O_4 molecule. An unambiguous determination of this number must await a determination of the radial distribution function with better resolution by recording the angular distribution of scattered neutrons to larger values of s. Such measurements will also determine whether the main density maximum of the distribution functions at 3.8 A is composed of a single or double shell of atoms.

ACKNOWLEDGMENTS

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[17] G. Herzberg, *Spectra of Diatomic Molecules* (D. Van Nostrand Company, Inc., Princeton, New Jersey, 1950), 2nd ed., p. 560.

[18] M. and B. Ruheman, *Low-Temperature Physics* (Cambridge University Press, New York, 1937), p. 228.

[19] G. N. Lewis, J. Am. Chem. Soc. **46**, 2027 (1924).