

*A Study of Magnetic Properties of Solid Oxygen,
Oxygen-Argon and Oxygen-Fluorine **

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Synopsis

To acquire information on the interaction between oxygen molecules in solid phase, studies have been carried out on the magnetic properties of solid oxygen, oxygen-argon and oxygen-fluorine.

Review of the studies on the interaction between oxygen molecules is cited.

Magnetic susceptibility was measured by the Faraday method as a function of temperature from 12° K to the melting point of them.

Pure oxygen both in α and β phase indicates paramagnetism corresponding to long-range antiferromagnetic order. Oxygen-argon mixtures of 92~66 mol% oxygen content indicate large susceptibility corresponding to δ phase, which can be interpreted in terms of the cluster of oxygen molecules in trimer.

Small paramagnetism was found for the oxygen-fluorine mixture even as dilute as 10 mol% oxygen content, which may be due to the strong antiferromagnetic interaction. This can be interpreted in terms of super-exchange interaction between oxygen molecules via fluorine molecule.

* based upon doctor thesis

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1. Introduction

1-1. General Introduction

Oxygen is known as one of the rare molecules that indicates a paramagnetism in gas phase. The magnetic susceptibility(χ) is described as a function of absolute temperature(T);

$$\chi = 1.01/T \quad (\text{emu/mol})$$

At 300 K, for example, it indicates considerably large paramagnetic susceptibility of 3.33×10^{-3} emu/mol. It is expected from the Curie law that at low temperature it would become larger, but solid oxygen indicates extremely small susceptibility.

Concerning the interaction among oxygen molecules which reduces paramagnetism in solid state, many investigations have been made with absorption spectra, magnetic measurement, X-ray and neutron diffraction and so on. These investigations have revealed antiferromagnetic interaction in solid oxygen. However, we can only find that a few studies on the magnetic interaction in solid oxygen have been carried out.

We present, in this study, the measurement of magnetic susceptibility of O_2 -Ar and O_2 - F_2 solid mixture of various O_2 concentration of oxygen molecule with its surroundings.

1-2. Review of the studies on the interaction between O_2

Since 1823, when M.Faraday first proposed to liquefy air, many kinds of gas were liquefied one by one until the first stage of 20th century. At the summit of them, H.Kammerlingh Onnes succeeded in liquefying helium and reached to the extremely low temperature, -269°C (4.2 K). Applying these technique to produce low temperature, studies of solid state physics have achieved great progress and as a branch of them, investigation on liquid and solid state of the materials which are gaseous at room temperature have been able to be conducted.

Attending to the fact that oxygen is a triplet in the ground state and indicate paramagnetism in gas phase, A.Perrier and H. Kammerlingh Onnes¹⁾ measured the susceptibility of oxygen in liquid and solid phase and also that of oxygen-nitrogen mixture in liquid phase. They showed that the susceptibility of pure oxygen decreases abruptly at the melting point, again decreased sharply around 33 K and is almost constant below 33 K. In oxygen-nitrogen liquid solution, the susceptibility decreases with increase of nitrogen

content.

Founding on the results of Perrier and Kammerlingh Onnes, G.N. Lewis²⁾ advocated that an association of two oxygen molecules may occur in solid and liquid phase to form O_4 molecule which is diamagnetic. He assumed an equilibrium relation as $O_4 \rightleftharpoons 2O_2$ and obtained from the temperature dependence of equilibrium constant 128 cal/mole as a heat of the dissociation of O_4 .

W.F.Giauque and H.L.Johnston³⁾ measured the specific heat of solid oxygen and discovered the existence of three phases, α , β and γ . Transition temperature and latent heat obtained by them and later by the other workers are listed in Table 1.

Table 1. Transition temperature and latent heat of oxygen

	Transition point (K)	Latent heat (joule/mole)
Boiling point	90.17	6820
Triple point	54.36	442+2 (445+1)
β - γ	43.78	742+5 (743+1)
α - β	23.89	~ 0 (94)

() --- W.F.Giauque and H.L.Johnston.³⁾

Others --- C.H.Fagerstroem and A.C.H. Hallett.⁴⁾

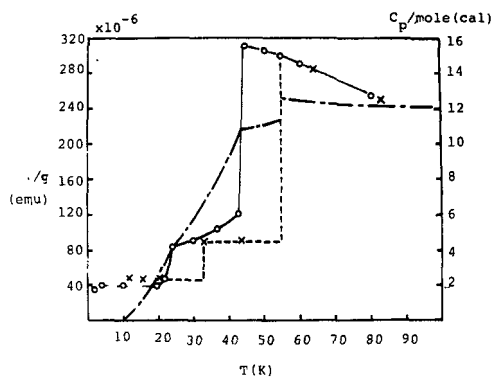


Fig.1. Magnetic susceptibility and specific heat of solid oxygen

—; Kanda et al.⁶⁾

---; Perrier and Kammerlingh Onnes¹⁾

---; Specific heat value by Giauque and Johnston³⁾

On the other hand, the absorption spectra of liquid oxygen were studied by several workers and in 1933 J.W.Eliss and H.O.Kneser⁵⁾ could assign the spectra in visible and ultraviolet region assuming that, besides the known excited states $^1\Delta$ and $^1\Sigma$, there exist combination terms $^1\Delta+^1\Delta$, $^1\Delta+^1\Sigma$, $^1\Sigma+^1\Sigma$ due to O_4 molecule. Moreover, they considered that the absorption spectra corresponding to $^3\Sigma \rightarrow ^1\Delta$ and $^3\Sigma \rightarrow ^1\Sigma$ are intensified by the production of O_4 molecule and the lift of prohibition. The concentration of O_4 molecule estimated from the absorption intensity indicates good agreement

with Lewis' estimation that there exists about half of the associated oxygen.

Twenty years after, in 1954, E.Kanda et al.⁶⁾ has again measured the susceptibility from 2 K to the melting point with a Hartshorn A.C. bridge. Their results are shown in Fig.1 with that of Perrier and Kammerlingh Onnes¹⁾ and also that of Giaque and Johnston.³⁾ A fairly good agreement was obtained between magnetic transition points and the thermal ones by Giaque and Johnston, different from the results by Perrier and Kammerlingh Onnes. At the transition point from γ to β phase, the susceptibility decreases sharply to one third. In β phase, it diminishes gradually with the temperature to the next transition point from β to α phase, where it decreases abruptly once again to a half. They make a doubt upon the previous belief that the dimer molecule O_4 is diamagnetic, because their results showed an apparent paramagnetism down to 2 K where all molecules should form the dimer according to Lewis' theory. They suggested that oxygen in liquid and solid phase is rather antiferromagnetic.

From about that time, in the field of optical spectroscopy also, many reports have been published. V.I.Dianov-klov⁷⁾ studied absorption spectra of condensed oxygen in the $1.26 \sim 0.3 \mu$ region. The intensities of all absorption bands depend on square of the pressure in atmospheric and condensed oxygen (Fig.2), which indicates the determining role of pair collisions. The life-time of the colliding pair in the gas was estimated from the band half-width and the rotational splitting as $3 \times 10^{-13} < \tau < 2 \times 10^{-11}$ sec.

C.W.Cho et al.⁸⁾ measured absorption intensity of infrared and red band region in pure oxygen in the pressure range $50 \sim 150$ atm and in O_2-N_2 , O_2-Ar and O_2-He mixture up to 3000 atm. They showed that induction effects in O_2-N_2 , O_2-Ar and O_2-He

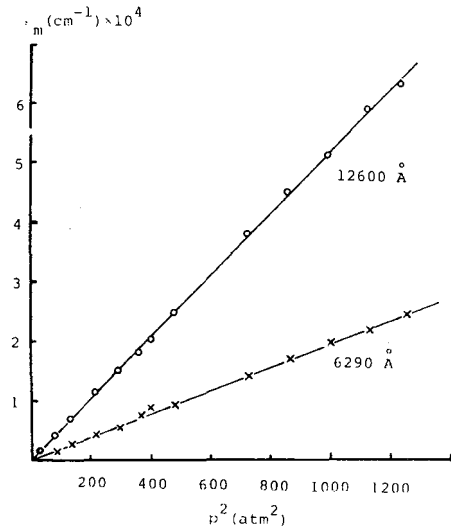


Fig.2. Variation of the peak intensity of the absorption bands with the square of the pressure (Dianov-klov⁷⁾).
o; 12600 Å, x; 6290 Å

pairs were much smaller than those in O_2-O_2 pairs. It was thought probably more preferable to explain in terms of the formation of O_4 molecules.

In the emission bands also, the spectra due to the combination terms was found. J.S.Arnold et al.⁹⁾ found weak bands at 6340 and 7030 Å in discharged oxygen. L.W.Bader and E.A.Ogryzlo¹⁰⁾ reported that the intensity of 6340 Å band emission was proportional to the square of O_2 concentration.

Lately, C.A.Long and G.E.Ewing¹¹⁾ reported the infrared spectra $1480\sim 1800\text{ cm}^{-1}$ at temperature $77\sim 300\text{ K}$. In the paper, the energy of formation of O_4 , as determined from the temperature dependence of the doublet which appeared below 90 K, was shown to be -530 cal/mole. The lifetime of O_4 was estimated from the doublet band half-width to be $\sim 10^{-12}$ sec. Comparing this with intermolecular interaction times of $\sim 10^{-13}$ sec for colliding pair, they considered the dimer structure somewhat rigid.

The crystal structure of solid oxygen was revealed with the development of low temperature technique in crystal analysis. T. H.Jordan et al.¹²⁾ showed with X-ray diffraction that the crystal structure of γ -oxygen is very similar to that of β -fluorine. The unit cell is cubic, space group is $Pm\bar{3}n$, and has a lattice dimension $a=6.83\text{ Å}$. As is shown in Fig.3, the unit cell contains eight oxygen molecules. Oxygen molecules located at the center and corner of the cube rotate freely, and each oxygen in the face of the cube rotate in the plane perpendicular to the face.

The crystal structure of β -oxygen was investigated with electron diffraction by E.M.Hörl.¹⁸⁾ He found a rhombohedral structure of the space group $R\bar{3}m$. Its corresponding hexagonal cell has the dimensions $a=3.307$, $c=11.250\text{ Å}$ and contains three oxygen molecules with their axis parallel

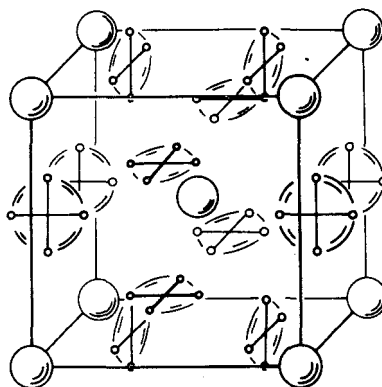


Fig.3. The structure of γ - O_2 . The balls forming the body-centered part of the cell represent freely rotating or nearly isotropically disordered O_2 molecules. The disorder of the other O_2 is mainly constricted to a plane as shown (T.H.Jordan et al.¹²⁾).

to the hexagonal axis. The unit cell of β -oxygen is shown in Fig. 4.

C.S.Barrett et al.¹⁴⁾ investigated with X-ray diffraction the crystal structure of α -oxygen. The unit cell is monoclinic with $a=5.403$, $b=3.429$, $c=5.086$ Å, $\beta=132.53^\circ$, volume= 69.44 Å³, calculated density 1.530 g/cm³. The cell contains two molecules centered at the lattice points 000 and $1/2 1/2 0$, which are symmetry centers. The nearest center-to-center distances between molecules is 3.20 Å and the O-O bond axis was found to be perpendicular to the ab plane within an experimental accuracy of a few degrees. The crystal structure revealed by them is shown in Fig. 5.

These results on the crystal structure of solid oxygen revealed that O_4 dimer does not exist in any phase of solid oxygen.

Since existence of O_4 molecule is denied, the susceptibility of solid oxygen have to be interpreted in terms of antiferromagnetism not in terms of diamagnetism, as was indicated by Kanda et al. Several studies were conducted to confirm antiferromagnetism in solid oxygen, especially in α -phase.

Neutron powder patterns of solid α - and β -oxygen were taken by M.F.Collins¹⁵⁾ in 1966. He observed two magnetic lines that have d spacings of twice the value for the nuclear lines in α -phase (Fig. 6). In β phase no magnetic line was found. He concluded that α -oxygen is antiferromagnetic whilst β -oxygen exhibits only short-range antiferromagnetic order.

Resting on the basis, C.S.Barrett et al.¹⁴⁾ interpreted Collins'

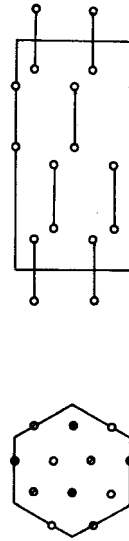


Fig.4. The structure of β -O₂.

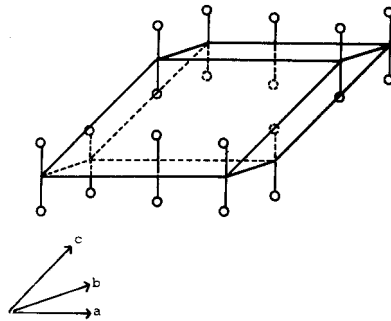


Fig.5. The structure of α -O₂.

neutron diffraction results and presented a magnetic structure. They indicated that the magnetic line with 4.78 \AA has index $\bar{1}01$ on the cell and also the line $d=3.99 \text{ \AA}$ has index 100 , and expected that the magnetic dipoles of the molecules in the ab plane in Fig.5. at 000 are antiparallel to those at $1/2 \ 1/2 \ 0$. With this arrangement of the magnetic moments, the eight nearest neighbors of each molecule have oppositely directed moments, which they thought, is a configuration that is entirely reasonable. About the relation of a molecule with its nearest-neighbor, they pointed out the molecular packing in the lattice. Projection of molecules with 0.002 contours of electron density on (001) and $(\bar{2}01)$ plane of monoclinic lattice in α -oxygen was compared with that in β -oxygen on (001) plane of hexagonal lattice. Close packing in α -oxygen would result in larger exchange interaction and more perfect alignment of spin than in β -oxygen.

Yu.G.Litvinenko et al.¹⁶⁾ studied the effect of the anti-ferromagnetism on the absorption spectra of solid oxygen. As shown in Fig.7. the intensity of the absorption band was constant up to $14 \sim 17 \text{ K}$ and decreases rapidly above the temperature. Red shift with increase of temperature and with dilution was observed. They

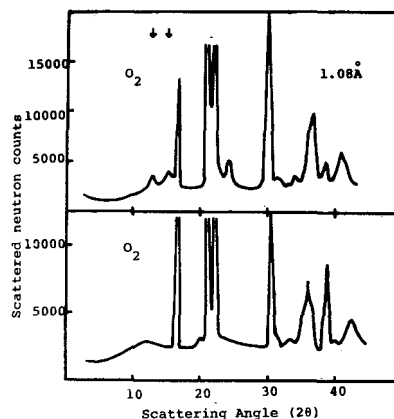


Fig.6. Neutron powder patterns from α - and β - oxygen at 4.2 K and 27 K . The first two lines for α -oxygen indicate the presence of an ordered structure. (M.F. Collins¹⁵⁾)

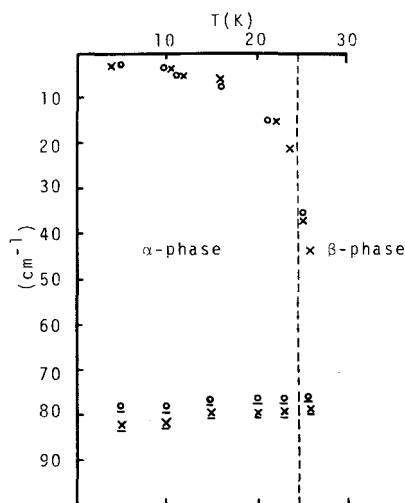


Fig.7. Temperature dependence of the band frequency shift of the transition $2^3\Sigma \rightarrow 2^1\Delta$ (Yu.G.Litvinenko et al.¹⁶⁾
 o; 0-1 transition
 x; 0-2 transition
 the bar -- $85\% \text{ O}_2 + 15\% \text{ N}_2$

concluded that the transition are induced by the exchange interaction and presumed the existence of magnon excitation.

Magnon excitation predicted by Litvinenko et al. was directly observed in the far-infrared absorption spectra by T.G.Blocker et al.¹⁷⁾ They reported a temperature-dependent absorption near 27 cm^{-1} which appears to be an antiferromagnetic resonance mode (Fig.8).

E.J.Wachtel and R.G.Wheeler¹⁸⁾ showed that the absorption near 27 cm^{-1} is definitively associated with magnon rather than phonon in the crystal indicating the absence of an isotopic mass shift. They estimated the magnitude of the exchange interaction $J = 4.0\text{ cm}^{-1}$

P. M. Mathai and E. J. Allin¹⁹⁾ also observed the magnetic excitation in Raman spectra at 27.2 cm^{-1} and assigned it to the magnon mode of $k=0$.

Magnetic susceptibility of oxygen molecules diluted in argon was measured to determine the exchange interaction between oxygen molecules by T.G.Blocker et al.²⁰⁾ They analysed the data using a statistical molecular field theory and estimated that $4J/3k=5\text{ K}$ for O_2 molecules separated by $3.4\sim 3.8\text{ \AA}$ in the lattice.

From the investigations hitherto described, we can put in order the results about the interaction between O_2 molecules as follows.

(a) When oxygen molecules are close each other, there occurs considerable exchange interaction between them. This exchange interaction induces simultaneous and induced transitions.

(b) In gas phase, oxygen molecules interact each other by collision. The life time of $(\text{O}_2)_2$ dimer molecule is estimated at the order of 10^{-12} sec.

(c) In solid phase, there exists no $(\text{O}_2)_2$ dimer molecules but the exchange interaction between oxygen molecules generates antiferromagnetic molecular field at each oxygen molecule. As a results, long-range order of antiferromagnetism exists in α -oxygen but there

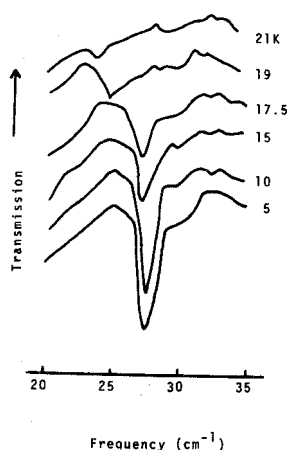


Fig.8. Temperature dependence of far-infrared absorption in α -oxygen (T.G.Blocker et al.¹⁷⁾).

exists only short-range order in β - and γ -phase oxygen.

2. Experimental Procedures

2-1. Preparation of O_2 -Ar mixture

Gases of oxygen and argon were first stored in a gas bulbs of known volume at appropriate pressure and were mixed each other. Then the gaseous mixture was condensed thoroughly through the capillary tube into the quartz ampoule (5 mm in diameter and 15 mm in length) at liquid helium temperature and the capillary tube was sealed off with oxyhydrogen flame. To avoid choking the capillary with solidified oxygen and argon, raising and lowering the temperature of capillary part was repeated several times until the mercury indicated almost at the vacuum level. The oxygen and argon gas were obtained from commercial sources (O_2 :99%, contain a small amount of Ar and N_2 as impurities. Ar:99.99%) and were passed through liquid nitrogen traps to remove water. The composition of each sample is listed in Table 2.

2-2. Preparation of O_2 - F_2 mixture

Gases of Oxygen and fluorine at appropriate pressure were mixed in the tube of known volume and the mixture was condensed thoroughly into the quartz ampoule (5 mm in diameter and 100 mm in length) at liquid helium temperature and the capillary tube was sealed off with oxyhydrogen flame as was carried out with oxygen-argon mixture. Oxygen and fluorine gas were obtained from commercial sources and were passed through liquid nitrogen traps to remove water and hydrogen fluoride.

* % is always mol% in this paper.

Table 2. Oxygen and argon content of each O_2 -Ar sample

Sample	O_2 (mg)	Ar (mg)	mole concentration of O_2 (%) [*]
1	8.38	0.52	95
2	8.68	0.91	92
3	5.65	0.85	90
4	5.22	1.59	81
5	5.71	2.33	75
6	5.94	3.88	66

Table 3. Oxygen and fluorin content of each O_2 - F_2 sample

Sample	O_2 (mg)	F_2 (mg)	mole concentration of O_2 (%) [*]
1	6.96	2.77	74
2	5.52	3.82	60
3	4.64	4.90	50
4	3.71	5.68	41
5	2.78	7.15	29
6	2.00	7.84	21
7	0.93	8.72	10

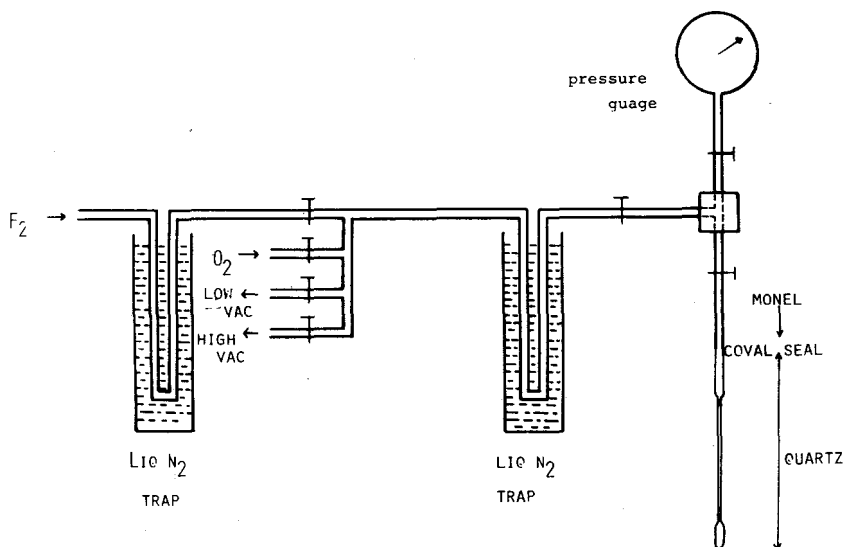


Fig.9. Apparatus for preparing of O_2-F_2

Much care is necessary in sampling fluorine. If there is even a little water remained in the glass ampoule, fluorine reacts with water to produce hydrogen fluoride, which corrodes a silica glass. To avoid this corrosion, water in the glass ampoule had to be eliminated as completely as possible. Following the advice of a technical expert for glass works, silica glass which contain least amount of water was adopted and the glass works were carried out with no breathing. Quartz ampoule thus produced was baked in vacuum at $1050^\circ C$ for three hours. This baking was expected to eliminate the water almost in the glass. Moreover, after setting the ampoule to the preparation system, baking again was carried out at $500^\circ C$ for more than ten hours. These treatment, however, did not remove the water in the ampoule completely, but improve the resisting power of the ampoule to some extent. Transparency of the glass was kept at least for an hour.

Almost all parts of the preparing system were composed of monel metal to avoid corrosion with fluorine or hydrogen fluoride. Coval seal was employed for the joint of the monel and the quartz. Ampoules containing the mixture were kept in liquid nitrogen. At the low temperature corrosion did not occur at all. The composition of each sample is listed in Table 3.

2-3. Measurement of magnetic susceptibility of O_2 -Ar and O_2 -F₂ solid mixture

The magnetic susceptibility measurements were carried out by observing the force acted on the sample in the inhomogeneous magnetic field (Faraday method). Figure 10 shows the apparatus for the measurements. The magnetic field was set at about 9000 Oe and $H(dH/dx) = 4.7 \times 10^6 \text{ Oe}^2/\text{cm}$. The value of $H(dH/dx)$ was calibrated by measuring the susceptibility of sucrose, the susceptibility of which was taken to be $-0.566 \times 10^{-6} \text{ emu/g}$ and to be independent of temperature.

The thermal history of the sample was as follows: The sample in the quartz ampoule was cooled down to about 80 K and kept at this temperature for more than ten minutes in order to liquefy and mix the components. This liquid mixture was solidified at about 50 K. After this treatment, it was cooled to 12 K within less than 15 min.

To facilitate the heat exchange between the liquid helium and the sample, helium gas (about 30 mmHg), which had been purified by passing it through the active charcoal trap at liquid nitrogen temperature, was admitted around the sample. Measurements were carried out continuously from 12 K to each melting point. The measurement of the temperature was carried out with an Au:Co-Cu thermocouple referenced with ice-water.

The out-put of the micro-

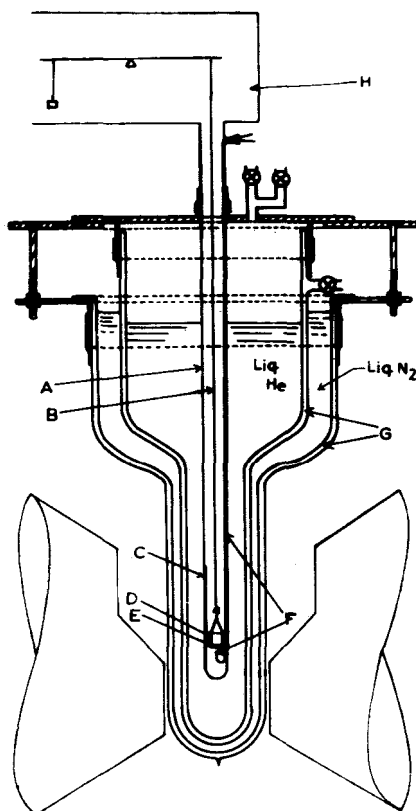


Fig.10. Apparatus for the measurement of the susceptibility.

A: glass tube, B: glass string, C: copper film, D: quartz ampoule, E: sample. F: Au:Co-Cu thermocouple, G: Dewar vessel, H: micro-balance

balance was recorded on a X-Y recorder (Yokogawa 3708) as a function of the e.m.f. of the thermocouple.

As the thermocouple was placed a bit apart below the sample cell, the temperature of the sample was calibrated by the phase transition temperature of oxygen such as 90.1 K(bp), 54.4 K(mp), 44.8 K(β - γ transition point) and 23.8 K(α - β transition point). Calibration was also done by measuring several times the susceptibilities of the paramagnetic salts whose susceptibilities are known to obey the Curie law, Tutton's salts $(\text{Mn}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O})$ and $(\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O})$ under the same condition.

The rate of raising of the temperature was set at about one degree per minute between 12 \sim 55 K by controlling the vacuum pressure in the wall of the inner Dewar vessel. The Dewar vessel was placed between the Sucksmith-type pole pieces with a pole gap of 5 cm as is illustrated in Fig.10. The sample was suspended by a Pyrex glass string from the arm of a vacuum balance, a Sartorius Electrono Microbalance. The sample cell was adjusted so as to be located at the plateau of $H(dH/dx)$.

3. Results

3-1. Oxygen-argon mixture

The results are shown in Figs.11 \sim 13, in which the axis of abscissa is absolute temperature and the axis of ordinate is magnetic susceptibility per gram of oxygen. The susceptibility is corrected for the diamagnetism of the quartz ampoule.

The results of pure oxygen is in good agreement with the previous work.

In case of the 95% O_2 , the behavior of the magnetic susceptibility was very similar to that of pure oxygen. Susceptibility below 25 K is rather large and the transition point becomes ambiguous. At the transition around 42 K, the starting point is lower by 4 K and the susceptibility increased less steeply than in pure oxygen.

On the other hand, with further increase in argon content, the magnetic susceptibilities showed some behaviors very different from those of pure oxygen and the 95% O_2 mixture. The susceptibility below about 28 K is considerably larger than that in the temperature range 33 \sim 40 K. The transition temperature becomes higher with increase of the argon content. Below 20 K,

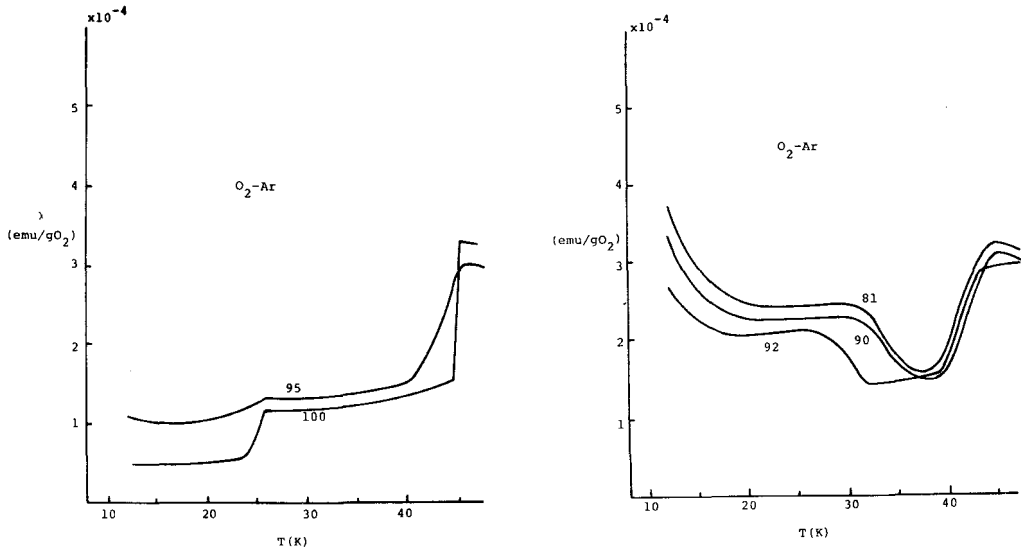


Fig.11. Susceptibility vs. temperature curve for pure oxygen and O_2 -Ar of 95%, 92%, 90%, and 81% oxygen content.

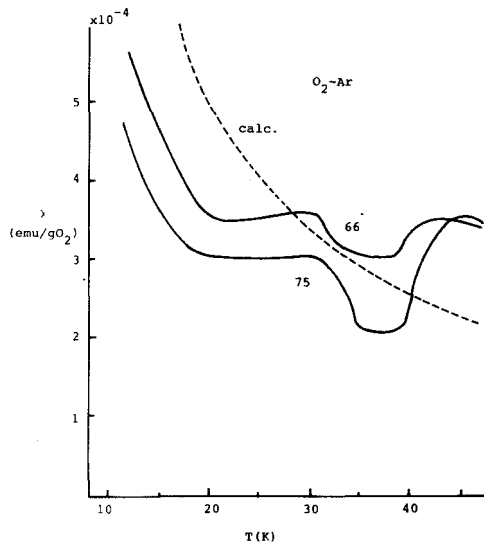


Fig.12. The temperature dependence of the magnetic susceptibility of O_2 -Ar of 75% and 66% oxygen content. ---: Calculated for δ -phase.

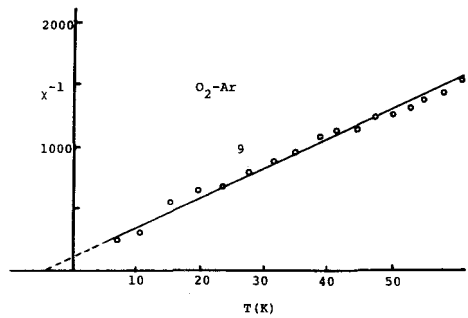


Fig.13. Inverse susceptibility vs. temperature of O_2 -Ar of 9% oxygen content.

the susceptibility can be fit $1/T$ curve, that is the Curie-Weiss law.

Figure 13 shows that the magnetic susceptibility of the 9% O_2 -91% Ar mixture is almost governed by the Curie-Weiss law with Weiss temperature of about 5 K, which agrees well with that of Blocker et al.²⁰⁾

3-2. Oxygen-fluorine mixture

Figures 14 and 15 show the temperature dependence of the magnetic susceptibility at each oxygen molar ratio, corrected for the diamagnetism of the quartz ampoule.

The mixture of 75% O_2 shows different behavior from others. Three temperature regions exist, judging from the temperature dependence of the susceptibility, one below 28 K, the other between 28 and 46 K and the third 46~50 K. Rather large susceptibility of the phase below 28 K is characteristic, which resembles the situation of O_2 -Ar mixture of 75% O_2 content.

In case of the other mixture than that of 75% O_2 content two regions exist, one below 48 or 49 K, the other above this temperature. The fall of the susceptibility towards low temperature, is highest of all in 10% O_2 and becomes lower with increase of oxygen concentration.

The large susceptibility at low temperature obeys the Curie law, which may be due to free spin of oxygen molecules randomly dispersed. To remove the effect of the free spin, appropriate amount of susceptibility, which is proportional to $1/T$ (dotted line in the figures), is subtracted and then appears almost linearly temperature dependence of susceptibility below 45 K, which is shown with dashed lines in the figures.

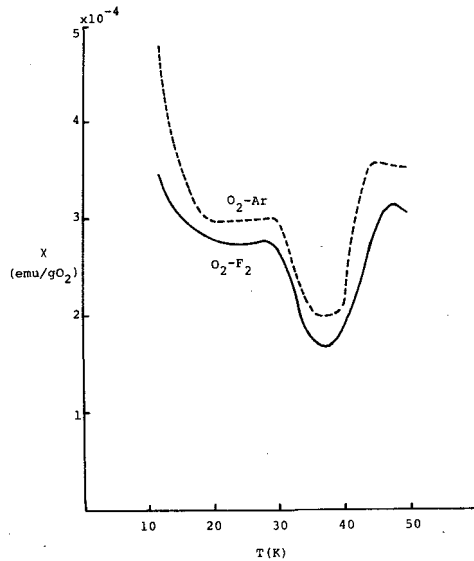


Fig.14. Susceptibility vs. temperature curve for O_2 75% - F_2 25% mixture with that for O_2 75%-Ar 25% mixture.
 — : O_2 - F_2 mixture.
 ---- : O_2 -Ar mixture.

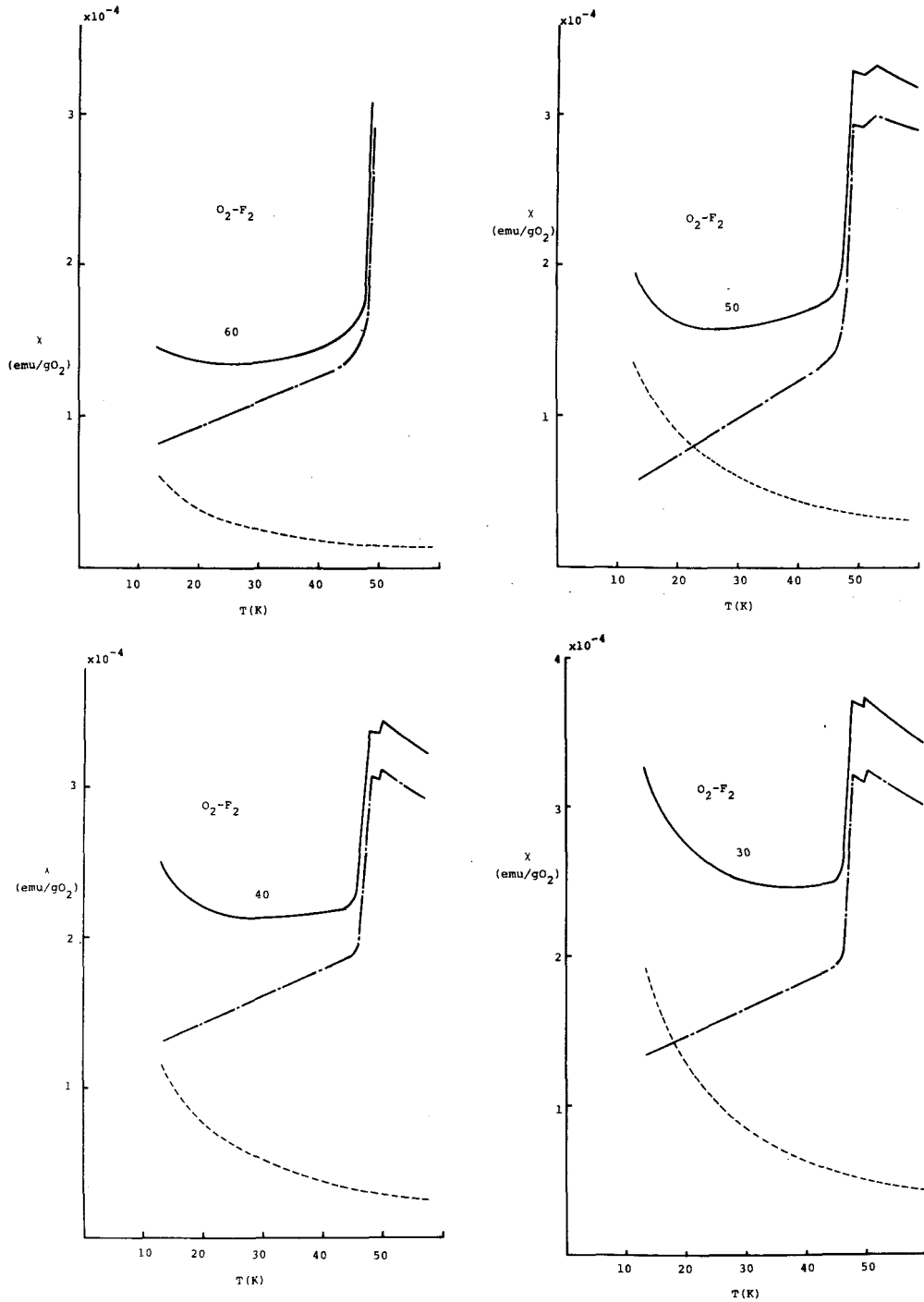


Fig.15. Magnetic susceptibility vs. temperature curve for O₂-F₂ of 60, 50, 40, 30, 20, 10% O₂ content.

—: measured susceptibility, ---- : Curie's paramagnetism,
 -.-: residual susceptibility.

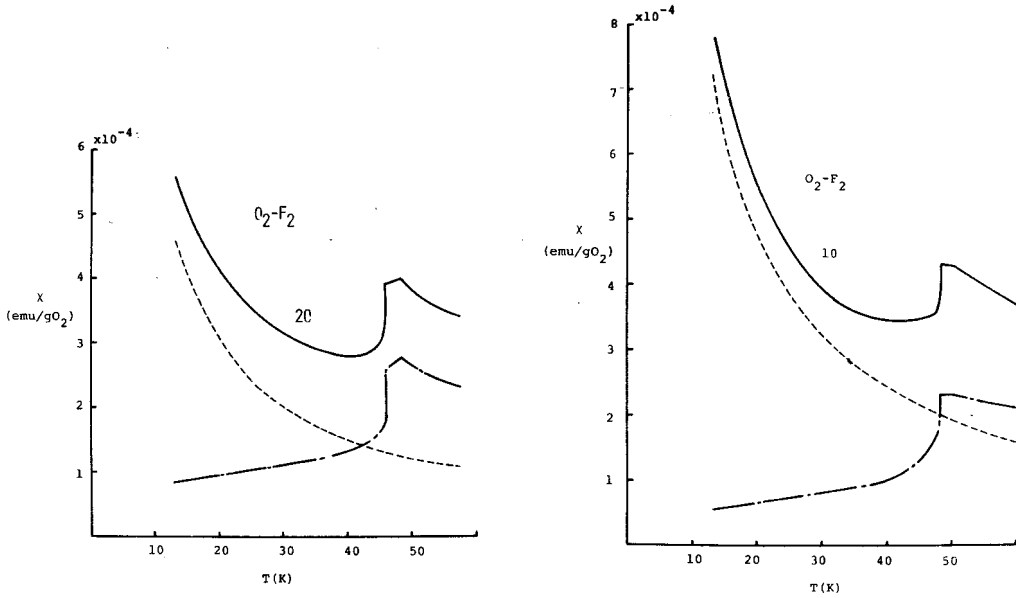


Fig.15. (continued)

4. Discussion

4-1. Antiferromagnetic interaction in α - and β -oxygen

In case of pure oxygen sample, the result is in good agreement Kanda et al.⁶⁾ In α -phase below 24 K, small paramagnetic susceptibility corresponds to antiferromagnetic order. According to Collins¹⁵⁾ and Barrett et al.¹⁴⁾ the magnetic dipoles of the oxygen molecules in the ab plane in Fig.5 at 000 are antiparallel to those at $1/2\ 1/2\ 0$. Following the model some discussion will be made to estimate the magnitude of the exchange interaction from magnetic susceptibility in pure oxygen.

According to the molecular field theory, the susceptibility of an antiferromagnet obeys the Curie-Weiss law, $\chi = C/(T - \theta)$, above the Néel point, $T_N = (A - B)/2$, where $C = Ng^2 \mu_B^2 S(S + 1)$, $\theta = -(A + B)C/2$, N Avogadro's number, g g -factor, μ_B Bohr magneton, S spin and A or B molecular-field constant of each super-lattice. Below the Néel point, anisotropic susceptibility is lead. Susceptibility perpendicular to the magnetisation (χ_{\perp}) is $1/A$, independent of temperature and that parallel to the magnetisation (χ_{\parallel}) leads to $1/A$ at the Néel

point, decreases towards low temperature and becomes zero at 0 K. In a polycrystalline sample, the susceptibility averaged for all orientation ($\bar{\chi}$) represents $(1/3)\chi_{\parallel} + (2/3)\chi_{\perp}$, and so is $1/A$ at the Néel point and $2/(3A)$ at 0 K. Feature of the temperature dependence of the susceptibility derived is shown in Fig.16.

In case of α -oxygen, we assume that (a) a molecule interacts only with eight nearest neighbor, and (b) interaction in (001) plane is equal to that in ($\bar{2}01$) plane. These assumption may be justified in the semiquantitative estimation.

Considering that $\bar{\chi}_i$ near $T=0$ is almost $(3/2)\chi_{\perp}$, we can estimate from the experimental results χ_{\perp} at 2.4×10^{-3} emu/mol. Using this value of χ_{\perp} , we obtain the exchange interaction $J=3.1 \times 10^{-15}$ erg/molecule. This is about 15 cm^{-1} or 22 K. This J value is four or five times larger than was obtained by Wachtel et al.¹⁸⁾ from magnon spectra and by Blocker et al.²⁰⁾ from the susceptibility of O_2 -Ar mixture. In their study of magnon spectra, Wachtel et al. determined J as one of the parameters in the equation to decide the intensity ratio and they might take another value if other parameters assumed by them take different values. In the experiment of O_2 -Ar in the oxygen concentration range 0~40%, crystal structure changes to fcc or hcp and the distance between oxygen molecules differs from that in α -phase. Therefore, it is no wonder that exchange interaction obtained in O_2 -Ar becomes small compared with that in pure oxygen. Of course, in the present study with only semiquantitative analysis, the value may be estimated larger than is really the case.

T_N is estimated at about 210 K. This value of T_N is consistent with considering that χ around 20 K can be a substitute of that at $T=0$. It is revealed from this that in α -oxygen antiferromagnetic order would maintain at higher temperature, If the crystal structure did not change at 24 K. This situation is shown in Fig.17. Almost

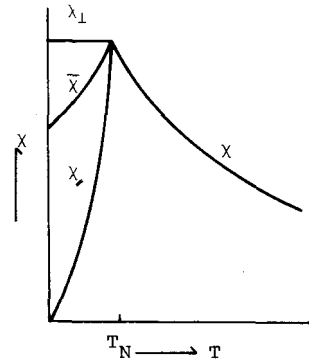


Fig.16. Temperature dependence of the susceptibility from the molecular-field model of an antiferromagnet.

χ_{\parallel} : parallel susceptibility.

χ_{\perp} : perpendicular suscept.

$\bar{\chi}$: powder suscept.

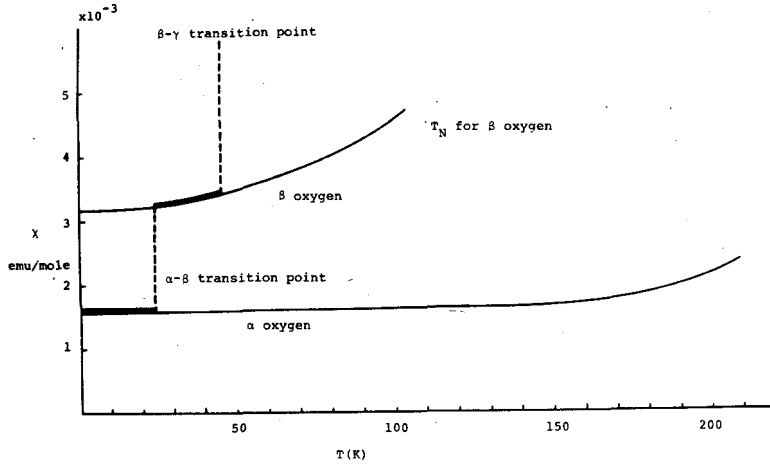


Fig.17. Susceptibility vs. temperature curve based on the molecular-field theory.

constant susceptibility in α -phase is understood as in the lower temperature part of the antiferromagnetic ordered state. The exchange energy value of the previous works is considered to be too small to explain the constant susceptibility.

In β -phase of pure oxygen, susceptibility decreased gradually from about 140 emu/g at 44 K to 110 emu/g at 24 K. This behavior is the characteristics of the state below Néel point. As has been done with α -oxygen, molecular field theory is adopted to the β -oxygen. Susceptibility vs. temperature curve is extrapolated to 0 K and the virtual $\bar{\chi}$ can be estimated at about 100 emu/g, i.e. 3.2×10^3 emu/mol. From this we obtain that $\chi_{\perp} = 4.8 \times 10^{-3}$ emu/mol, $A = 210$ and that $T_N = 105$ K. This situation is shown in Fig.17 with that in α -phase and the tendency of susceptibility vs. temperature curve in experimental results is well represented.

According to this conception, there occurs in β -oxygen long-range antiferromagnetic order, inconsistent with the results and interpretation by Collins¹⁵⁾ with the diffraction. However, if only a short-range order is taken into consideration, β -oxygen corresponds to the state above the Néel point and then the susceptibility has to increase towards lower temperature obeying the Curie-Weiss law, which is contradictory to the susceptibility measurement.

4-2. Interaction in oxygen-argon mixture

In case of 95% oxygen content

In case of 95% oxygen, the behavior of the magnetic susceptibility was very similar to that of pure oxygen. This shows that the antiferromagnetic properties characteristic of each crystalline phase, α , β , γ of solid oxygen are not so much affected at these low concentration of argon. It is true, but the long-range order in α -phase is somewhat disturbed, which is shown in increase of the susceptibility in the temperature range.

From the view point of the dynamics of the crystallisation, this solid mixture was found to behave differently from pure oxygen. The transformation temperature from β to γ is lowered to about 40 K. In the transition process, an abrupt change of the susceptibility at each transition temperature as in pure solid oxygen was not observed in this mixture, even at the slowest rate of temperature rise (1 °C/min), which was controlled by changing the vacuum in the Dewar vessel. Because of this experimental design, the susceptibility did not reach equilibrium during the transformation. In the transition of the pure oxygen, molecules may not move so far from their position, but in that of mixture, oxygen and argon molecules move to rearrange their position and find more stable state. Then transformation takes more time in the mixture than in pure oxygen. These dynamical effects resulting from the addition of argon to the oxygen lattice have been observed in a determination of the oxygen-argon system by Barrett et al., and also through the measurement of the specific heat.

In case of 92, 90, 81, 75 and 66% oxygen content

With further increase in argon content, the magnetic susceptibility showed some behaviors very different from those of pure oxygen and the 95% O₂ mixture. They are consistent with the appearance of a novel homogeneous phase " δ " discovered by Barrett et al. This phase appears, by Barrett et al., in the composition range between 55% and 80% O₂, while the monoclinic phase disappears. They showed that the upper limit of oxygen content at which this phase appears can be extended to 90% when the mixture is cooled from the γ -phase down to liquid hydrogen temperature within less than an hour.

The stable temperature region of this phase can be estimated from 30~31 K for the 90, 81, 75 and 60% oxygen mixture. In case of 92% O₂ mixture, similar decrease in susceptibility was also observed, but at a slightly lower temperature of about 26 K. These transformation temperature do not agree in detail with that of the phase

diagram. According to the diagram of this region the temperature, at which δ -phase begins to transform, increases from 25 K to 30 K with increase of the argon concentration. This discrepancy is considered to arise from the fact that magnetic susceptibility measurement cannot reflect such a delicate partial change as the X-ray diffraction does.

In the temperature range of β -phase, susceptibility of the 92% and 81% O_2 is almost equal to that of pure oxygen and with the increase of argon content from 25% to 34%, the susceptibility of this range indicates larger value.

The phase diagram shows that solid solution of Ar and O_2 is made to maintain the β -structure in case of 80~100% oxygen content

and that two phases coexist in 50~80% case. It may be concluded from the facts above that the antiferromagnetic interaction in β -oxygen is hardly disturbed with argon atoms, and that in hcp structure, of which the oxygen concentration is lowered to about 50%, the interaction is considerably disturbed, which results in the increase of the susceptibility.

The temperature and concentration dependence of the susceptibility in the δ phase region can be interpreted on the crystal structure determined by Barrett et al.²¹⁾ According to their work, the unit cell has a body centered cubic lattice with $a=13.23 \text{ \AA}$ and $z=64$, which is a superlattice of the γ -structure of pure oxygen with $a=6.83 \text{ \AA}$ and $z=8$ (Fig.3). The position of the argon atoms in the structure have not been exactly determined, but some plausible models were suggested. One of them is illustrated in Fig.19. In this model, the argon and oxygen molecules are placed in a periodic sequence as ---Ar, O_2 , O_2 , O_2 , Ar, O_2 , O_2 , O_2 --- in the rows across the middle of the cube faces denoted " γ rows". The distance between the oxygen in a γ row is 3.31 \AA , which is equal to the

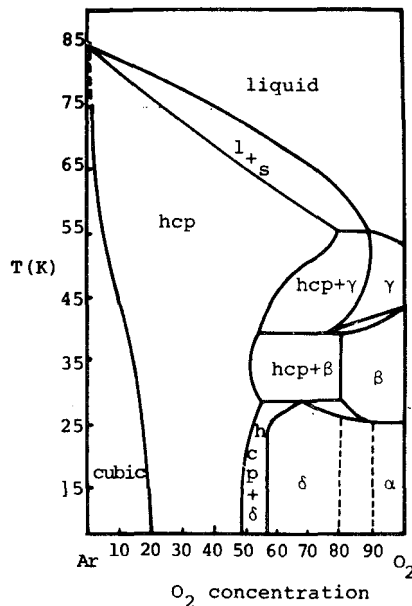


Fig.18. Phase diagram of O_2 -Ar (C.S.Barrett et al.)

nearest-neighbor distance in β -oxygen and is about 0.1 \AA shorter than that in γ -oxygen. So, we can expect that there exists a fairly strong antiferromagnetic exchange interaction between these oxygen molecules in a γ row. Through the interaction, spin of each oxygen molecule, which is originally free, couples each other in a γ row and the total spin of these molecules decreases to one in appearance.

The clusters of these oxygen molecules in the γ rows are separated by the argon atoms from each other and the total spin made in a cluster may be considered almost free and obey the Curie law.

If none of the Ar atoms are in the corner and center sites in each unit cell, there will be 12 out of 64 sites occupied by Ar and composition will be 81.2% O_2 . At the other extreme, if Ar atoms occupy all of the corner and center sites, these 16 Ar sites together with the 12 sites in the γ row will give a composition of 56.8% O_2 . In the intermediate case, substitution of one Ar atom for one O_2 molecule in the unit cell decreases O_2 concentration by 0.9%. Therefore, in this study, the composition of 81% O_2 corresponds to zero Ar atom occupying the center and corner sites, 75% O_2 to 4, and 66% O_2 to 10 Ar atoms. In the present experimental results in the temperature range of δ -phase, magnetic susceptibility increases with the

decrease of O_2 concentration. This indicates that oxygen molecules in the corner and center sites play a certain role to the spin ordering. In the case that all corner and center sites is occupied by Ar atom, trimer of oxygen molecules, $---\text{O}_2 \text{ O}_2 \text{ O}_2---$, in the γ row is completely surrounded by Ar atoms and the total spin made in the trimer behaves as a free spin. The susceptibility may probably obey the Curie law, $\chi = C'/T$ (emu/mol O_2), where C' equals 3.33×10^{-1} , that is a third the value for oxygen gas. This may reflect roughly the

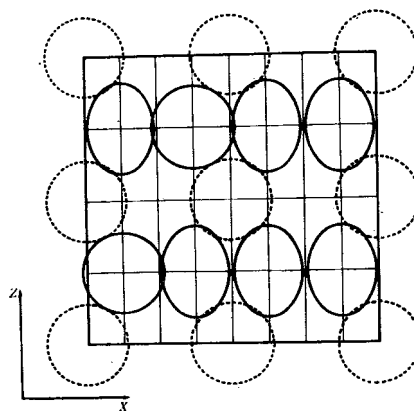


Fig.19. The (010) face of the unit cell of the δ -phase with close-packed non-intersecting rows " γ rows" containing argon atoms and oxygen molecules in some periodic, non-random sequence (C.S.Barrett et al.²²)

outline of the experimental results, but does not show an exact accord especially in the flat part between 20 and 30 K. This flat part of the magnetic susceptibility may be due to that the exchange coupling in the trimer $--O_2 O_2 O_2--$ becomes weak relative to the temperature and the spin on each oxygen molecule begins to be free.

In case of 9% oxygen content

In this case, oxygen molecules are dispersed randomly in the lattice of argon, which is cubic or hcp from the diagram, and are surrounded almost perfectly by argon atoms. Therefore, the spin on the oxygen molecule behaves almost freely with the influence of weak molecular field produced by the other oxygen molecules at some distance from it.

4-3. Interaction in oxygen-fluorine mixture

4-3-1. In case of 10, 20, 30, 40, 50 and 60% oxygen content

In O_2-F_2 mixture containing 10~60% O_2 , the susceptibility decreases abruptly at about 45K and diminishes gradually below the temperature. This small and gradually diminishing susceptibility is characteristic of antiferromagnetism. The crystal structure and the arrangement of oxygen and fluorine molecules in the lattice has not been known. Then, the mechanism for the antiferromagnetism cannot be determined definitely, but some possible models will be presented to interpret this character.

Assumption on the crystal structure

The crystal structure of O_2-F_2 solid phase has not yet been investigated. The crystal structure of solid oxygen and fluorine in various phases, however, has been clarified by several workers, and we can use these results to estimate an outline of the crystal structure of the mixture. In Table 4 is cited the list of these results.

It is reasonable to consider that in the temperature range below 45K there exists only one phase, as no magnetic transition was found in the range. In this range, oxygen takes two phases, α and β , of which the crystal structure is monoclinic and rhombohedral, respectively. Fluorine takes only one phase, α , of which the crystal structure is monoclinic. Monoclinic unit cells of both oxygen and fluorine α -phase resemble very much each other. The unit cell of α -fluorine is only twice that of α -oxygen along the c-axis, i.e., so called superlattice. Besides the crystal structure, shapes and sizes of oxygen and fluorine molecule resemble one another. At the

0.002 a.u. contour of the total molecular charge density, which includes over 95% of the molecular charge, the size of the O_2 molecule is 4.18 Å long and 3.18 Å wide and that of F_2 molecule is 4.18 Å long and 2.86 Å wide.³³⁾

The shapes of them resemble cocoons. Because of the resemblance of the crystal structure and molecular shape and size, it is natural to suppose that the crystal structure of $O_2:F_2=1:1$ mixture below 45 K should be monoclinic.

About the homogeneous distribution of O_2 and F_2 , it might at least be supposed that oxygen molecules would not segregate together to be clusters. If the clustering occurs, the transition of oxygen should be observed in magnetic susceptibility, which was not found.

There are two ways of homogeneous distribution, ordered and disordered, but it cannot be decided as far which phase is really taken. In the case of such a low oxygen concentration as 10%, an ordered distribution is hard to be realized. It is reasonable to think that oxygen molecules are distributed randomly in the lattice of fluorine. In the case of 1:1 mixture, on the other hand, ordered distribution can be realized and on account of the periodicity it is probably more favorable for the long-range magnetic order. In Fig.20 are cited some models of the distribution in $O_2:F_2=1:1$ mixture. Model (a) and (b) are more probable to be realized than (c), because the short axis of fluorine molecule is a little shorter than that of oxygen by 0.32 Å and the alternate distribution of the two species in the ab plane may induce less distortion in the lattice.

Superexchange interaction

Table 4. Crystal structure of the various phases of oxygen and fluorine.

Oxygen	T (K)	Fluorine
Liquid	54.36	Liquid
γ phase cubic a 6.83 Å	50	β phase cubic a 6.67 Å
	43.78	45.55
β phase rhombohedral (hexagonal) a 3.307 Å c 11.250 Å	40	α phase monoclinic a 5.50 Å b 3.28 Å c 10.01 Å (5.00 Å × 2) β 134.66°
	23.89	
α phase monoclinic a 5.403 Å b 3.429 Å c 5.086 Å β 132.53°	20	
	10	

It is characteristic of O_2-F_2 mixture that even the mixture of 10% oxygen concentration indicates an abrupt decrease of susceptibility at 45 K and the magnitude of the decrease is comparable with that of higher oxygen concentration. In case of O_2-Ar mixture, on the other hand, the mixture of 9% oxygen obeys the Curie-Weiss law and no transition was observed below the melting point. According to Blocker et al.,²⁰⁾ susceptibility of O_2-Ar obeys the Curie-Weiss law even to the 50% oxygen. Generally, the interaction which induces long-range order decreases with increase of non-magnetic material, mixed in the magnetic lattice. As the O_2-F_2 mixture of 10% O_2 , however, indicates the characteristics of strong anti-ferromagnetic order below 45 K, it must be thought that fluorine molecules do not only contribute to the magnetism of mixture as non-magnetic material but play an active role in producing the long-range order. There are many examples of such a case as non-magnetic material play an important role in antiferromagnetism. Their theoretical surveys also have been presented by several workers to the mechanism of the phenomenon.^{25,26,27)}

In regard to O_2-F_2 mixture, it is noticed that the molecular orbitals of oxygen which concern with the magnetic dipole moment resemble closely d-orbital of the transition metal (Fig.21). According to the figure, charge distribution of $1\pi_g$ orbital of oxygen is much alike that of d_{xy} or d_{zx} of transition metal if the molecular axis is taken to be the z axis. This resemblance of the orbitals gives us a prospect to explain the mechanism in F_2-O_2 mixture as has been done with ionic crystals of transition metal.

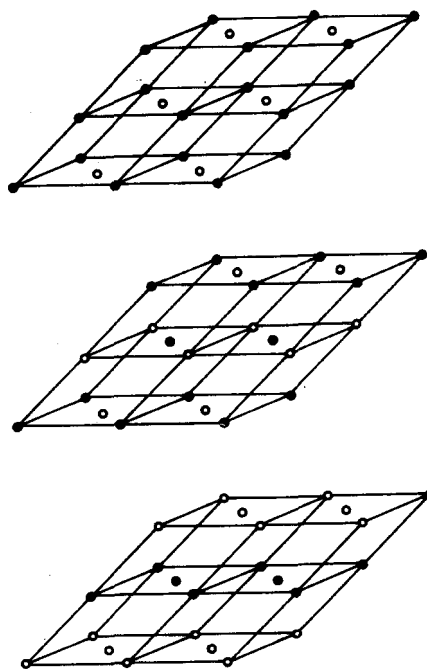
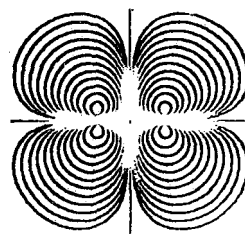
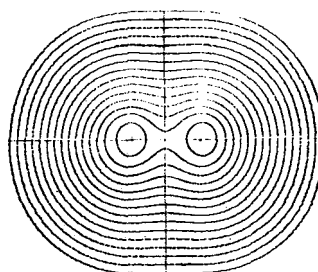


Fig.20. Examples of the ordered models for $O_2:F_2=1:1$ mixture.

●: oxygen molecules
○: fluorine molecules.

In order to investigate the interaction, a model of arrangement of O_2 and F_2 in ab plane will be considered as in Fig.22, where A, B, C and D are denoted for oxygen and F for fluorine. It is the question how occurs interaction between these molecules. First, interaction between A and C, or similarly B and D, will be treated. The distance between A and C is about 6.4 \AA and too long to interact directly. Then, the possibility of superexchange interaction via F must be investigated. Though the geometry of the molecular orbital cannot be determined as is done with transition metal in ionic crystal under the crystal field of non-magnetic ions, an appropriate feature is assumed as in Fig.22. Compared with p -orbital of O^{2-} or F^- ion in such an ionic crystal as MnO or MnF_2 , highest occupied orbital of fluorine molecule, $1\pi_g$, extends its lobes to oxygen molecule, which may be advantageous for the interaction because of large overlap integral.

Described in Anderson's manner, mechanism of superexchange interaction is as follows: Part of the electron on the orbital of F transfers to the $1\pi_g$ orbital of one of the neighboring O_2 , for example A, that is occupied by one electron. If up spin state of the $1\pi_g$ orbital of A is already occupied, the electron from F is restricted to down spin from the Pauli principle and so the electron left on F must be up spin. As the exchange integral between $1\pi_g$ orbitals of F and C is negative, the electron spin of the $1\pi_g$ orbital of C is ordered antiparallel to that on F, i.e., down spin. In the other case if down spin state of $1\pi_g$ on A is already occupied, up spin is induced on C. At any rate antiferromagnetic interaction exist between A and C.

Oxygen molecule $1\pi_g$ orbital

Oxygen molecule total electron density

Fig.21. Electron density contours of oxygen molecule (A.C. Wahl³²⁾ and R.F.W.Bader et al.³³⁾).

If Goodenough's mechanism is employed, simultaneous partial covalent bond between O_2 $3\sigma_u$ and F_2 $1\pi_g$ is considered. This mechanism also predicts anti-ferromagnetic interaction between oxygen molecules.

Next, the interaction between A and B is treated. The distance between them is about 5.0 Å, which is also too long to induce strong direct interaction. Then, superexchange interaction via F will be introduced. Geometry assumed is drawn in Fig.22. The situation is thus: One $1\pi_g$ orbital of F overlaps considerably with $1\pi_g$ orbital of A but little with $1\pi_g$ orbital of B, while the other $1\pi_g$ orbital of F overlaps with $1\pi_g$ of B but little with $1\pi_g$ of A. This situation is a modified one of the case in the Kanamori's semi-empirical rule for "90° position". If A-F-B angle was accurately 90°, exchange integral between the $1\pi_g$ of B and one of the $1\pi_g$ of F should become positive, which should induce ferromagnetic interaction between A and B. However, in the present case, as the angle A-F-B is much larger than 90°, the overlap integral between the orbitals does not become zero and so the exchange interaction does not necessarily act to induce ferromagnetism. In any case, this interaction may be considered to be rather weak.

Another mechanism can be presented as follows. Partial electron of one $1\pi_g$ of F transfer to $1\pi_g$ of A and simultaneously partial electron of the other $1\pi_g$ of F transfer to $1\pi_g$ of B. As a result of this transfer of electron from $1\pi_g$ orbitals of F, partial spin is left on each orbital restricted by the spin state of A and B, respectively. Because the two $1\pi_g$ orbitals of F are degenerate, internal exchange interaction forces the spins on the orbitals to align paral-

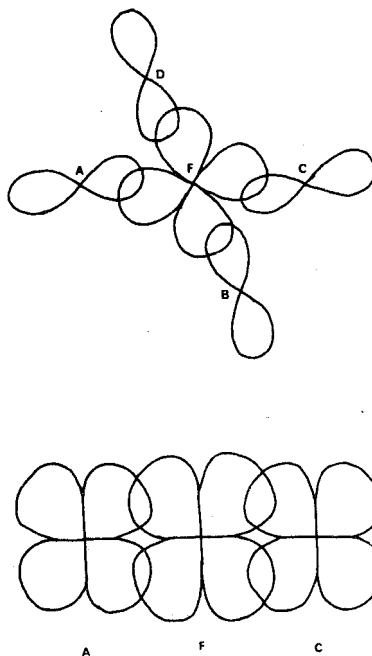


Fig.22. A projection chart of $1\pi_g$ orbitals of oxygen and fluorine molecules. Above is on the ab plane, and below on the plane perpendicular to the ab plane.

1el(Hund rule). Therefore, ferromagnetic interaction is induced between A and B.

Goodenough's mechanism also suggests that there is ferromagnetic interaction between A and B. Partial bonding between $3\sigma_u$ of A and one $1\pi_g$ of F orbitals and also between $3\sigma_u$ of B and the other $1\pi_g$ of F is simultaneously formed and the unpaired spins on $1\pi_g$ orbitals interact with each other. From Hund rule, spins are ordered ferromagnetically.

Between A and D, distance is estimated $3.2\sim 3.4 \text{ \AA}$ from that of the α -structure of O_2 and F_2 . The shape of F_2 is narrower than O_2 by 0.32 \AA , which would decrease the distance between A and D in comparison with the case of the pure oxygen. Such a closed packing induces direct exchange interaction between A and D, which may perhaps be antiferromagnetic. In addition to this direct interaction, superexchange interaction also may be allowed as in the case between A and B. Nearly "90° position" of A-F-D induces ferromagnetic interaction between A and D. It is the question which of the direct-antiferromagnetic or the indirect-ferromagnetic interaction is stronger, but the actual spin alignment is determined under the balance of all interaction acted on the spin. For instance, because A and B are parallel and B and D antiparallel mentioned above, A and D are apt to be antiparallel.

Then how are the interactions in the other plane than ab plane? In the monoclinic unit cell of O_2 or F_2 solid α -phase, one molecule has four near-neighbor molecules in the $(\bar{2}01)$ plane at a center-to-center distance of about 4.2 \AA . Nearly closed packing in this plane suggest the interaction in this plane. As has been treated with the interaction in the ab plane, a possible model for the distribution of molecules is considered and also the direction of molecular orbitals is assumed. If such a situation is actually realized, the same reasoning as in the ab plane suggests the possibility of superexchange interaction. According to this, there should be antiferromagnetic interaction between the oxygen molecules too far from each other to interact directly. In this case also, considerable overlaps of $1\pi_g$ orbitals of O_2 and F_2 contribute to induce the interaction.

Now that superexchange interaction above is introduced, one oxygen molecule, of which eight nearest neighbors are all fluorine molecules, can interact with the other oxygen molecules far apart. For, example, if an ordered distribution of O_2 and F_2 are assumed as

in Fig.20, in which each oxygen molecule is surrounded by fluorine molecules, before-mentioned mechanism predicts an antiferromagnetic pattern cited in Fig.23. Figure 24 shows another example of a mixture of 12.5% O_2 , in which long-range order cannot occur without superexchange interaction. Thus it can be interpreted by introducing superexchange interaction via fluorine molecule that even the mixture of low oxygen concentration indicates long-range antiferromagnetism.

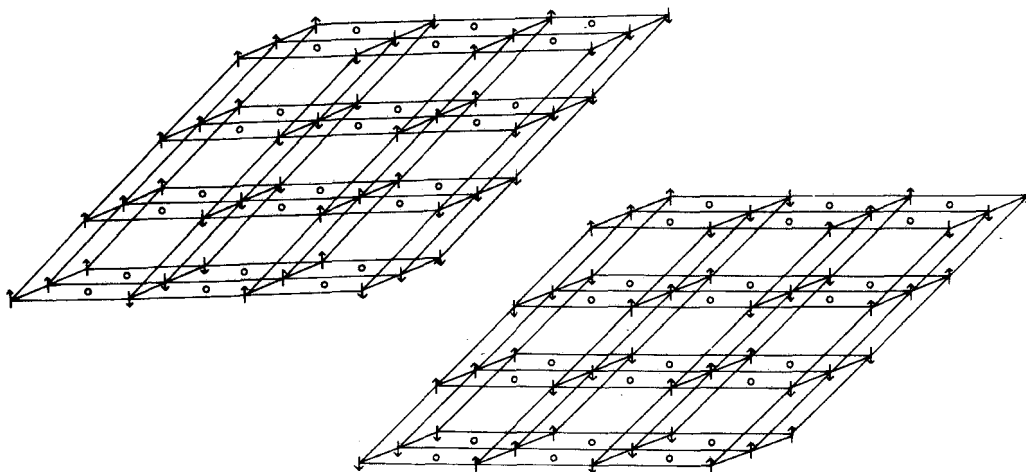


Fig.23. Examples for the antiferromagnetic lattice pattern in $O_2:F_2=1:1$ mixture.

o: position of the fluorine molecules.

↑: magnetic moment of the oxygen molecules.

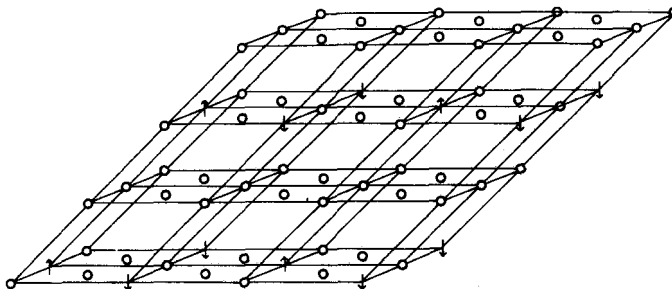


Fig.24. An example of the antiferromagnetic lattice pattern for O_2-F_2 of 12.5% O_2 content.

o: position of the fluorine molecules.

↑: magnetic moment of the oxygen molecules.

There remained, however, a significant point of question in the superexchange mechanism above. It lies on the possibility for the transfer of partial electron from F_2 to O_2 . Taking into consideration that ionization potential of F_2 is $15.686 \text{ eV}^{28)}$ and electron affinity of O_2 is $0.43 \text{ eV}^{29)}$ we can expect too small a contribution of this charge transfer configuration to induce strong superexchange interaction. This difficulty might be relieved in the crystal formation.

On the other hand, the ionization potential of O_2 is $12.07 \text{ eV}^{30)}$ and electron affinity of F_2 is $3.0 \text{ eV}^{31)}$ These values indicate that it is rather easier for the electron to transfer from O_2 to F_2 than F_2 to O_2 . Therefore, it might be probable that unpaired electron on O_2 interact via the empty $3\sigma_u$ orbital of F_2 , different from the mechanism above. This mechanism qualitatively predicts that there occurs in the ab plane, antiferromagnetic interaction between A and C and also between A and B. In the case of "90° position", opposite result is predicted. Effect on the strength of O_2 and F_2 is also different between the two mechanisms. In the mechanism that electron transfer from F_2 to O_2 , the bond strength of F_2 may increase because electron of antibonding orbital is removed and the bond strength of O_2 may decrease because antibonding orbital is additionally occupied. In the mechanism that electron of O_2 transfers to F_2 , opposite results are expected to come out.

4-3-2. In case of 75% O_2 content

Sample of 75% O_2 -25% F_2 indicates a transition at about 27 K and rather large susceptibility below this temperature, which very much resembles the case of 75% O_2 -25% Ar mixture. For O_2 -Ar, there appears below 27 K a novel δ -phase of which the crystal structure is cubic and very similar to that of the γ -phase. For O_2 - F_2 , without a knowledge of the crystal structure the definite interpretation cannot be made, but it is probable that there would occur supercooling from around 50 K and that the cubic lattice would be quenched to the lowest temperature.

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