表1. 本研究におけるパラマグネティック・スペンサシビリティーの測定結果

<table>
<thead>
<tr>
<th>優者</th>
<th>希望素系</th>
<th>希望素系のラベル</th>
<th>希望素系のラベル</th>
<th>希望素系のラベル</th>
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<tbody>
<tr>
<td>KANDA Eizo, HASEDA Taiichiro, OTSUBO Akio</td>
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文献詳細

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Paramagnetic Susceptibility of Solid Oxygen

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The Research Institute for Iron, Steel and Other Metals

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Synopsis

The susceptibility of solid oxygen was investigated at temperatures ranging over from 2 to 77°K by using Hartshorn A.C. bridge method. A fair agreement was obtained between magnetic transition points and thermal ones. The susceptibility did not change at the melting point (54.3°K), but was almost of the same magnitude as in the liquid state. At the transition point from γ to β phase (43.7°K), the susceptibility decreased sharply to $130\times10^{-6}$. In β phase, it diminished gradually with the temperature to the next transition point (23.7°K) from β to α phase, where it decreased abruptly once again to $50\times10^{-6}$. Antiferromagnetic nature was expected from many evidences. The nature and the origin of $(O_2)_2$ molecule were discussed briefly.

1. Introduction

Oxygen and nitric oxide are the only two common paramagnetic gases. There have been, however, only a few investigations about the magnetic properties of oxygen at low temperatures.

The susceptibility $\chi$ of solid oxygen was measured in 1914 by Perrier and Kamerlingh Onnes in Leiden University\(^1\). They found that $\chi$ decreased at the freezing point to one third of the value at the liquid state and sharply decreased again at about 33°K. The specific heat measurement made by Giauque and Johnston\(^2\) in 1929 showed that there existed two phase transitions in solid state at 23.7° and 43.7°K. Neither of these transition points does correspond to the magnetic one, which the Leiden’s authors found at 33°K. $\chi$ of liquid mixture of oxygen and nitrogen was also measured by the Leiden’s authors\(^3\). Weiss constant $\delta$ calculated from their data numerically increases rapidly with the concentration and reached $-60°K$ in pure liquid oxygen. These results were attributed to the existence of the large molecular field or the molecular interaction in liquid state. Assuming the diamagnetic $(O_2)_2$ molecule in liquid state, Lewis obtained\(^4\) 180 cal/mole as the dissociation energy of $(O_2)_2$ molecule from the Leiden’s data. On the other hand, it is well known that two nitric oxide molecules associate with each other, forming the diamagnetic dimer in the liquid state\(^5\).

It is, however, very doubtful even from the Leiden’s data that $(O_2)_2$ molecule is diamagnetic, as will be discussed later.

It was intended to measure $\chi$ of solid oxygen in detail at the temperature range.

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* The 779th report of the Research Institute for Iron, Steel and Other Metals.

(1) A. Perrier and H. Kamerlingh Onnes, Leiden Comm. 139C (1914).
(3) A. Perrier and H. Kamerlingh Onnes, Leiden Comm., 139d (1914).
(5) H. Bizette and B. Tsai, Compt. Rend., 206 (1938), 1288.
from 2 to 77K to investigate (1) the relation between the magnetic transition points and the thermal ones and (2) the magnetic properties of (O₂)₂ molecule at low temperatures.

II. Apparatus and procedure

The apparatus is shown in Fig. 1. Procedure to set the sample is as follows: At first, the tube A is surrounded by another Dewar vessel containing liquid nitrogen, and oxygen is condensed to liquid in the cell B through C. When a definite amount (about 3 c.c.) of the liquid is obtained, the space S is evacuated and the tube A is set in Dewar D. After the liquid helium is poured in D, vacuum in space S is once again broken by a small amount of helium gas to solidify the liquid oxygen in the cell B and to cool down the sample to the helium temperature. The temperature of the sample is controlled by the heat conduction through helium gas in S and by the heat supply through thin copper wires H which are attached to the heater E located sufficiently apart from the measuring coil to avoid the magnetic disturbance. Au(Co 2 per cent)-Ag(Cu 0.2 per cent) thermoocouple J is available over the whole range of temperature of the sample. χ was measured by Hartshorn A.C. bridge at about 1000 c/s(6). F and G are the primary and secondary coils respectively. The measurement of χ and thermal analysis were made simultaneously to ascertain the homogeneity of temperature of the sample, especially at the transition points.

III. Experimental results

Measured values of χ are shown in Fig. 2. Different from the previous results, the magnetic transitions occurred at 23.7° and 43.7K. The fair agreement of the magnetic transition points with the thermal ones was ascertained by the thermal analysis. In α-phase, χ was about $50 \times 10^{-6}$, being almost constant down to 1.9K. No transition was expected in lower temperatures as supported by the specific heat measurement(2),(7). Hence, it may be concluded that oxygen is paramagnetic, or not diamagnetic at least down to the extreme low temperatures. At 23.7K, χ increased sharply to $100 \times 10^{-6}$ and in β-phase it gradually increased to $130 \times 10^{-6}$ at 43.7K, the transition point to γ-phase. At this point, it increased abruptly, to $320 \times 10^{-6}$ while in γ-phase it lay almost on the extension of the curve for the liquid state. At the

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(6) for instance, H.B.G. Casimir, and F.K. Du Pré, Physica, 8 (1941), 449.
melting point, it did not change appreciably, only its slope being slightly changed.

![Graph showing susceptibility vs. temperature](image)

*Fig. 2.*

- ....... \( \chi \) by Leiden's authors; 1914.
- --- \( \chi \) by present authors; 1954.
- ---- specific heat by Giauque and Johnston; 1929.

IV. Discussion

The magnetic transition points found in the present experiment agree well with the thermal ones, at which the latent heat and the change in the crystalline structures have been known to be accompanied. Unfortunately, as the crystal structure of each phase was not exactly determined, it is impossible to treat them as a crystalline statistical problem, and to discuss the magnetic structure in each phase. So the problem about the magnetic properties of \((O_2)_2\) molecule will be discussed mainly. It will be worth-while to take some considerations about the characteristics of \( \chi \) in each phase before going into this problem. \( \chi \) of \( \gamma \)-phase was almost the same as that of the liquid phase. Our present result is quite different from the Leiden's data which showed an abrupt decrease in \( \chi \) at the melting point. As it is known from X-ray investigation that the structures of \( \gamma \) and liquid phases are very alike\(^8\). Our result is rather consistent with this fact. It is necessary to note here that there have been somewhat ambiguous descriptions about the nature of \( \gamma \)-phase. For instance, it has been said to be glassy or transparent\(^9\). So, we are likely to reserve some definite explanation about the true equilibrium nature


of $\gamma$-phase. About $\beta$ and $\alpha$ phases, we can only say that the $\chi \sim T$ relation, on the whole, resembles well that of antiferromagnetics. The large negative Weiss constant may also support this idea. It is not reasonable, however, to ascribe the transition point of 43.7 K to Curie point in antiferromagnetics, because there exists a large structural change accompanying the latent heat.

Next, some considerations will be made about the magnetic properties of $(O_2)_2$ molecule. The existence of the dimer molecule $(O_2)_2$, in liquid and solid states has been known from various experiments, for instance, infra red and Raman spectra\(^{(10)}\), and X-ray investigations\(^{(8)}\). It has been believed to be diamagnetic by various authors\(^{(11)}\). If it is true, however, $\chi$ must show diamagnetism at the lowest temperatures, because all molecules should form the dimers in low temperatures. Our results completely contradict with this expectation but rather show an apparent paramagnetism at the temperature down to 1.9 K.

Now, the related data about $(O_2)_2$ molecule will be quoted here. The dissociation energy of the dimer is about 150 cal/mole. $O_2-O_2$ distance is about 3.5 Å. It is especially noticeable that the electronic structure of the composed molecule is $^3\Sigma$ in $\alpha$-phase like in the gaseous state \(^{(12)}\). From these facts, the following conclusion may be drawn: two oxygen molecules are coupling very weakly at the distance considerably apart from each other and having the same electronic structure as the individual molecule. The origin of this interaction may first be attributed to the free spins in those molecules. The electric quadrupole interaction or charge transfer interaction may also be worth-while to be considered. The former, however, is much weak at the distance of about 3.5 Å and the latter is not likely to occur in this case.

The electronic structure of oxygen has been computed by many authors\(^{(13)}\) and its energy state and eigenfunction of ground state have been determined definitely. $2p\pi^\pm$ are responsible to its two unpaired electrons. It is well known, in general, that, when the distance between two atoms is small, the exchange of all electrons in both atoms must be accounted for and that it gives the exchange repulsion in the case of the interaction between the closed shells. In oxygen, however, there are two unpaired electrons, giving rise to the energy difference between $\sigma$- and $\pi$-interaction. Since the exchange repulsion coming from the orbits other than $2p\pi^\pm$ also predominates, the total interaction will be repulsive at a small distance, whereas, at larger distance where the van der Waals attraction appears, there will be some difference in the depth of energy minimum between $\sigma$- and $\pi$-state in the exchange part. In our opinion, the dissociation energy of about 150 cal/mole will correspond to this difference. To make some rough estimate


about the order of this energy or the sign of the exchange integral which determines the magnetic property, it will be sufficient to study the nature of $2\sigma - 2\sigma$ interaction at this large distance. From the calculation made by Bartlett\(^{(14)}\), the ground state of $2\sigma_{zz}$ is $3\Sigma$ at about 0.5$-$1.0Å. According to the calculation\(^{(15)}\) by Dr. Sugawara in our Laboratory using Kotani's table\(^{(16)}\), the exchange integral changes its sign at large distance. If 4.0 is taken for the screening constant of oxygen, it will change at 1.3Å and $1\Sigma$ is stable at larger distance, at least, of about 2Å. Unfortunately, as no study about the interaction at larger distance had been reported, the order of magnitude or even its sign at the distance of 3$-$4Å could not be determined. Though no picture about $(O_2)_2$ can be made, it is interesting to compare the van der Waals distance with the inter molecular distance of various dimer molecules. In table 1 the distances and the dissociation energy are listed.

<table>
<thead>
<tr>
<th>Monomer</th>
<th>dimer</th>
<th>dissociation energy</th>
<th>references</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\varepsilon_0$</td>
<td>$\gamma_0$</td>
<td></td>
</tr>
<tr>
<td>NO</td>
<td>260 cal/mol</td>
<td>3.25 Å</td>
<td>4Kcal/mol</td>
</tr>
<tr>
<td>O$_2$</td>
<td>230 &quot;</td>
<td>3.68 &quot;</td>
<td>0.15 &quot;</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>370 &quot;</td>
<td>4.60 &quot;</td>
<td>3 &quot;</td>
</tr>
</tbody>
</table>

* Averages in gaseous state obtained from the second virial coefficient, or viscosity.

In the cases of NO and CO$_2$, the dimer distance is very much smaller than van der Waals distance. It is clear that the other cause of attraction such as electrostatic force prevails against the exchange repulsion. The dissociation energy is large in these cases. The nearly same distance and very small dissociation energy in oxygen show that only the exchange effect is important.

**Summary**

The susceptibility solid oxygen was thoroughly investigated in the temperature between 2 and 77K. The magnetic transitions occur at 23.7° and 43.7K, which agree well with the results from thermal investigation. From the large negative Weiss constant in liquid and the figure in $\beta$-phase, it may be concluded that oxygen is antiferromagnetic at low temperatures. Some theoretical consideration was attempted, but it was found very hard on account of the present imperfect knowledge about the crystal structure of oxygen and the lack of the calculation about the $2\sigma-2\sigma$ interaction in large distances.

**Acknowledgement**

The authors wish to express their sincere thanks to Prof. H. Masumoto, director of the Institute and the government authorities for their good offices and expenditure to equip the Institute with the Helium Cryostat and other facilities for cryogenic researches, with which the present researches have been completed.

\(^{(15)}\) Private communication