Magnetic Susceptibility of the Solid Oxygen-Fluorine Mixture

Akira SAKAKIBARA,* Yoshihiro MORI,** and Hiroo INOKUCHI
The Institute for Solid State Physics, The University of Tokyo, Roppongi, Minato-ku, Tokyo 106

(Received June 13, 1974)

The magnetic susceptibility of an oxygen–fluorine solid mixture with a 20—75% oxygen content was measured from 12 K to each melting point. The small susceptibility found below 45 K with a 20—60% oxygen content is interpreted in terms of direct- and super-exchange interaction. The supercooling of the cubic phase is suggested in the case of a 75% oxygen content.

Oxygen and fluorine are neighbouring elements of the second row of the Periodic Table, and their molecular sizes and shapes 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 O_2 molecule is 4.18 Å long and 3.18 Å wide, while the F_2 molecule is 4.18 Å long and 2.86 Å wide.1) Besides, the packings of the molecules in the solid phase resemble one another: solid oxygen occurs in three phases, α, β, and γ,*** of which the crystal structures are monoclinic (C2/m),2) rhombohedral (R$\bar{3}$m)3) and cubic (Pm3n)4) respectively. On the other hand, the crystal structures of α- and β-fluorine**** are monoclinic (C2/m)5) and cubic (Pm3n),6) strikingly similar to those of the α- and γ-solid oxygen. Because of these similarities, we can expect that oxygen and fluorine molecules mix well to form solid solution.

Concerning the physical properties of these solid phases, previous workers7) have established that antiferromagnetic spin ordering exists in the α-phase, while in the β- and γ-phases the ordering is limited to a short range. As for the magnetic properties of the O_2–Ar solid solution system, Blocker *et al.* have investigated lower concentrations of oxygen molecules in an attempt to determine the exchange interaction between oxygen molecules:8) argon molecules serve to dilute the oxygen concentration and intercept the magnetic interaction among the oxygen molecules. When there is a higher concentration of O_2 in the O_2–Ar system, however, we have found from our magnetic susceptibility measurements that argon molecules directly affect the antiferromagnetism and also the crystal transformation of the solid oxygen.9) Therefore, it seemed that it would be interesting to study the magnetic properties of solid solution of oxygen and another molecule such as fluorine, which more strongly interacts with oxygen.

In this paper, the results of the magnetic susceptibilities of oxygen–fluorine mixtures will be presented and discussed in terms of the exchange interaction.

Experimental

The magnetic susceptibility measurements were carried out from 12 K to each melting point of the oxygen–fluorine mixture by the Faraday method, as has previously been described.10) The magnetic field was set at about 9×10^3 Oe throughout the measurements. The $H(\partial H/\partial x)$ value was calibrated by measuring the susceptibility of sucrose, the mass susceptibility of which was taken to be -0.566×10^{-6} emu/g.

A gaseous mixture of oxygen and fluorine in various ratios, but containing 2—8 mg of oxygen, was thoroughly condensed into a small quartz tube cooled at the temperature of liquid helium, after which the tube was quickly sealed off with an oxyhydrogen flame.

Because of the reactivity of fluorine, especially with even a trace of water, the preparation process was carried out carefully as follows. Each of the oxygen and fluorine gases (commercially obtained) was passed through a liquid-nitrogen trap. Quartz tubes were at first baked for 3 hr at 1050 °C and then treated for a further 12 hr at 500 °C in a vacuum before introducing the sample into the tubes. The tubes and valves for the preparation system, composed of monel metal were also baked at 200 °C. The quartz tube was joined to the monel metal with coval metal, not with a seal using O rings, with attention paid to the resistivity to the heat treatment. The quartz-tube ampoules containing the O_2–F_2 mixture were placed in liquid nitrogen. In spite of the use of such a careful method for preparation and storage, however, the inner wall of the quartz ampoule containing the mixture was partially corroded; therefore, the final molar ratio of oxygen and fluorine is estimated to be larger by at least a few percent.

This quartz ampoule (5 mm in diameter and about 100 mm in length) was suspended by a Pyrex glass string from the arm of a vacuum balance, a Sartorius Electrono Microbalance, and cooled down to about 50 K; warming and cooling were then repeated around the melting point. After this, it was cooled down to 12 K in less than ten minutes. The temperature was measured with an Au: Co–Cu thermocouple placed below the ampoule and calibrated by the phase-transition points of pure oxygen and also by measuring the susceptibilities of the paramagnetic Tutton's salts, ($Fe(NH_4)_2(SO_4)_2\cdot6H_2O$) and ($Mn(NH_4)_2(SO_4)_2\cdot6H_2O$). Measurements of the temperature dependence of the magnetic susceptibility were started about three hours later, at a time when the temperature of the sample rose naturally after the evaporation of the liquid helium. The susceptibility was corrected for the diamagnetism of the quartz ampoule, but not for that of the sample itself, which would be negligible in this case.

Results and Discussion

Figures 1—3 show the temperature dependence of the magnetic susceptibilities of the oxygen–fluorine mixture (O_2–F_2). In case of a mixing O_2–F_2 ratio of

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* School of Engineering, Okayama University, Okayama 700.

** Faculty of Pharmaceutical Sciences, Toyama University, Gofuku, Toyama 930.

*** α: below 23.88 K, β: 23.88—43.76 K, and γ: 43.76—54.39 K.

**** α: below 45.6 K and β: 45.6—53.5 K.

50: 50 or 60: 40 in Fig. 1, there exists only one phase transition, at 45 K; no transition was found around 24 K, corresponding to the α-β phase transition temperature in pure solid oxygen and also in the 95% O_2–5% Ar mixture.[9] This finding indicates that the solid phases of oxygen and fluorine are not segregated from each other, but that solid solutions are preferably formed below 45 K.

The rapid increase in the susceptibility toward the low-temperature region is due to the free spins of the oxygen molecules isolated in the fluorine matrices. The ratio of the oxygen molecules contributing to this paramagnetism is at most a small percentage at those contents.

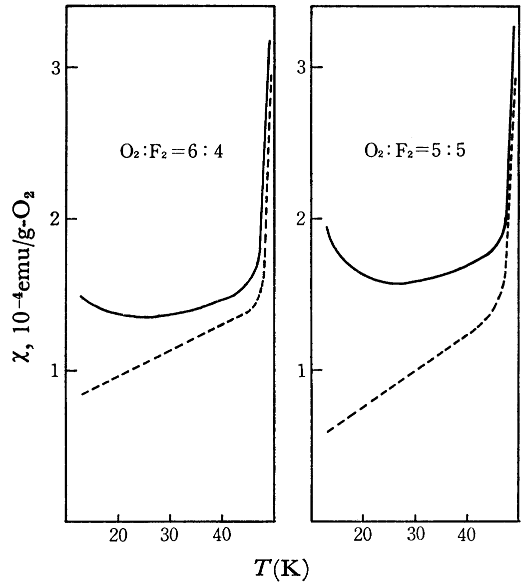

Fig. 1. Magnetic susceptibility for O_2: F_2=60: 40 and 50: 50 mixture as a function of temperature.
——: Measured susceptibility
----: Susceptibility removed of Curie's paramagnetism.

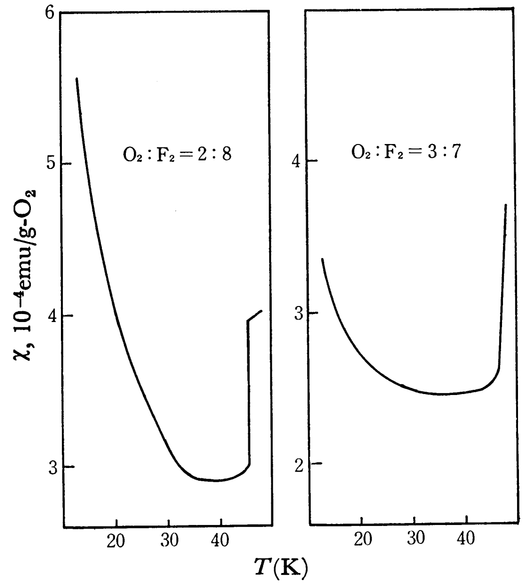

Fig. 2. Magnetic susceptibility for O_2: F_2=20: 80 and 30: 70 mixture as a function of temperature.
——: Measured susceptibility.

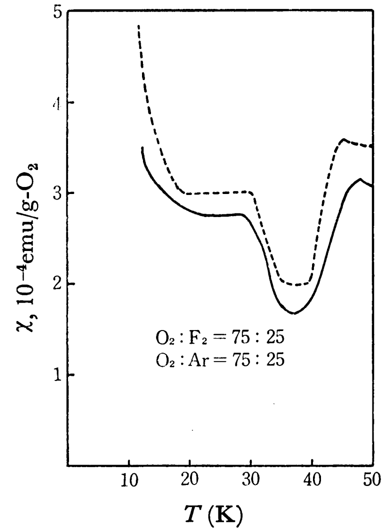

Fig. 3. Magnetic susceptibility for O_2: F_2=75: 25 compared with O_2: Ar=75: 25 mixture as a function of temperature.
——: O_2–F_2, ----: O_2–Ar

The dotted lines in Fig. 1 show the susceptibilities, with their paramagnetism removed by 4% for the 50: 50 mixture and 2% for the 60: 40 mixture according to Curie's law. The exact contribution of this paramagnetic oxygen could not be determined. There appears, then, a monotonously decreasing susceptibility below 45 K (dotted lines in Fig. 1). This temperature dependence of the magnetic susceptibility suggests that there exists a strong antiferromagnetic interaction in these solids, as in the α-phase of pure oxygen. A possible model for this antiferromagnetism of the O_2: F_2=50: 50 solid solution is presented below.

No experimental data for the crystal structure of the O_2–F_2 mixture in the solid phase have been reported. However, considering that the lowest-temperature phases, monoclinic, of both oxygen and fluorine and the molecules resemble each other in shape and size, as has been mentioned above, the crystal structure of the O_2–F_2 solid solution below 45 K can be expected

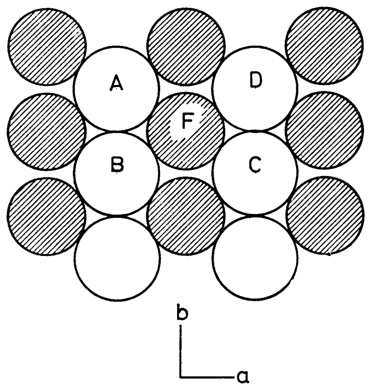

Fig. 4. A possible model for the molecular packing of O_2 and F_2. The contour is at the 0.002 a.u. of the total molecular charge density, which includes over 95% of the total charge. The lattice parameter, a or b, in the model is taken to be an average of that for α-oxygen and α-fluorine. Shadowed are fluorine molecules and non-shadowed are oxygen.

to be monoclinic. In Fig. 4, one of the possible models for the arrangement of oxygen and fluorine molecules in the ab plane is presented. The molecular packing of this arrangement can be predicted to be a nearly closed-packed one judging from that of the α-phase of oxygen and fluorine, and also from the molecular size. Because the fluorine molecule is narrower in width than the oxygen molecule, the distance between A and B may decrease in comparison with that of the same pairs in pure oxygen, 3.43 Å. Then the orbital overlap between them will so increase that the spin of the A oxygen strongly interacts with that of B antiferromagnetically. This direct antiferromagnetic exchange interaction is the most important factor.

The direct-exchange interaction between A and C or A and D can be neglected because of the long distance between them. However, the spin of the A oxygen may indirectly interact with that of the C oxygen through the F fluorine, as there may be a large overlap between the orbitals of A and F and between those of C and F, as is to be expected from their molecular packing shown in Fig. 4. This indirect interaction can be understood in terms of the super-exchange interaction, which has proceeded in some antiferromagnetic ionic compounds. That is, the electron of the $1\pi_g$ orbital of the A oxygen molecule interacts with that of the $1\pi_g$ of the C oxygen molecule, including the electron transfer from fluorine to oxygen. Then the spins of A and C are ordered in antiparallel fashion. The same interaction through F also occurs between A and D. In this case, the spin of A may be ordered parallel to that of D, because the two $1\pi_g$ orbitals of the F fluorine which interact with A and D are orthogonal.

In the $(\bar{2}01)$ plane of the monoclinic lattice also, the molecular packing may be nearly closed, as in α-oxygen, in which case exchange interaction will occur directly or indirectly *via* a fluorine molecule.

As a matter of fact, it is still questionable whether or not an ordered distribution of O_2 and F_2 occurs, but in any case, including a randomly distributed model, the antiferromagnetic ordering in this solid solution would be realized by the direct- and also the super-exchange mechanism described above.

The magnetic susceptibilities of the O_2: F_2=20: 80 and 30: 70 mixtures at low temperatures are rather large in comparison with that of the 50: 50 mixture, but the decrease in the susceptibility around 45 K, though a little smaller, was also observed in these mixtures with lower oxygen contents. On the other hand, the susceptibilities of O_2–Ar mixtures of the same ratio do not decrease around 45 K and show a Curie-Weiss paramagnetism in this temperature region.[8] Therefore, in this case of O_2–F_2, oxygen molecules may not be distributed more thinly in one region and may be more concentrated in the other region.

For the case of O_2: F_2=75: 25, the temperature dependence of the susceptibility is very similar to that for O_2–Ar of the same ratio, O_2: Ar=75: 25. The large susceptibility at lower temperature, and the transition at about 27 K are characteristic. For the case of O_2–Ar, there appears a novel phase below 27 K, the crystal structure of which is cubic and very similar to that of the γ-phase.[11] This novel phase can be observed even at a composition and temperature where the monoclinic phase is stable when a rapid cooling quenches the structure of a higher temperature.[9,11] For the case of O_2–F_2 also, supercooling occurs from around 50 K and the cubic lattice is quenched to the lowest temperature.

The authors are much indebted to Drs. G. Fujisawa, M. Iwasaki, and S. Tsujimura of the Tokai Research Establishment, Japan Atomic Energy Research Institute, for preparing the sample and to T. Takeda for his skillful glass work. We are also grateful to Dr. H. Kawamura for helping us to prepare the apparatus.

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