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LETTERS

Anomalous Magnetic Behaviors of O_2-CO_2 Mixed Solid

A. Tohdoh and K. Kaneko*,[†]

Physical Chemistry, Material Science, Graduate School of Natural Science and Technology, and
Center for Frontier Electronics and Photonics, Chiba University, 1-33 Yayoi, Inage, Chiba 263, Japan

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The temperature dependence of the magnetic susceptibility (χ) of O_2 and CO_2 mixture was measured as a function of the mole fraction of CO_2 over 1.9−100 K. The χ value was remarkably depressed by the coexistence of CO_2, although a change in χ due to $\alpha-\beta$ and $\beta-\gamma$ phase transitions of solid O_2 was observed. The remarkable depression of the χ of the CO_2-O_2 mixture indicated the presence of new compound having the temperature independent-magnetic susceptibility. The relationship between the temperature-independent magnetism and the CO_2-O_2 composition intensively suggests the formation of stoichiometric compounds of CO_2 and O_2, such as clathrate compounds.

Introduction

The ground state of O_2 is triplet, showing a typical paramagnetism in the gas phase. It is well-known that solid O_2 (s-O_2) has three polymorphs of α, β, and γ. The $\alpha-\beta$ and $\beta-\gamma$ transitions show explicit anomalies in the magnetic susceptibility due to the corresponding phase transitions at 23.8 and 43.8 K.[1,2]

The binary mixture of simple gases such as O_2, N_2, CO_2, and rare gases have been studied as model molecular systems. X-ray diffraction study gave the phase diagram of O_2 and N_2, which indicates many phase transitions in the solid phase.[3] Raman study[4] suggested the presence of a new phase transition that was not observed by the X-ray diffraction approach. The fundamental understanding of the O_2 and N_2 mixture should be helpful to design a new air separation technology.

In the case of O_2-Ar binary system, X-ray diffraction study showed the absence of solid-phase transition in the mole fraction range of Ar from 0.5 to 0.8. The mixture of Ar and O_2 of the above composition has a hexagonal close packed structure, which is completely different from the structure of pure solid O_2.[5] On the other hand, the heat capacity measurement of the $Ar-O_2$ system indicated the presence of a "hump"-type phase transition at 0.6 of Ar mole fraction and 14−25 K, not evidenced with X-ray diffraction.[6] Thus, the fundamental study on the O_2 based-molecular solid should be carried out not only by X-ray diffraction, but also by other techniques such as Raman spectroscopy.[7−11] Furthermore, magnetic susceptibility measurement is a potential method for O_2 based molecular solids because the magnetic interaction is quite sensitive to the local structure around an oxygen molecule. The structural study on the O_2 based-molecular solids should provide a new aspect for the intermolecular interaction.

As a CO_2 molecule has a great quadrupole moment,[12] the presence of CO_2 molecules should intensively affect the solid O_2 structure. The magnetic susceptibility of the solid O_2 can quite sensitively detect the local structural change of an oxygen molecule. The low-temperature magnetic susceptibility of the O_2-CO_2 mixture was measured over the temperature range from 1.9 to 100 K in this study. The present work describes a remarkable effect of the coexistent CO_2 on the magnetism of solid O_2.

[†] Center for Frontier Electronics and Photonics.

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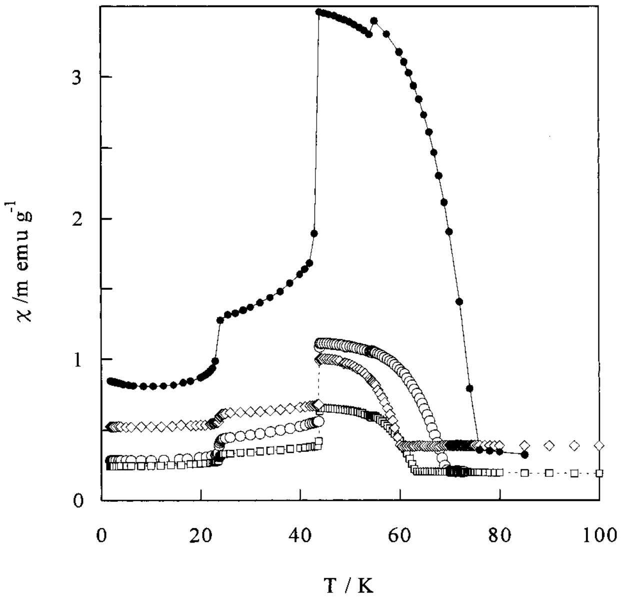

Figure 1. Temperature dependencies of the magnetic susceptibility of the solid O_2-CO_2 system as a function of the CO_2 mole fraction x. ●: $x = 0$, ○: $x = 0.2$, □: $x = 0.3$, and ◇: $x = 0.5$.

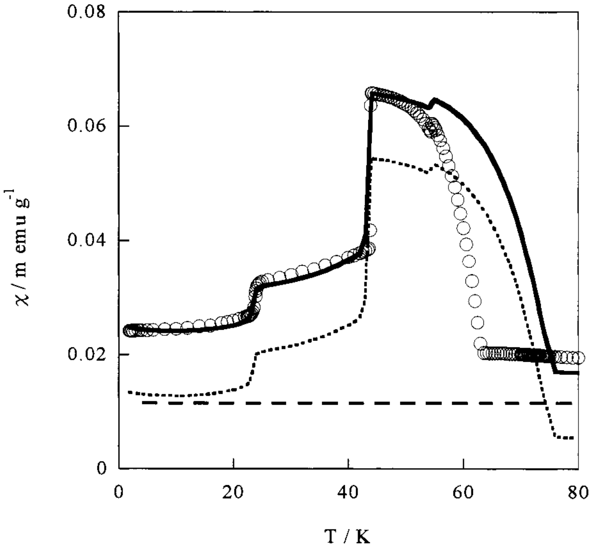

Figure 2. Fitting procedure of the magnetic susceptibility of the O_2-CO_2 system of $x = 0.3$. ○: Experimental data, — — —: χ_{ti}, - - -: $b_O\chi_O$, and —: $(\chi_{ti} + b_O\chi_O)$.

Experimental Section

CO_2 and O_2 gases of high purity (99.99%) were used after repeated vacuum distillations. The mixed gas of CO_2 and O_2 were kept for 90 min at 303 K after their mixing. The gas mixture was introduced into an ESR quartz tube (length: 90 mm, diameter: 5 mm), and then the quartz tube was sealed. The composition of the gas mixture was determined through measurement of the O_2 and CO_2 partial pressures at 303 K. The mole fraction of CO_2 is designated as x. The quantity of O_2 was determined from the O_2 pressure and the volume of the sealed quartz tube. The magnetic susceptibility, χ, was measured with a SQUID magnetometer system MPMSR2 (Quantum Design) over the temperature range from 1.9 to 100 K at a magnetic field of 1*T*. The magnetic susceptibility, χ, of the quartz tube was subtracted.

Results and Discussion

Temperature dependences of the magnetic susceptibility χ of the O_2-CO_2 system are shown in Figure 1 as a function of mole fraction x of CO_2. Pure O_2 shows explicit anomalies at the phase transition temperatures of 23.9 K($\alpha-\beta$), 43.8 K($\beta-\gamma$), and 54.4 K($\gamma-$liquid), which agree with the literature values.[1,2] The anomalies due to $\alpha-\beta$ and $\beta-\gamma$ transitions are preserved at the same temperatures, even in the O_2-CO_2 system, although the χ is remarkably depressed by the coexistence of CO_2. As the CO_2 molecule has no spin, the observed changes in the magnetism stem from the change in the O_2-O_2 and/or O_2-CO_2 intermolecular structure. In this work, the magnetic susceptibility data of liquid and gaseous O_2 above 54.4 K are not sufficiently discussed.

The magnetic susceptibility depression is not proportional to the CO_2 mole fraction x. Therefore, we assumed that the coexistent CO_2 changes the magnetic interaction between O_2 molecules through the formation of a weakly interacted compound such as clathrate compound. We introduce the temperature-independent magnetic susceptibility (χ_{ti}) due to the above compound formation. As the O_2-CO_2 system should consist of pure O_2 and the O_2-CO_2 compound, the observed magnetic susceptibility χ_{ob} is expressed by χ_{ti} and the magnetic susceptibility of pure O_2, χ_O, as given by

$$\chi_{ob}(T) = \chi_{ti} + b_O\cdot\chi_O\,(T) \quad (1)$$

Here χ_{ti} and the constant b_O are determined by the fitting procedure, as shown in Figure 2. The fitting over the temperature range from 1.9 to 50 K is well done. Nevertheless, the calculated $\chi_{ob}(T)$ using eq 1 deviates above 50 K, and the deviation becomes significant with increasing temperature. This is because the O_2 partial pressure of the O_2-CO_2 system is different from that of pure O_2, shifting the boiling temperature of liquid O_2. Figure 3 shows χ_{ti} and b_O with x. The χ_{ti} increases with the increase of x. Hence, O_2 molecules must form a compound with CO_2 molecules, as suggested above. On the other hand, the b_O decreases until $x = 0.2$ and oscillates with the increase of x.

The above interesting data must be explained by the constant b_O, which indicates the contribution of pure O_2 in the O_2-CO_2 system. We can presume that the pure O_2, which is not associated with the compound formation with CO_2, shows the same magnetism as the pure solid O_2. Then, the contribution of the pure O_2 and the component O_2 in the O_2-CO_2 compound to the observed magnetism can be separatively determined as follows. The total weight of O_2 is described by the sum of the weight of pure O_2 and that of the component O_2 in the O_2-CO_2 compound, as given by eqs 2 and 3

$$m_O = m_{O,p} + m_{O,c} \quad (2)$$

$$m_{O,p} = b_O\cdot m_O \quad (3)$$

Here, m_O is the total weight of O_2 in the sample cell, $m_{O,p}$ is the weight of the pure O_2, and $m_{O,c}$ is the weight of the component O_2. Then, b_O and m_O can express $m_{O,c}$

$$m_{O,c} = (1 - b_O)\cdot m_O \quad (4)$$

The mole fraction x_{comp} of CO_2 in the O_2-CO_2 compound is described by $m_{O,c}$ and m_{CO}, as shown by eq 5

$$x_{comp} = \frac{m_{CO}}{m_{O,c} + m_{CO}} = \frac{m_{CO}}{(1 - b_O)\cdot m_O + m_{CO}} = \frac{x}{b_O(x - 1) + 1} \quad (5)$$

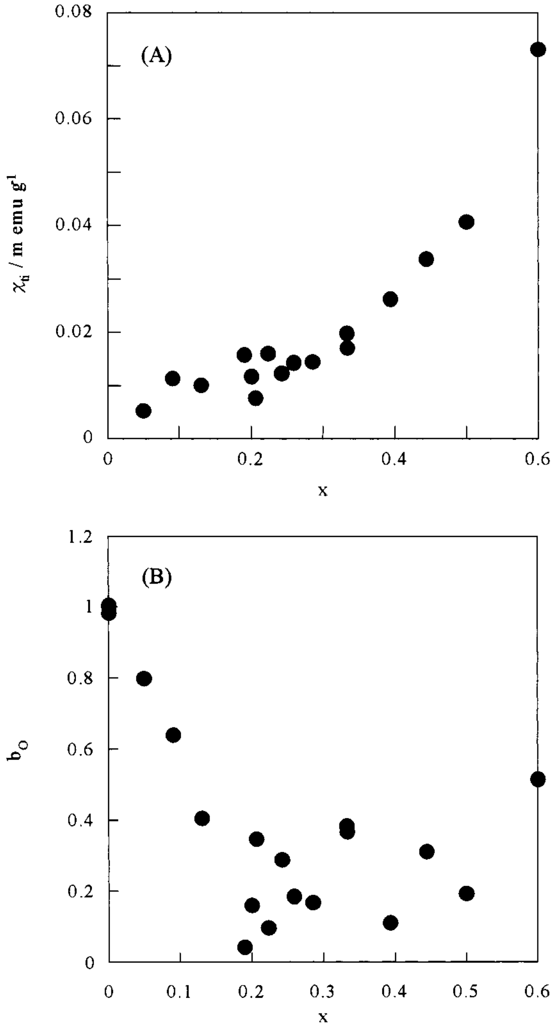

Figure 3. Changes of χ_{ti} and b_O with x. (A): χ_{ti} vs x and (B): b_O vs x.

Here, m_{CO} is the weight of CO_2 in the sample cell. The temperature independent magnetism should stem from the O_2-CO_2 compound. Therefore, the observed χ_{ti} must be recalculated using the weight of O_2 in the O_2-CO_2 compound to get the correct magnetic susceptibility $\chi_{ti,c}$ per unit mass of the component O_2 in the O_2-CO_2 compound with eq 6

$$\chi_{ti,c} = \chi_{ti}\cdot\frac{m_O}{m_{O,c}} = \chi_{ti}\cdot\frac{1}{1-b_O} \qquad (6)$$

Thus, the variations of $\chi_{ti,c}$ and x_{comp} with x are obtained, as shown in Figure 4. There are clear stepwise relationships for both of $\chi_{ti,c}$ and x_{comp}. Although the relationship between b_O and x above $x = 0.2$ is complex, simple $\chi_{ti,c}$ versus x and x_{comp} versus x relations can be obtained by the separation of O_2 into pure O_2 and the component O_2. So far, we cannot determine precisely the step position in Figure 4. However, these stepwise changes strongly suggest the formation of the stoichiometric compound of O_2 and CO_2 whose composition depends on the CO_2 content. Unfortunately, only magnetic susceptibility data cannot determine directly the structure of the O_2-CO_2 compound showing the temperature-independent magnetism, although the temperature-independent magnetism suggests the antiferromagnetic interaction between O_2 spins.

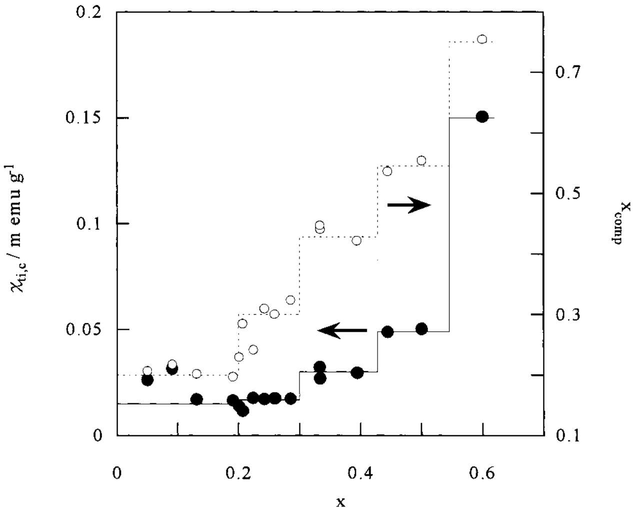

Figure 4. Changes of the temperature independent magnetism $\chi_{ti,c}$ of O_2 and the CO_2 mole fraction, x_{comp}, of the O_2-CO_2 compound with the mole fraction x of CO_2.

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