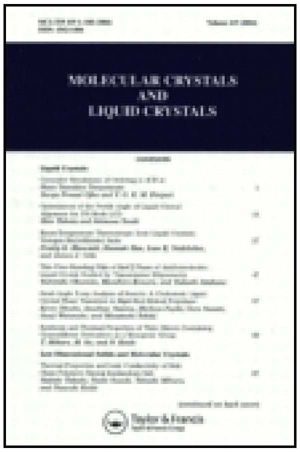

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Magnetic Properties of Oxygen Physisorbed in Cu-Trans-1,4-Cyclohexanedicarboxylic Acid

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MAGNETIC PROPERTIES OF OXYGEN PHYSISORBED IN Cu–TRANS–1,4–CYCLOHEXANEDICARBOXYLIC ACID

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Abstract Magnetic properties of oxygen physisorbed in Cu–trans–1,4–cyclohexanedicarboxylic acid having one–dimensional micropores are studied. O_2 is well known as a magnetic molecule with S=1. In the case of the low adsorption, temperature dependence of the susceptibility shows the Schottky–type broad peak and the high–field magnetization process has a step at around 34T with saturation moment of $2\mu_B/O_2$. These results are interpreted by the dimer model of S=1/2 with an antiferromagnetic exchange interaction. Broadening of the step of magnetization with increasing the adsorption may be due to the inter–dimer interaction or the distribution of the intra–dimer exchange interaction. Linear magnetization process which is characteristic of one–dimensional Heisenberg antiferromagnet has not been observed even in the full pore region.

INTRODUCTION

Oxygen molecule O_2 is well known as a simplest magnetic molecule with S=1.[1] Magnetic systems of adsorbed O_2 are of interest in terms of its characteristic circumstances and of expected ideal low–dimensionality. Various studies for two–dimensional system such as O_2 adsorbed on graphite[2] have been carried out, while one–dimensional system has not been investigated. If O_2 forms S=1 Heisenberg antiferromagnetic chain, the quantum effect such as Haldane gap and spin–Pierls transition may be expected.

We report the magnetic properties of O_2 adsorbed in Cu–trans–1,4–

cyclohexanedicarboxylic acid (CCHD) having one-dimensional micropores. The supposed structure of CCHD is shown in Fig.1. CCHD consists of stacked square lattices of $Cu_2(OOC-C_6H_4-COO)$ forming one-dimensional micropores. The diameter of the pore is experimentally estimated as 4.5A.[3] It is also confirmed that CCHD adsorbs N_2, Ar, Xe as well as O_2. Since Cu^{2+} ions with $S=1/2$ form the magnetic dimer with $J/k_B=-248K$, the magnetic contribution from Cu^{2+} ions is negligible in the present temperature range of $T<80K$ where the adsorption of O_2 is completed.

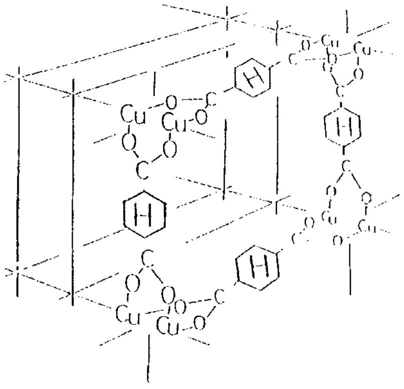

Fig.1 Crystal structure of Cu-trans-1,4-cyclohexanedicarboxylic acid (CCHD).

EXPERIMENTAL

Temperature dependence of O_2 adsorption was measured using a magnetic balance. In zero field, we measured the temperature dependence of the total mass of the adsorbed O_2 and the powder sample of CCHD in oxygen atmosphere. Susceptibility measurements were carried out using both a magnetic balance and a SQUID magnetometer. High-field magnetization process was measured using a pulsed magnet with a pulse duration of about 0.4 msec at the Research Center for Materials Science at Extreme Conditions, Osaka University and another pulsed magnet with a pulse duration of about 10 msec at Institute for Solid State Physics, University of Tokyo.

In the high-field magnetization process and the susceptibility measurement using SQUID magnetometer, we prepared adsorption cells consisted of O_2 gas and CCHD powder. The cell was made of quarts in order to avoid the paramagnetism due to magnetic impurities. CCHD powder was tightly fitted into the cell. After degas and dehydration out of CCHD at 100℃, an appropriate amount of O_2 gas was adsorbed into CCHD at liq. N_2 temperature. Finally, the quartz cell was enclosed by a gas burner.

RESULTS

Adsorption

Temperature dependence of O_2 adsorption measured using a magnetic balance is

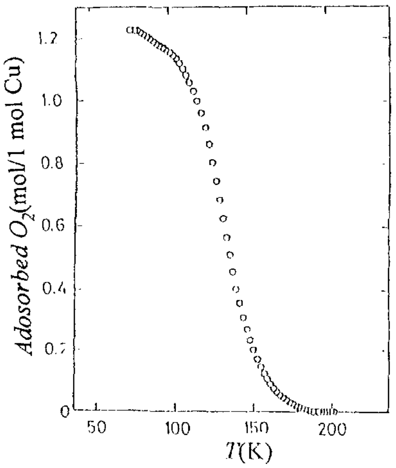

Fig.2 Temperature dependence of O_2 adsorption into CCHD.

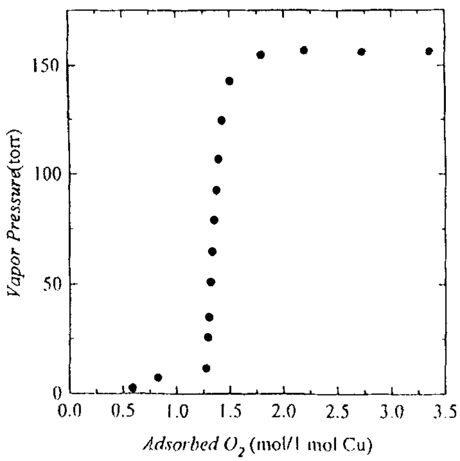

Fig.3 Adsorption isotherm at T=77K.

shown in Fig.2. The adsorption increases gradually below 150K and saturates below 100K. The saturated value reaches 1.2 mol of O_2 per 1 mol of Cu in CCHD at T=77K. The adsorption shows no hysteresis against temperature, which indicates that O_2 is physically adsorbed in the micropores of CCHD. Figure 3 shows the adsorption isotherm measured at T=77K. The vapor pressure increases rapidly at 1.25 mol/Cu and reaches the saturated vapor pressure. The steep slope just above 1.25 mol/Cu indicates that the adsorption on the surface of the CCHD powder is smaller negligiblly than the adsorption in the micropores since the adsorption isotherm shows a broad slope in the case of the adsorption on the surface such as graphite.[1]

Susceptibility

Temperature dependence of magnetic susceptibility in two cases of low adsorption and full pore region is shown in Fig.4. We show the data measured using a SQUID magnetometer which agree with those measured using a magnetic balance. The susceptibilities show a broad maximum at around T=25K and 30K in the low adsorption case of O_2/Cu=0.18 and the full pore case of O_2/Cu=1.11, respectively. The broad maximum is considered to show the short range order. Below 10K, the susceptibility increases rapidly, which has nearly paramagnetic temperature dependence.

Magnetization Process

High-field magnetization process shown in Fig.5 was obtained at T=1.3K using a pulsed magnet with a pulse duration of about 0.4 msec. These data agree with those

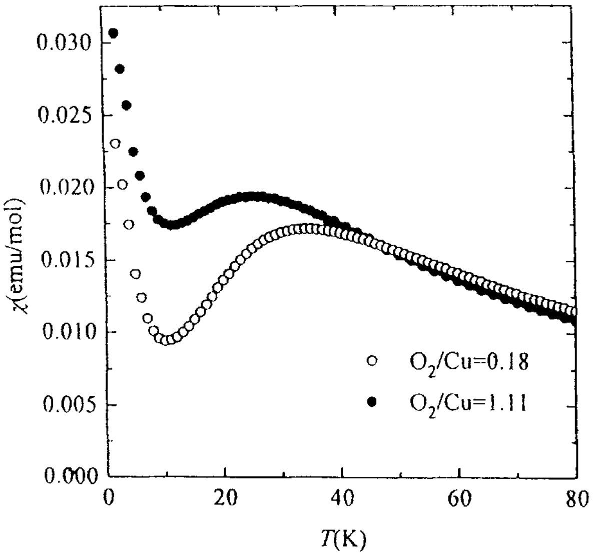

Fig.4 Temperature dependence of susceptibility in two cases of low adsorption and full pore region.

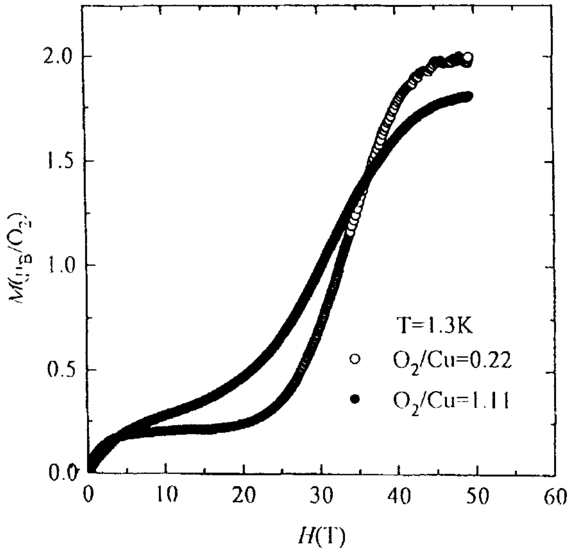

Fig.5 High-field magnetization process at T=1.3K in two cases of low adsorption and full pore region.

measured using a long-pulse magnet with a pulse duration of about 10 msec. We confirm experimentally that the background magnetization from both CCHD and quarts cell is negligibly small.

In the low adsorption region, the magnetization shows small paramagnetic behavior in the low field. With increasing the field, the magnetization increases rapidly at around H=34T and saturates at around the highest field of H=50T. The saturated magnetization reaches $2\mu_B/O_2$ which is expected value in the case of S=1, g=2.0. In the full pore region, both the paramagnetic behavior in lower field and the rapid increase of magnetization in higher field show considerable broadening. We cannot observe a linear magnetization expected for one-dimensional Heisenberg model even in the full pore region.

DISCUSSIONS

The characteristic magnetization process having a step at around 34T is observed in the low adsorption region and has been dominant even in the full pore region. The characteristic behavior cannot interpreted by S=1 Heisenberg model. In the case of magnetic dimer described in the Hamiltonian:

$$H = -2JS_1 \cdot S_2 + g\mu_B S \cdot H, \quad J<0, \tag{1}$$

the magnetization process should change by two steps in the field $H=-2J/g\mu_B$ and $-4J/g\mu_B$, respectively. Since the present results were obtained by using powder sample, we may reject the possibility that a step is caused by the single ion anisotropy DS_z^2. The D-value of isolated O_2 molecule has been known as $D/k_B \sim 5.5K$[4,5] which is smaller than the energy gap of Δ/k_B=23K corresponding to the critical field of 34T. The present result is different clearly from the magnetization in S=1 Heisenberg antiferromagnetic chain. Though Haldane gap exists in this case, the magnetization shows almost linear behavior where the magnetization increase at $H=-0.41J/g\mu_B$ and the saturated field is $-4J/g\mu_B$.[6-8] For S=1 Heisenberg alternating chain, the magnetization process is considered to show an intermediate behavior between the dimer and the uniform chain.

Therefore, we employ S=1/2 dimer model described by Hamiltonian (1) for the present result. In this case, the magnetization process shows a step at $H=-2J/g\mu_B$. Subtracting the paramagnetic magnetization in the low field, the experimental result can be interpreted as the S=1/2 dimer model with J/k_B=−23K and g=2.0. Assuming the small distribution for J, the agreement between the experimental result and the calculated one becomes better. Broadening of the magnetization step in the full pore region may arise from the considerable inter-dimer interaction. Temperature

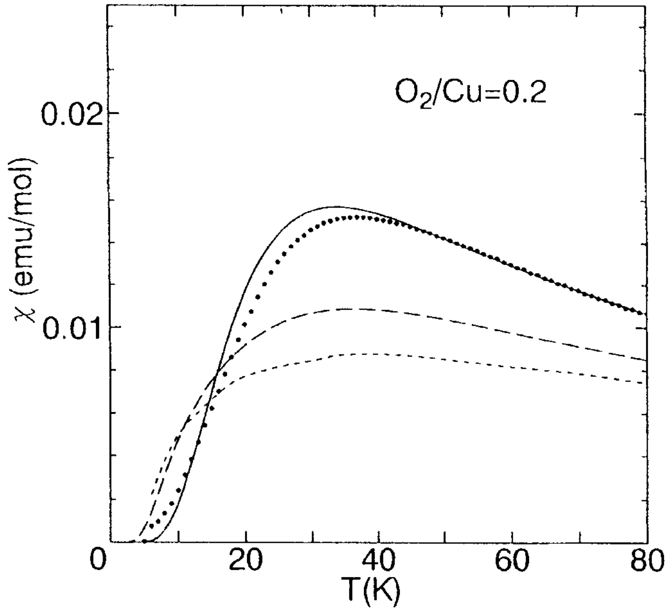

Fig.6 Temperature dependence of susceptibility in the low adsorption region. The paramagnetic susceptibility at low temperatures is subtracted. Respective curves indicate the calculated one for S=1/2 dimer model (solid line), S=1 dimer model (broken line) and S=1 Heisenberg antiferromagnetic chain (dotted line).

dependence of susceptibility in the low adsorption region can be also fitted by the S=1/2 dimer model with J/k_B=−27K and g=2.4 as shown in Fig.6 where the paramagnetic susceptibility at low temperatures is subtracted by assuming the Curie–Weiss law. In this case, the critical field is obtained as H=34T. Disagreement with S=1 dimer model or S=1 Heisenberg antiferromagnetic chain[9] is clear from Fig.6.

We note the possibility that the inter-dimer interaction of Cu^{2+} spins with S=1/2 changes when CCHD adsorbs O_2. We also measured the susceptibility of CCHD absorbing N_2. Adsorption isotherm at T=77K shows the similar behavior with the adsorbed O_2 and the full pore adsorption of N_2/Cu=1.1. The susceptibility in the sample of N_2/Cu=1.1 agrees with that of CCHD without N_2. Therefore, we can reject the possibility that the magnetization of Cu^{2+} ions is observed in the present experiment of adsorbed O_2.

We speculate that the origin of S=1/2 may arise from the instability of S=1 state in O_2 molecule. Spin 1 of O_2 comes from two parallel spins in degenerate antibonding p_π orbital. If the two levels separate due to adsorption, the magnetic moment of O_2 is expected to be described by antiferromagnetic dimer model of S=1/2. The oxygen may exist as the monatomic oxygen in the micropores. Though we tried the Raman-spectroscopy in this system, the signal of oxygen cannot be observed due to large background signal of CCHD.

CONCLUSION

We investigated the magnetic properties of O_2 physisorbed in CCHD having one-dimensional micropores. The Schottky-type broad peak of susceptibility and the high-field magnetization process having a broad step at around 34T may be interpreted as the dimer model of S=1/2 though the origin of S=1/2 is still not clear.

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