MLF Experimental Report	提出日 Date of Report
課題番号 Project No. 2012B0067 実験課題名 Title of experiment Magnetic excitation in O_2 supercrystal realized in nanoporous compound 実験責任者名 Name of principal investigator Takatsugu Masuda 所属 Affiliation Institute for Solid State Physics, the University of Tokyo	装置責任者 Name of Instrument scientist Kenji Nakajima 装置名 Name of Instrument/（BL No.） BL14 実施日 Date of Experiment 21st Nov – 29th Nov.

試料、実験方法、利用の結果得られた主なデータ、考察、結論等を、記述して下さい。（適宜、図表添付のこと）
Please report your samples, experimental method and results, discussion and conclusions. Please add figures and tables for better explanation.

1. 試料 Name of sample(s) and chemical formula, or compositions including physical form.

Cu-Trans-1,4-Cyclohexanedicarboxylic Acid

2. 実験方法及び結果（実験がうまくいかなかった場合、その理由を記述してください。）
Experimental method and results. If you failed to conduct experiment as planned, please describe reasons.

In some types of nanoporous metal organic complex, gas molecules can be adsorbed in its porous and a possibility of supercrystal is suggested. For example in a Cu complex, CPL-1, the adsorbed O_2 molecules, S=1 magnetic entity, forms dimer like structure in the one dimensional cylindrical porous [1]. Recently we studied the magnetic excitation of the adsorbed O_2 by inelastic neutron scattering technique [2]. The observed spectrum was beautifully explained by singlet-triplet excitation of S=1 dimer model and the realization of O_2 magnetic supercrystal was identified. Furthermore a characteristic behavior due to soft framework of the supercrystal was observed in the temperature dependence of neutron cross section. Thus the newly developped area of O_2 supercrystal is a forefront of condensed matter science.

A Cu complex, Cu-Trans-1,4-Cyclohexanedicarboxylic Acid, (Cu-CHD) is another interesting material. In O_2 atmosphere Cu-CHD includes O_2 molecules in its microporous as shown in Fig. 1 [3]. Magnetic susceptibilities and magnetization show spin gap behavior with non-magnetic ground state for lightly

oxygen adsorbed sample and non-spin-gap behavior with magnetic ground state for heavily adsorbed sample as shown in Fig. 2 and 3. The data is not explained by conventional spin models including S=1 dimer, S=1 chain, S=1/2 dimer etc. Hence we performed cold neutron scattering experiment to reveal a spin Hamiltonian of O_2 supercrystal realized in nanoporous compoumd.

5g of powder sample was prepared. We used ORANGE type cryostat to achieve 1.5 K. At 100 K we introduce O_2 gas at less than 1 atm into sample container thorough oxygen gas introduction probe. In this process O_2 gas is adsorbed in Cu-CHD. After completion of a set of neutron scattering experiments on O_2-included sample, we proceed to background measurements on non-O_2-included sample. We heat the sample up to room temperature and evacuate the sample container to eliminate O_2. Then we cool down the sample to measure the background. Neutron experiment was performed at AMATERAS spectrometer installed in J-PARC MLF.

Neutron scattering spectrum of lightly O_2 adsorbed Cu-CHD is shown in Fig. 4. The data after background subtraction is presented. Dispersionless excitations are observed at E = 2meV and 4 meV. The energy widths are wider than experimental resolutions. Intensities decrease with the increase of Q. Hence the observed excitations are those from magnetic clusters. We assume that the supercrystal in the porous consists of two types of dimers with distributed exchange interactions J's. The data are reasonably explained by the model and the obtained parameters are J=4.27meV, D=0.41meV, σ =1.69meV, R=2.70Å for one dimer and J=2.26meV, D=0.41meV, σ =1.27meV, R=5.50Å for another dimer. Here D is single ion anisotropy, σ is J's distribution, and R is intradimer distance of O2 molecules. Figure 5 shows the spectrum of heavily O_2 adsorbed Cu-CHD. A new excitation is observed at 0.4meV in addition to 2meV and 4meV. Considering the bulk measurements we assumed S=1 trimer model with single ion anisotropy. The model explain the data reasonably and the obtained parameters are J_1 = 3.94meV, J_2=0.98meV, D=0.41meV, σ=1.54meV, R_1=2.25A, and R_2=2.98A. Here J_1 and J_2 are intratrimer interactions and R_1 and R_2 are intratrimer distances. While neutron scattering spectrums are explained by the clusters models, bulk properties are not reproduced. Consider that the calculated spectrum including intermolecule potentials in O_2 dimers deviates from purely spin Hamiltonian [4] we deliberately lower the energy levels of eigenstates with S ~ 2 and 3. Consequently the bulk properties are reproduced.

In conclusion we performed neutron scattering experiment on O_2 molecules adsorbed in nano-porous complex Cu-CHD and it is revealed that the realized supercrystal is dimer for lightly adsorbed sample and trimer for heavily adsorbed sample.

References

[1] R. Kitaura et al., Science 298, 2358 (2002).

[2] T. Masuda et al., J. Phys. Soc. Jpn. 77, 083703 (2008).

[3] S. Takamizawa et al., Angew. Chem., Int. Ed. 43, 1368 (2004).

[4] B. Bussery and P.E.S. Wormer, J. Chem. Phys. 99, 1230 (1993).

2. 実験方法及び結果（つづき） Experimental method and results (continued)

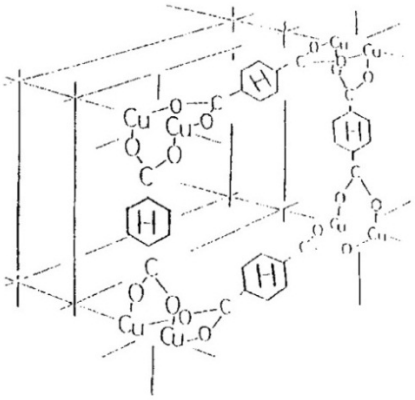

Figure 1: Crystal structure of Cu-CHD. Oxygen molecule is adsorbed in nano scale porous.

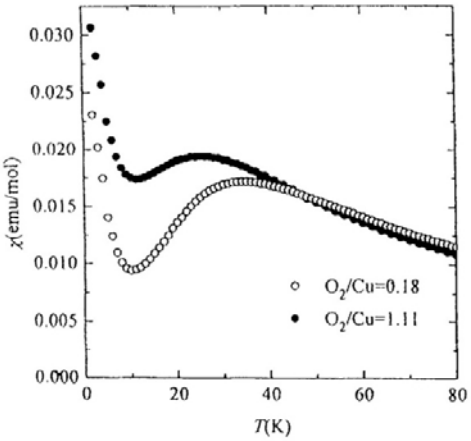

Figure 2: Magnetic susceptibility of O_2 adsorbed Cu-CHD with heavy concentration (filled circles) and light concentration (open circles).

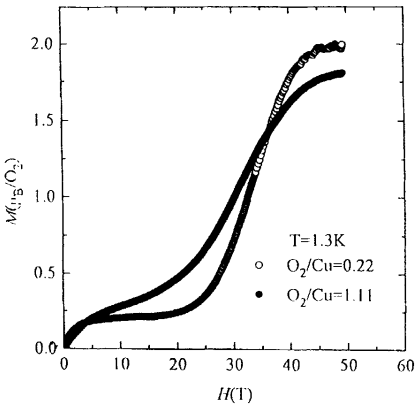

Figure 3: Magnetization of O_2 adsorbed Cu-CHD with heavy concentration (filled circles) and light concentration (open circles).

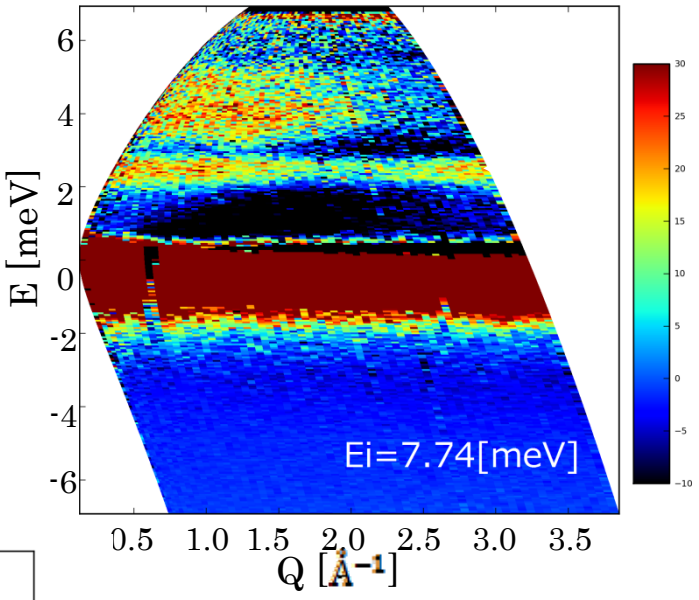

Figure 4: Neutron spectrum of lightly adsorbed Cu-CHD.

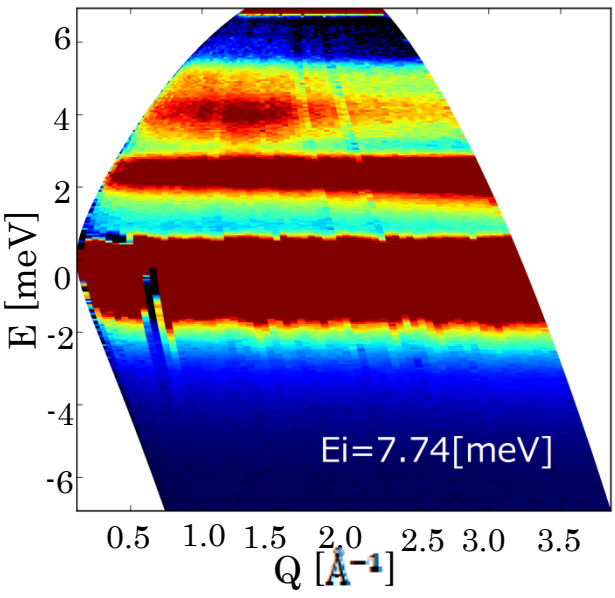

Figure 4: Neutron spectrum of heavily adsorbed Cu-CHD.