Neutron scattering in O_2 adsorbed CPL-1

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In some metal-organic compounds O_2 molecules are adsorbed in nano-scale microporous structure [1, 2]. Since $S = 1$ spins are localized at O_2 molecules, of which the electronic structure is $^3\Sigma_g^-$, and the array of the O_2 molecules is determined by the geometry of microporous in host compounds, O_2 adsorbed microporous compound is a new research field for designing quantum spin magnets. So far magnetism of artificially controlled oxygen molecules has been restricted to surface adsorption on graphite [3] or Aluminum. The amount of oxygen is very small: monolayer or multilayer at best. In contrast in microporous compound, bulk amount of adsorbed oxygen form bulk $S = 1$ quantum spin magnet. Here we report the observed spin dynamics of O_2 molecules adsorbed in the prototypical microporous compound CPL-1 ($C_{16}H_{12}Cu_2N_6O_{10}$) by thermal neutron inelastic scattering technique.

The crystal structure of O_2 adsorbed CPL-1 is determined by x-ray powder diffraction [2]. A saturated amount of adsorption of O_2 molecules is two moles per one mole of CPL1. Since O_2 molecules forms ladder structure, the spin-gap is expected in the O_2 based magnet. Indeed the magnetic susceptibility [2] and magnetization measurements [4] suggests the spin gap of $60 \sim 88$ K ($5.2 \sim 7.6$ meV). Hence we utilize the thermal neutron scattering technique to study the spin dynamics.

20 g of the powder sample of CPL-1 (protonated sample) was prepared by Takamizawa *et al.* The sample is put in Al can (ϕ 20 mm $\times$ 80 mm) with specially designed sample probe for O_2 adsorption experiment. The spacer of 10 mm height is put in the bottom of Al sample can for the extra O_2 reservoir. The O_2 pressure was maintained at 0.8 MPa down to 90 K for the adsorption [2]. ORANGE type cryostat was used to achieve the temperature of 1.5 K. The neutron inelastic experiment was performed at PONTA spectrometer at 5G beam line in JRR3 in JAEA Tokai. The sollar collimation of open - 80′ - sample -radial collimation - open with $E_F = 14.7$ meV was used. PG filter was put after sample and horizontally focusing analyzer was used to obtain better statistics. We paid special attention to background subtraction. Since we have large background due to protons in the host compound, we performed the exactly same scans for both with and without O_2 molecule. This means that it takes two times as much as usual experiment. Though large background with peak structure is observed in the constant q scan without O_2, the enhanced intensity is clealy observed in O_2 adsorbed sample. Three peaks are observed at 5meV $\leq \hbar\omega \leq$ 16 meV in the subtracted data. Among them the peaks at $\hbar\omega \sim 10.5$ and 14 meV are supposed to be non-magnetic origin because they are temperature independent. In contrast the sharp peak at $\hbar\omega \sim 8$ meV is suppressed by the increasing temperature. In addition, the peak position is q independent in wide q range and the peak intensity is suppressed with the increase of q. These results mean that the 8 meV peak is due to magnetic excitation of isolated spin clusters. Constant energy scan at $\hbar\omega = 8$ meV is shown in Fig. 1. The scan at 6meV is used as background. There seems a maximum around 1.0 meV. In addition peak structure around 3 meV *probably* exists but seems smeared out due to poor statistics.

The most probable model for the observed spin cluster is S = 1 spin dimers due to adsorbed O_2 molecules. From crys-

tal structure consideration, the intradimer distance is 3.206 Å [4] and the inter-dimer distance is 4.688 Å. The empirical relation between the spin exchange constant and inter-molecule distance of oxygen suggests that the latter is reasonably weak and can be neglected. Hence we draw the spin dimers neutron cross section including presumed O_2 form factor (dashed-dotted line in Fig. 1) [5]. In spite of rough calculation, the curve reproduce maximum at $q \sim 1.0$ $Å^{-1}$.

In summary we observed spin dynamics of O_2 molecules adsorbed in microporous compound CPL-1.

References

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[5] Form factor of oxygen is extensively studued in P.W. Stephens, Phys. Rev. B **31**, 4491 (1985). In this memo I simply used exponential decay formula. Further analysis will be done later.

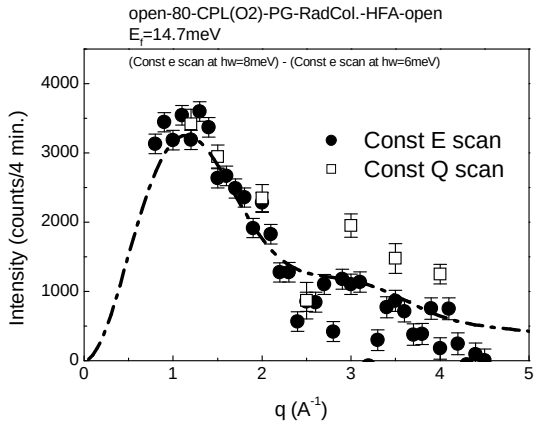

Fig. 1. Constant *E* scan.