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 ($C_{16}H_{12}Cu_{2}N_6O_{10}$) 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 ($\phi 20$ 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 solar 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 clearly 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 O₂ 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 O₂ molecules adsorbed in microporous compound CPL-1.

References

Fig. 1. Constant E scan.