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Light induced excited-states x-ray crystallography of multi-nuclear d^{10} transition-metal complexes

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Multinuclear metal complexes of d^{10}-metals such as Cu(I) and Ag(I) display a wide variety of structure form as well as different emissive behavior. Some of these clusters with halogen and N-donor ligands show strong long-lived luminescence under ultraviolet irradiation. Those strong emissions have been assigned to triplet cluster-centered excited states. If the metal cluster orbitals are involved in photo-excitation, the elections may migrate from non-bonding metal *d*-orbitals to bonding *s*-orbitals. Thus the cluster core will shrink at the excited states. We have tried to observe molecular distortion directly by single crystal diffraction analyses.

X-ray diffraction experiments were performed by using the low temperature vacuum x-ray camera with multiple-exposure IP method[1]. At this time we have tried to measure by a newly developed exposure mode[2] in which photo irradiation and x-ray source were interrupted periodically by mechanical choppers, in order to reduce temperature difference in a crystal between light-on and -off phenomena. A single crystal of a tetranuclear copper cluster $[Cu_4I_4(3\text{-pic})_4]$ was mounted on a carbon fiber and kept 30 K. The crystal was subjected to light irradiation by a He-Cd CW laser (442 nm, 100 mw) introduced through fiber optics into the X-ray camera. X-ray source (22 keV) and laser were interrupted in 50 Hz.

Estimated temperature raise at the light-on period was less than 0.1 K which indicate no temperature factor corrections should be required. Difference Fourier syntheses of $|F_{on}|-|F_{off}|$ were performed to detect small change in molecular geometry between the light -on and -off data sets. The observed electron density maps only small peaks (< 0.5 e/Å^3) near copper and iodine atoms (**Fig. 1b**), in contrast to that of without chopper[3] (**Fig. 1a**). The new exposure method is effective for reducing heating problem at the light-on crystal. Further structure analyses are still in progress.

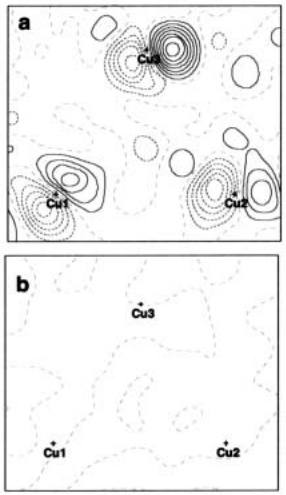

Fig.1 Difference Fourier map of a Cu, plane section in a tetranuclear copper core. a: without chopper[3], b: with chopper (50 Hz). Solid and dashed line indicate positive and negative density drawn at every 0.5 e/Å^3, respectively)

Reference

1) Y. Ozawa *et al.*, *Chem. Lett.*, **32**, 62 (2003).
2) Y. Ozawa *et al.*, *SPring-8 User Exp. Report* 2002B0602.
3) Y. Ozawa *et al.*, *SPring-8 User Exp. Report* 2002B0645 .

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A Study of the Structure of DyB_2C_2 at the Quadrupole Moment Ordered State

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Multi-pole moment ordering, or 'orbital' ordering has been attracted by many researchers in recent years. The nature of multi-pole moment ordering has been open for a long term because of a lack of direct probes. Recently, resonant x-ray scattering method using synchrotron radiation is proposed to be useful for investigating this field. However, the method is not perfectly suitable. As Neumann's principle describes in crystallography, the symmetry of any physical properties must include the symmetry operations of the crystal point group. Once multi-pole moment orders in a crystal, the local symmetry is reflected by the multi-pole. In other words, the crystal sometimes distorts according to the symmetry of multi-pole moment. One serious demerit of the resonant x-rays scattering is that it is usually sensitive to the lattice distortion as long as it uses the dipole ($E1$) transition. Another strong probe using x-rays is non-resonant x-ray diffraction. In this method, we can observe the electron density of the multi-poles as it is, and the lattice distortion as well. We need to measure as many reflections as possible in order to separate two contributions, one from the multi-pole, and the other from the lattice distortion. In DyB_2C_2, a quadrupole moment ordering appears at 25 K, and an antiferro- magnetic one appears at 15 K. We have done an experiment at the beamline BL02B1 firstly to clarify the atomic structure of the ordered state, and secondly to observe *directly* the ordered structure of the anisotropy of the 4*f* valence shell of the Dy ions. A sample in size of 0.4 mm x 0.45 mm x 0.25 mm was mount on a closed-cycle ^{4}He cryostat. The integrated intensities of 943 reflections have been gathered at T=17.5 K (above the Curie temperature).

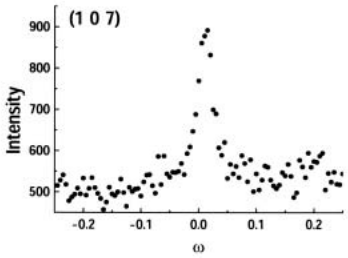

Fig. 1 shows the peak profile of (1 0 7) super-lattice reflection, which is forbidden at room temperature, observed at 17.5 K. Data analysis is in progress.