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Development of X-ray Molecular Orbital Analysis with highly accurate Synchrotron Radiation

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Under top-up operation of PF super accurate structure factor measurement became possible at BL14A, where four-circle diffractometer and APD are installed and programs for the measurement avoiding multiple diffraction are utilized. In order to assure the accuracy of the measurement highly accurate measurement of CeB_6 suppressing the statistical counting errors of all reflections less than 0.1% were successfully performed. XAO analysis revealed electron population on *4f* and *5d* orbitals at room temperature. Highly accurate structure factors are also necessary for X-ray molecular orbital analysis (XMO). Part of the recent results of the XMO analysis of diformohydrazido, $(NHCHO)_2$, is also stated.

1 Introduction

Highly accurate measurement of X-ray diffraction intensities under top-up operation became possible with the four-circle diffractometer installed at BL-14A equipped with an APD detector. BL-14A has also excellent programs made mainly by one of the authors, (Y.T.), which enable to measure effectively intensities avoiding multiple diffraction (MD).[1] Accordingly it is especially effective for the electron density measurement of heavy-atom compounds like rare-earth complexes and super conductors, since the effect of MD easily exceeds 1% of the observed structure factors in these compounds but the contribution of 4f or 5d electrons to structure factors is approximately 1% or less. The APD detector has made it possible to measure linearly up to 10^7 cps, as well as to reduce background to extremely low level. These characteristics made the diffractometer at BL14A one of the most accurate device in the world. In the present article highly accurate measurement of structure factors of all the reflections of CeB_6 with the statistical counting errors less than 0.1% is first reported.[2] Then our recent research on XMO analysis is reported.

X-ray atomic orbital analysis(XAO)[3] was applied to the investigation of the electron density distribution (EDD) of CeB_6. While conventional X-ray crystal structure analysis assumes each atom in the unit cell as the unit of diffraction of X-rays, XAO divides each atom further into sub-shells of *s*-, *p*-, *d*- and *f*-electrons, which share atomic position and atomic displacement parameter (ADP) and treat them independently to each other keeping the electro-neutrality of the unit cell. Atomic orbital and electron population of electrons in each sub-shell are refined with the least-squares method incorporating the constraint of orthonormal condition of orbitals.[4]

Molecular orbitals (MO) are expressed as a linear combination of atomic orbitals. The coefficients are determined by applying the least-squares method incorporating orthonormal relationships between orbitals in X-ray molecular orbital analysis (XMO). However all the coefficients cannot be determined by XMO, since the contribution of small coefficients to electron density is less than the experimental error. Therefore highly accurate structure factors are needed for the XMO analysis. The SR experiment at BL14A is essentially necessary for these investigations. In the present article present status of the XMO study on diformohydrazido (DFH) is briefly stated.

2 Highly accurate measurement with the statistical counting error of all reflections less than 0.1%

2.1 Experimental

In synchrotron-radiation measurements the chance for multiple diffraction (MD) to occur is expected to be rare since the incident beams diverge only a little. In fact FWHM (full width at half maximum) of CeB_6 crystal with the radius of 38mm is 0.017°. However in heavy-atom crystals it easily exceeds 1%. Therefore PF14A equipped with a 4-circle diffractometer with APDdetector which has one-order higher linear response to the incident X-rays than IP was selected since MD effect can be avoided with the ψ-scan, which can be done at PF14A after modifying the machine-controlling program. When we do the super-accurate structure-factor measurement, MD can't be neglected at all.

As the first step to the super accurate measurement, structure factors of all the reflections were measured with their statistical counting error less than 0.1% or more than $2.5x10^5$ counts for each reflection. 5899 reflections with $\sin\theta/\lambda$ up to $1.37Å^{-1}$ were measured in five days at room temperature. When reflections deviated more than 2% from the mean of the symmetry related reflections, they were measured again.

The reference reflections were not fluctuated more than 0.5% after the intensity normalization using the monitor counts measured with an ionic chamber. The stability of the incident beams is highly important for super accurate measurement

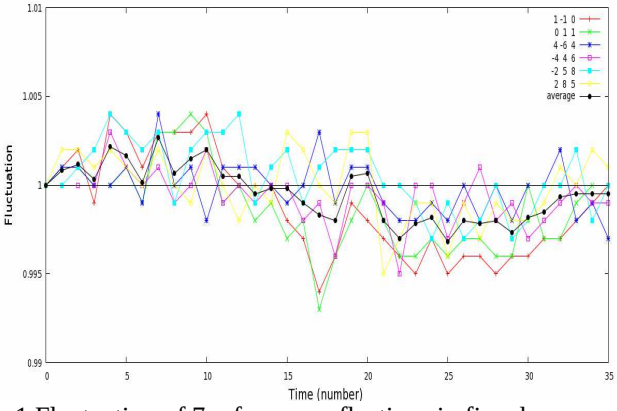

Fig. 1 Fluctuation of 7 reference reflections in five days
Top and bottom lines indicate ±1% fluctuation

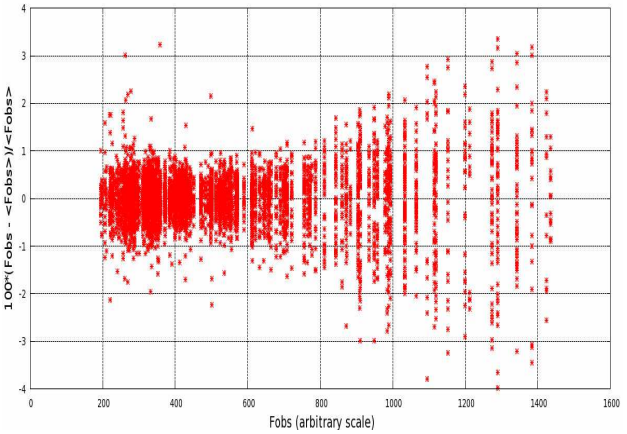

Fig. 2 The ratio of deviation of F_{obs} from the mean value of its equivalent reflections to F_{obs}, $(F_{obs} - \langle F_{obs,equiv}\rangle)/F_{obs}$ (vertical axis) and $F_{obs,}$ (abscissa)

and the present experiments also aims to test how effective the top-up operation is. Reference reflections measured were stable during the five days as illustrated in Fig. 1. Deviation from the mean of the equivalent reflections $(F_{obs} - \langle F_{obs,equiv}\rangle)/F_{obs}$ against $\langle F_{obs,equiv}\rangle$ are plotted in Fig.2. Evidently strong reflections deviate more than weak ones due to the anisotropic extinction effect in contrast to conventional measurements.

2.2 Results and Discussion

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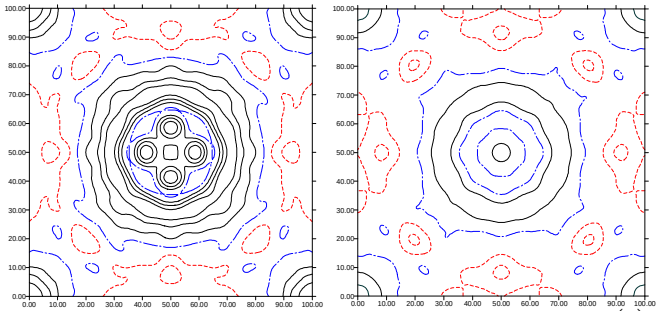
R factor after the conventional spherical-atom refinement assuming Ce^{3+} and B_6^{3-} are 0.536%. After the XAO analysis R factors reduced to 0.424%. Difference densities on (001) plane around Ce before the XAO analysis are illustrated in Figs.3 (a) and (b). Those around the B_4 moiety near the origin of the unit cell after the XAO analysis are shown in Figs. 4(a) and (b). There are peaks along <100> directions around Ce in Fig. 3(a) indicating *4f-Γ8(J=5/2)* electrons and also spherical and positive area surrounding the *4f*-EDD indicating 5d electrons. They are explained well by XAO analysis exhibiting 0.66(2) *4f-Γ8(J=5/2)* electrons and 0.57(2) *5d-Γ8(J=3/2)* electrons. The XAO analysis also revealed that the large negative holes around B in Fig. 3(b) corresponds to vacant B-$2p_x$(=$2p_y$) orbitals after the electron transfer from B to Ce. The top-up operation of PF succeeded to suppress the fluctuation of reference reflection less than 0.5% for five days as shown in Fig. 1. It, together with the excellent soft wares, makes us believe that the most accurate experiments are possible at BL14A. It is amazing that strong low order reflections deviate more than weak high order reflections. It indicates the anisotropic extinction correction is still important in future electron density analysis. It is desirable to have experimental method to correct for extinction.



(a)

(b)

Fig. 3 Difference density around Ce (a) before and (b) after the XAO analysis. Contours at 0.1eÅ^{-3}. Negative, zero and positive contours in red, blue and black lines

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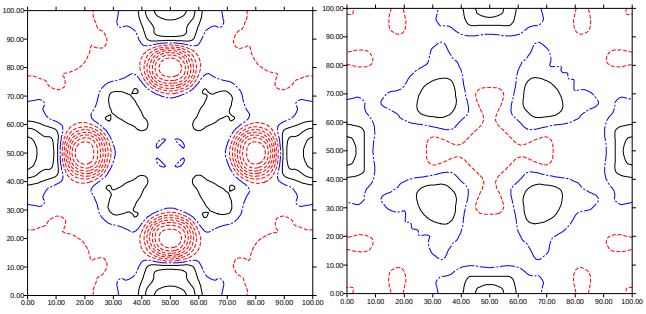
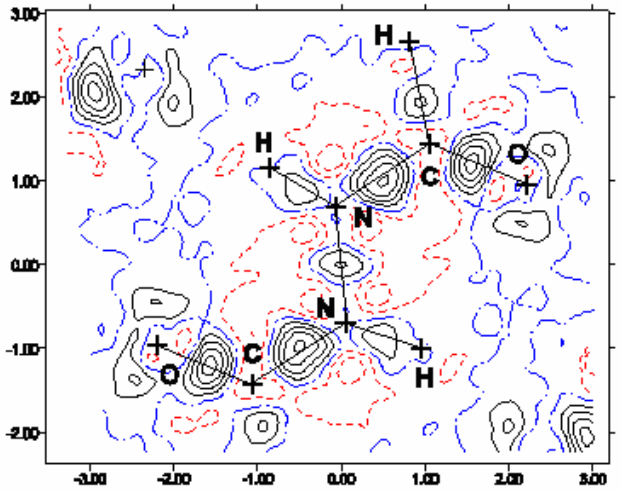


(a) (b)

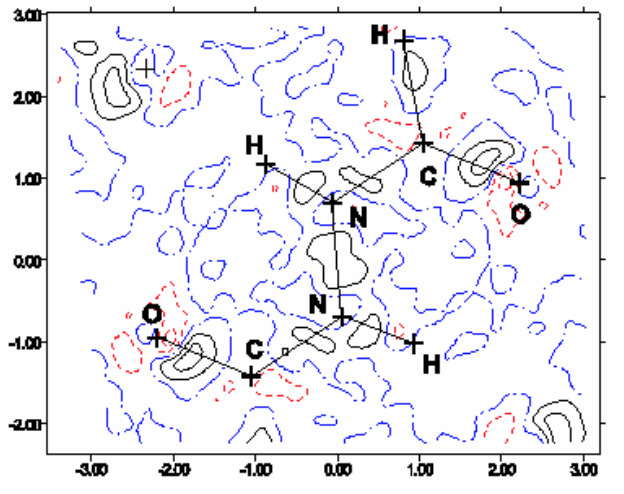
Fig.4 Difference density around B (a) before and (b) after the XAO analysis. Contours are the same as in Fig. 3.

3. XMO analysis of DFH

XMO analysis of DFH has been extensively studied using 4479 reflections measured at 100 K with the laboratory X-rays avoiding MD. Since non-linear least-squares method needs approximate values of MO, starting MO was calculated with HONDO. Since cusp at the nuclear position is not exactly represented by GTF used in MO theory, big negative hole is usually left at the nuclear positions of the difference density map. To avoid cusp problem, well-tempered basis functions by Huzinaga et al. [5] were employed. (10,10,1,1,1,1/5,1,1,1,1) for C,



(a)



(b)

Fig. 5 Difference density on the molecular plane of DFH (a) before and (b) after the XMO analysis. Contours at 0.1eÅ^{-3}. Negative, zero and positive contours in red, blue and black.

N and O atoms, which produce near Hartree-Fock wave functions, were successfully applied to eliminate high and sharp cusp-peaks at the nuclei. For H atoms contracted GTF basis set (2,1,1,1) by Stewart[6] was used. Accordingly MO's for $(NHCHO)_2$ are expressed in terms of 142=(6+5x3)x6+4x4 basis functions and 326 =(24+9x3)x6+5x4 GTF's. C_{2h} symmetry assumed for DFH and frozen core model reduce the number of unknown coefficients to 117. The XMO analysis reduced R-factor to 0.018 from 0.026 of spherical-atom refinement. Difference densities on the molecular plane before and after XMO analysis are illustrated in Figs. 5(a) and (b). Peaks due to the N-N, N-C, C-O bonds and lone pairs of the O atom reduced significantly. Moreover C-H bonds extends after XMO analysis from 0.901(3) Å to 1.072(9) Å, however N-H bond extends slightly from 0.873(3 Å) Å to 0.924(10) Å. The reason for shorter N-H bond seems to be due to the N-H…O intermolecular hydrogen bond, which is neglected in the present XMO analysis. However when the coefficients less than 0.18 were refined as the unknown parameters, least-squares refinement diverged. Since the square of each MO corresponds to the density of electrons of the MO, 0.18^2=0.032 (electrons) seems to be too small when they are distributed around the corresponding atom or bond. Although the value may become a little smaller when correlation between coefficients are carefully treated, it is the accuracy of intensity measurement that decide how small are the coefficients we can refine is. Thus the XMO analysis may presents an opportunity to test the accuracy of the measurement of each beam line.

The measurement at BL14A of diffraction intensities of DFH was tried at room temperature. However we do not succeed the measurement partly because number of significant reflections at room temperature is not enough due to large ADP's to do XMO analysis. Therefore the experiment at 100K is now planned combined with the neutron diffraction measurement of ADP's.

References

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