Observation of All-In Type Tetrahedral Displacement in Non-Magnetic Pyrochlore Niobates

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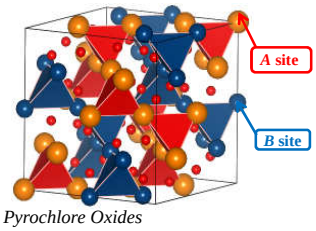
We observed all-in type Nb tetrahedral displacement in the pyrochlore niobates $A_2Nb_2O_7$(A=$Nd_{0.5}Ca_{0.5}$ and $Y_{0.5}Ca_{0.5}$) through neutron pair distribution function (PDF) analysis and the extended x-ray absorption fine structure (EXAFS). This all-in type displacement causes the diffuse scattering in the x-ray diffraction, and has the component of the resonant soft x-ray scattering (Nb L edge). The displacement is driven by the formation of the bond orbital, which has the character of a charge single state.

Introduction

The *f* spin frustration in the pyrochlore lattice provides an interesting phenomena such as the spin ice state. In *d* electron system, it is expected that the orbital will be hybridized with the neighboring site within the transition-metal tetrahedra. Its resultant atomic displacement and multimer formation have been reported in the compounds such as AlV_2O_4. In the pyrochlore niobate $YCaNb_2O_7$, it was reported that the Nb atoms are displaced inward or outward in the Nb tetrahedra by the neutron powder diffraction. We investigate the local order of the Nb atoms in $YCaNb_2O_7$ and $NdCaNb_2O_7$ through the diffraction methods and the two-body correlation, that is, the resonant (soft) x-ray diffraction (PF BL11B and BL4C), the neutron powder pair distribution function (PDF, J-PARC BL21(NOVA)), and the extended x-ray absorption fine structure (EXAFS, SPring-8 BL14B1).

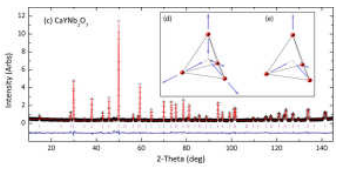


Pyrochlore Oxides $A_2B_2O_7$

$YCaNb_2O_7$ and $NdCaNb_2O_7$
$Nb^{4.5+}$ $(4d)^{0.5}$

Previous reports

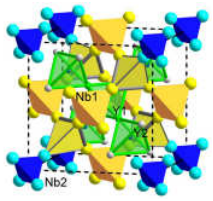
Neutron diffraction and structural analysis in the $YCaNb_2O_7$.



T. M. McQueen and R. J. Cava *et al.*, J. Phys.: Condense. Matter **20**,235210(2008)

In $YCaNb_2O_7$, the Nb atoms are displaced inward or out ward in the direction of the center of the Nb tetrahedra.

Theoretic study in $Y_2Nb_2O_7$.

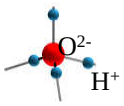


P. Blaha, *et al.*, Phys. Rev. let. **93**,216403(2004).

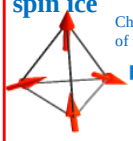
In $Y_2Nb_2O_7$, the Nb tetrahedral is formed charge singlet.

Concept

crystalline ice



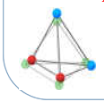
spin ice



Change the degree of freedom

Charge ice

Atomic displacement ice

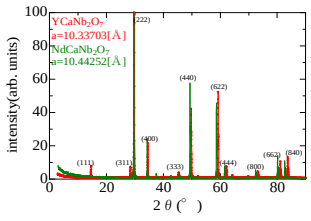


All-in type displacement

Experiments and results

Crystals Growth :
Floating Zone under Ar + H_2
in $NdCaNb_2O_7$ and $YCaNb_2O_7$.

Powder XRD

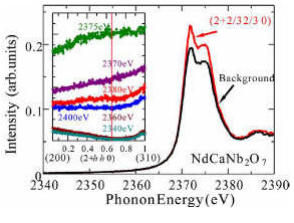


X-ray diffraction

・Diffuse scattering around (6 2/3 2/3)

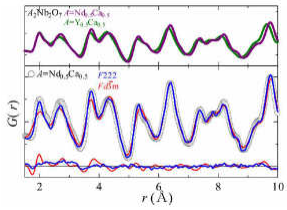
・The *T*-dep. of diffuse scattering is consistent with the resistivity anomaly.
⇒ The periodicity with a short range correlation.

Resonant soft x-ray diffraction (Nb L) @PF 11B

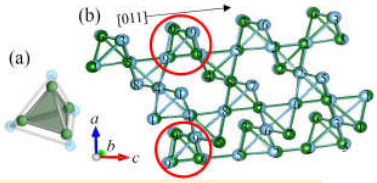


・Diffuse scattering around (2 0 0)
・The difference between (2.66 2.66 0) and background (3 0 0) gives a resonant component of the Nb atom.
⇒ The signal comes from the Nb displacement but also the difference in the valence and the oxygen octahedera between the Nb atoms.

PDF analysis @J-PARC BL 21NOVA



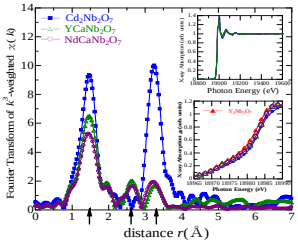
PDF *G*(r) in $NdCaNb_2O_7$ and $YCaNb_2O_7$
In the case of *F*d-3m :Rw=18.6%
In the case of *F*222:Rw=10.94%

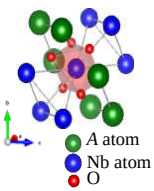


・In the Nb9 atoms, the all-in type tetrahedral displacement, which has the characteristic of charge singlet, occurs.
・ The periodicity (short range order) of the Nb displacement exists along the [011] direction.

Displaced Nb atom
Nb atom in the ideal pyrochlore structure

XAS @SPring-8 BL14B1





・XANE → $Nb^{4.5+}$ in $NdCaNb_2O_7$ and $YCaNb_2O_7$
・EXAFS → The deffernce in Nb-O distance in octahedral coordination of Nb-O.

・ The structure parameter in the EXAFS simulation is consistent with PDF analyasis.

S. Torigoe, *et al.*, Journal of Physics: Conference Series **320** 012078 (2011) .