

Crystal and magnetic structure determination of novel iron-based perovskite oxides containing unusual high valence ions

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Quadruple perovskite oxides containing unusual high valence Fe ions, $ACu_3Fe_4O_{12}$ ($A = Ca, Sr, \text{rare-earth ions}$) demonstrate various structural and electronic properties such as charge disproportionation/transfer, negative thermal expansion, metal-nonmetal transitions, and ferri-/antiferro-magnetism[1]. However, their magnetic structures are not investigated well because their severe synthesis conditions (15 GPa, 1273 K) prevent large volume syntheses for neutron diffraction experiments. $CeCu_3Fe_4O_{12}$ (CeCFO) is a novel quadruple perovskite displaying charge-disproportionation ($4Fe^{5+} + 3Fe^{3+} + Fe^{5+}$) and antiferromagnetic-like transitions below ~ 280 K. We performed neutron powder diffraction (NPD) measurements for CeCFO, obtaining its antiferromagnetic structure of predominant Fe^{3+} ions in charge-disproportionated phase.

The polycrystalline CeCFO sample of ~ 200 mg was prepared using a Kawai-type high-pressure apparatus. NPD data were collected using the WOMBAT diffractometer at ANSTO. Figure 1a shows NPD patterns at temperatures between 6 and 300 K. All Bragg reflection peaks at 300 K were assigned to nuclear diffractions of the cubic CeCFO phase whereas additional reflections such as 111 and 113 observed below 280 K were attributed to magnetic ones. Rietveld refinement using the RIETAN-FP program[2] revealed that CeCFO has a G-type antiferromagnetic structure similar to that of $LaCu_3Fe_4O_{12}$ [3]. Figure 1b shows temperature dependence of the Fe magnetic moment. The magnetic moment value of $\sim 2.5 \mu_B$ at the lowest temperature is smaller than that for a pure Fe^{3+} ions ($5 \mu_B$). This is attributable to the random occupation of Fe^{5+} ions at the quarter of

the Fe sites in the charge-disproportionated CeCFO phase. These results display a new magnetic state in $ACu_3Fe_4O_{12}$ perovskite oxides.

References

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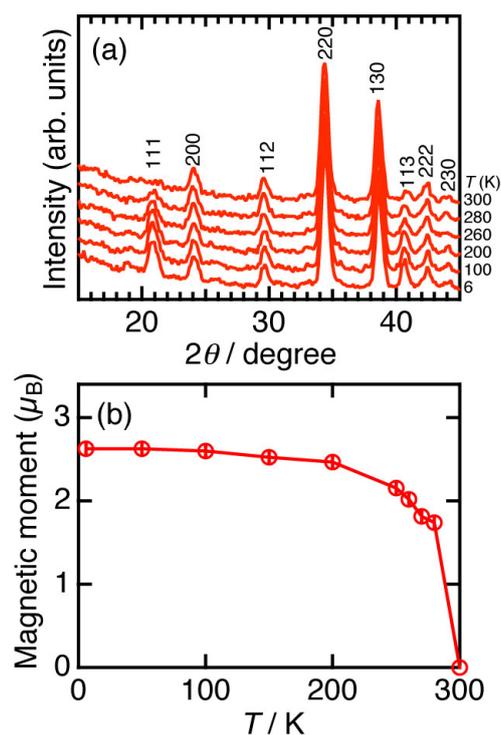


Fig. 1. Figure 1. (a) NPD patterns of CeCFO. (b) Temperature dependence of refined magnetic moment at Fe sites.