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Lattice-form-dependent orbital shape and charge disproportionation in charge- and orbital-ordered manganites

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Introduction

Electron self-organization is one of the most fascinating phenomenon in the area of material science. Especially, charge and orbital ordering in perovskite-related manganites has been extensively studied and some important questions about charge disproportionation (CD) between Mn^{3+} and Mn^{4+} sites and orbital shape (OS) in Mn^{3+} site are raised. Many diffraction and theoretical studies have reported the checkerboard-type charge order of Mn^{3+} and Mn^{4+} ion with 100% CD and stripe-type orbital order. However, in several recent studies, the model of less distinct CD has also been proposed. Another issue is which OS of the $(3y^2\text{-}r^2)/(3x^2\text{-}r^2)$- or $(y^2\text{-}z^2)/(x^2\text{-}z^2)$-type is realized at Mn^{3+} site in the orbital ordered phase. These problems are still debated extensively and need to be clarified from experimentally.

Experimental results and Analysis

We chose $Pr_{0.5}Ca_{0.5}MnO_3$ (PCMO), $Eu_{0.5}Ca_{1.5}MnO_4$ (ECMO), and $Pr(Sr_{0.1}Ca_{0.9})_2Mn_2O_7$ (PSCMO) with infinite-, single-, double-layered MnO_2 network, respectively, as target materials. The charge and orbital-ordering temperature (CO-OO) is at 230 K and 325 K in PCMO, and ECMO, respectively. In contrast, the successive CO-OO transitions are observed at 370 K (CO1) and 315 K (CO2) in PSCMO. It is noted that the 90 degrees rotation of orbital stripe-direction is observed at the phase transition from CO1 to CO2 in PSCMO [1]. The experiments were performed on a Rigaku DSC imaging plate system at the beamline BL1A. The energy of incident xrays was tuned at 18 keV. The twin-free single crystals of ECMO and PSCMO were grown by the floating zone method and were crushed to obtain small grains with a diameter of about 30 micro-meter.

A typical picture of imaging plate in CO-OO of ECMO is shown in inset of Fig. 1 (a). The white arrows indicate superlattice spots due to Jahn-Teller distortion. From these data, we can perform the crystal structural analysis. In Figs. 1 (a)-(c), observed structure factor (F_{obs}) is plotted against the calculated one (F_{cal}) for ECMO at 295 K (CO-OO) and PSCMO at 330 K (CO1) and 295 K (CO2), respectively. From these structural data, we can extract the informations of CD and OS. The CD can be estimated by using the bond valence sum calculation. On the other hand, the OS is related with the Jahn-Teller modes. From the analysis mentioned above, we can extract the full picture of CD and OS as depicted in Figs. 1 (d)-(g).

For the data of PCMO, we used crystal structure published in ref. [2]. In PCMO, the 22% CD and $(3y^2\text{-}r^2)/(3x^2\text{-}r^2)$-type OS of Mn^{3+} site are obtained. In contrast, the negligible 8% CD and $(y^2\text{-}z^2)/(x^2\text{-}z^2)$-type OS is observed for the single-layered ECMO. In the double layered PSCMO with an intermediate structure between PCMO and ECMO, 39% CD and the OS of intermediate type between $(3y^2\text{-}r^2)/(3x^2\text{-}r^2)$ and $(y^2\text{-}z^2)/(x^2\text{-}z^2)$ in CO1 phase. In CO2 phase, the OS turns into $(3y^2\text{-}r^2)/(3x^2\text{-}r^2)$-type without changing the CD. These results indicate that the OS and CD are sensitive to the dimension of MnO_2 network. Detailed informations are reported in ref. [3].

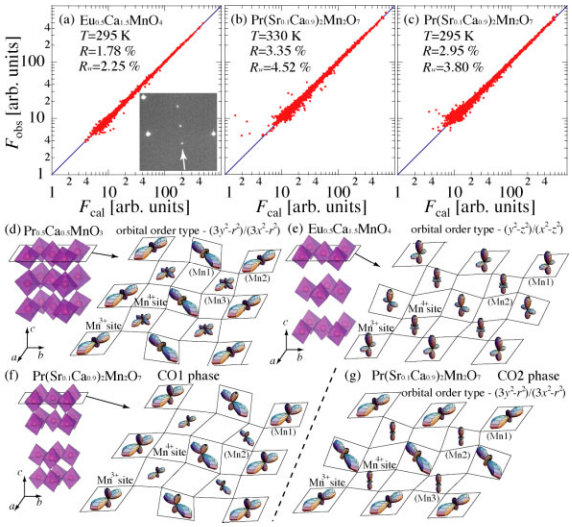

Fig. 1: The comparisons between F_{obs} and F_{cal} and the schematic views of charge and orbital order of (d) PCMO, (a,e) ECMO, (b,f) CO1 of PSCMO, and (c,g) CO2 of PSCMO, respectively.

References

[1] Y. Tokunaga et al., Nature Matter. **5**, 937 (2006).
[2] R. J. Goff et al., Phys. Rev. B **70**, 140404(R) (2004).
[3] D. Okuyama et al., Phys. Rev. B **80**, 064402 (2009).

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