

The electronic structure of mixed valence $\text{Na}_x\text{Ca}_{1-x}\text{Cr}_2\text{O}_4$ by X-ray absorption spectroscopy

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One of the most important concepts in a condensed matter physics is the mixed valence phenomenon (also denoted by the valence fluctuation or intermediate valence phenomenon) in a solid, which are closely related to the exotic physical properties in strongly correlated electron system. In this study, we investigated a mixed valence phenomenon in $\text{Na}_x\text{Ca}_{1-x}\text{Cr}_2\text{O}_4$ due to a Na doping [1]. The most characteristic of this material is that NaCr_2O_4 end member exhibits unconventional colossal magneto-resistance (CMR) effect, which are in sharp contrast to conventional CMR in the manganese oxides [2]. Such an unconventional CMR is expected to be caused by interplay of mixed valence, one-dimensional electronic correlations and geometrical frustrations. However, no experimental evidence has been provided so far. Here, we have succeeded in observing “self-doped states” with oxygen hole due to hole doping and its unusual mixed valence state.

The success was achieved by an X-ray absorption spectroscopy technique using a highly-energy resolution soft x-ray beam at HiSOR, which enables us to measure the detailed Na doping dependence of X-ray absorption spectra and to closely compare the experimental results with the theoretical calculations.

According to the conventional mixed valence picture, the ground state of NaCr_2O_4 should be described by the mixture of Cr^{3+} ($3d^3$) and Cr^{4+} ($3d^2$). However, throughout this study we clarified that Cr^{4+} site (hole doped site) will be described by $3d^3\bar{L}$ (self-doped) states rather than $3d^2$, suggesting that a generated hole by Na substitution will be primarily trapped in the oxygen sites rather than in Cr 3d states. Ultimately, an unusual mixed valence states that positive and negative charge transfer states coexist has been realized.

[1] M. Taguchi et al., Phys. Rev. B **96**, 245133 (2017).

[2] H. Sakurai et al., Angew. Chem. Int. Ed. Engl. **51**, 6653 (2012).