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# Crystallographic and Local Electronic Structures of Magnetic Nano-Checkerboards in Mn-Doped Cobalt Ferrite

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**Abstract** –Magnetically ordered nano-checkerboard structure has been successfully synthesized in Mn-doped cobalt ferrite by solid-state self-assembly. The nano-checkerboards, consisted of nanorods ~300 nm in length and a few nanometer in size, were formed through the chemical phase separation mediated by cooperative Jahn-Teller distortions associated with the Mn ions. Analyses of crystallographic and local electronic fine structures of the magnetic nano-checkerboards have been carried out by (scanning) transmission electron microscopy ((S)TEM) and electron energy-loss spectroscopy (EELS). Jahn-Teller distortions associated with the Mn ions are found to play a very critical role for both the crystallographic and electronic fine structures.

In this study, we focused on a new magnetic spinel system Mn-doped $CoFe_2O_4$ (with nominal composition $Co_{0.6}Fe_{0.9}Mn_{1.5}O_4$), which can be viewed roughly as a proper mixture of $CoFe_2O_4$ and $CoMn_2O_4$ spinels, respectively. At room temperature, $CoFe_2O_4$ is ferromagnetic and adopts a cubic phase ($a \approx 8.3$ Å, $T_c$ ~800 K), whereas $CoMn_2O_4$ is a tetragonal paramagnetic phase ($a \approx 8.1$ Å, $c \approx 9.3$ Å, $T_c$ ~100 K). Magnetically ordered nano-checkerboard structure has been successfully synthesized in the Mn-doped cobalt ferrite by solid-state self-assembly. Crystallographic microstructures of the ordered magnetic nano-checkerboards are nicely revealed by the analyses of high resolution TEM images and the corresponding electron diffraction patterns. We find that the Mn-doped cobalt ferrite is phase-separated into two distinct nanorod-type domains, the magnetic Fe-rich domains and the non-magnetic Mn-rich domains, which are alternately stacked in a checkerboard pattern [1]. The typical dimensions of a nanorod-type domain, which could be controlled by annealing temperatures and time, were ~300 nm in length and a few nm in cross-section. The Mn-rich domains are found to be tetragonal and the Fe-rich domains cubic in structure, leading to a slight zig-zag variation of the domain boundaries.

Electronic fine structures of Oxygen K-edge, $L_{2,3}$-edges of Co, Fe, and Mn were also obtained by EELS/STEM. Distinct near edge fine structures of the oxygen K-edge were found between the magnetic and the paramagnetic domains, as shown in Fig. 1, whereas only slight differences in fine structures were observed for the $L_{2,3}$-edge of Co, Fe, and Mn ions. Theoretical calculations reveal that the Jahn-Teller distortions due to the Mn ions play the most critical roles for the oxygen K-edge fine structures.

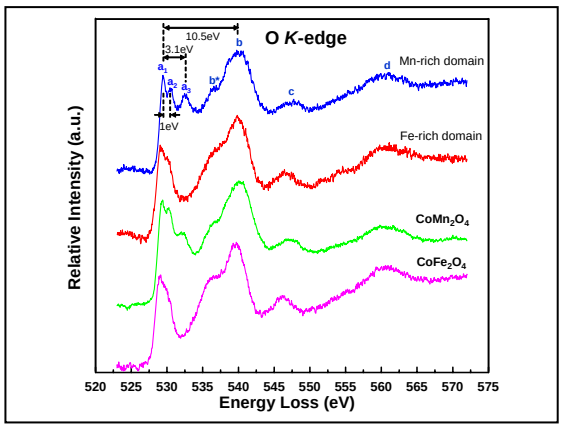


**Figure 1:** Oxygen K-edge fine structures for the Mn-rich and Fe- rich domains. For comparison, oxygen K-edge spectra for the pure compounds, $CoFe_2O_4$ and $CoMn_2O_4$ are also shown.

## References

[1] C. L. Zhang, C. M. Tseng, S. Yeo, Y. J. Choi, C. H. Chen, and S-W. Cheong, Appl. Phys. Lett. 91 (2007) 233110.