Effect of Mn Impurities on the Superconductivity in $Na_xCoO_2{\cdot}yH_2O$

Yu-Jen Chen (陳裕仁)[1,4], Chia-Jyi Liu (劉嘉吉)[2], Jung-Sheng Wang (王忠勝)[2], Jiunn-Yuan Lin (林俊源)[1], Chia-Pin Sun (孫家彬)[3], Shih-Wen Huang (黃詩雯)[4], Jenn-Min Lee (李振民)[5], Jin-Ming Chen (陳錦明)[5], Jyh-Fu Lee (李志甫)[5], Din-Goa Liu (劉定國)[5], and Hung-Duen Yang (楊弘敦)[3]

[1]Institute of Physics, National Chiao Tung University, Hsinchu, Taiwan
[2]Department of Physics, National Changhua University of Education, Changhua, Taiwan
[3]Department of Physics, National Sun Yat-Sen University, Kaohsiung, Taiwan
[4]Department of Electrophysics, National Chiao Tung University, Hsinchu, Taiwan
[5]National Synchrotron Radiation Research Center, Hsinchu, Taiwan

$Na_xCoO_2{\cdot}yH_2O$ has stimulated researchers due to its exotic superconductivity, the electronic frustration on the triangular Co lattice, and the characters of the strongly correlated electron systems. There is no doubt that $Na_xCoO_2{\cdot}yH_2O$ has been recognized as one of the most interesting superconductors since the high-T_c superconductor era. The superconducting order parameter of $Na_xCoO_2{\cdot}yH_2O$ has remained elusive. To gain more insights into the nature of the superconductivity in $Na_xCoO_2{\cdot}yH_2O$, the impurity scattering effects could provide one useful venue [1].

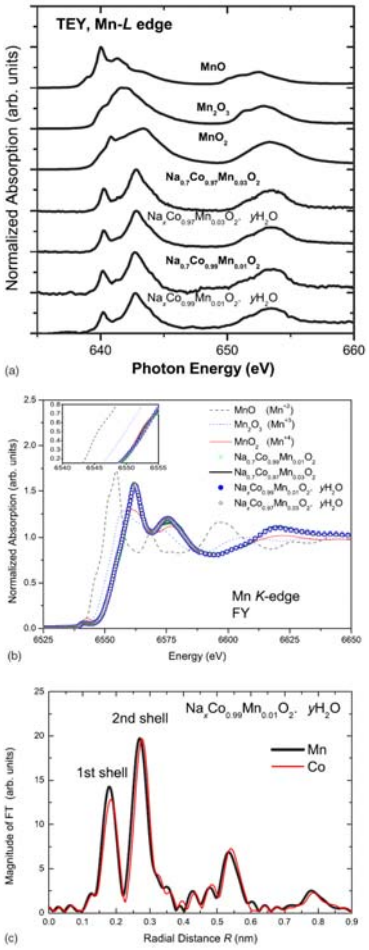

FIG. 1. (Color online)Mn (a)L-edge and (b) K-edge XANES of $Na_xCo_{1-z}Mn_zO_2{\cdot}yH2O$ and the standard samples; (c) FT magnitudes with phase correction of the k3-weighted EXAFS data at Mn K edge. Inset of (b) shows the enlarged edge region. All the Mn-doped samples have similar spectra in (a) and (b).

For the first time, x-ray absorption spectroscopy (XAS) shows that the doped Mn ions indeed occupy the Co sites. However, the unitary impurity scattering by Mn does not lead to strong T_c suppression. To reconcile the weak T_c suppression by impurities with other experiments, coexistence of *s*-wave and the unconventional pairings is proposed.

To characterize the samples, x-ray absorption spectroscopy (XAS) (including XANES and EXAFS) was carried out for Mn K- and L-edges as well as Co K-edge. For further characterizations of the doped Mn ions, Fig. 1(a) shows Mn *L*-edge XANES spectra of $Na_xCo_{1-z}Mn_zO_2{\cdot}yH_2O$ together with those of MnO_2, Mn_2O_3 and MnO. It is clear that all the Mn-doped samples have similar spectra distinct from those of the starting material Mn_2O_3 and two other common manganese oxides. Moreover, judged by the edge energy around 6550 eV in Fig. 1(b), Mn ions in all the doped samples, hydrated or not, have a valance close to +4. The first spectroscopic evidence of Mn^{4+} is provided here for Mn ions on the triangular lattice. Fig. 1(c) shows the Fourier transform (FT) amplitudes and profiles of EXAFS data at Co and Mn *K*-edges for $Na_xCo_{0.99}Mn_{0.01}O_2{\cdot}yH_2O$. FT amplitudes and profiles of EXAFS for both Co and Mn show identical features, indicating that Mn ions are in the same environment as Co ions and no other local structure of any second phase is present. FT peak position for the first shell of Co is 0.187 nm (Fig. 1(c)), identical to the Co-O bond length of $Na_xCoO_2{\cdot}yH_2O$ from the neutron diffraction. Also shown in Fig. 2(c), the Mn-O bond length is found to be 0.181 nm. This implies that the Mn^{4+} ionic radius (r_I) of 0.052 nm might be smaller than that of the Co ions which valance is between +3.3 and +3.4 (r_I=0.065 nm for Co^{3+}; r_I for Co^{4+} not available).

[1] Y.-J. Chen, C.-J. Liu, J.-S. Wang, J.-Y. Lin, C. P. Sun, S. W. Huang, J. M. Lee, J. M. Chen, J. F. Lee, D. G. Liu, and H. D. Yang, Phys. Rev. B **76**, 092501 (2007).