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Induced magnetic moment by Mn doping in $Na_xCo_{1-z}Mn_zO_2 \cdot yH_2O$

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Abstract

Impurity effects on $Na_xCoO_2 \cdot yH_2O$ are studied by Mn doping. Spectroscopic evidence reveals that the doped Mn ions occupy the Co sites and the valence is +4. The magnetic local moment induced by Mn doping was observed and $\mu_{eff} = 3.20\,\mu_B$. The induced local moment could lead to magnetic pair-breaking and is likely to be responsible for the T_c suppression by Mn impurities in $Na_xCo_{1-z}Mn_zO_2 \cdot yH_2O$.
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1. Introduction

Na_xCoO_2 has been intensively studied due to its large thermal electric power at high temperatures. Whether the physical properties of Na_xCoO_2 at low temperatures can be described as those of a Fermi liquid near the quantum critical point remains controversial [1]. This system, with varying Na content x, has a rich phase diagram, and is generally regarded as a strongly correlated electron system (SCES). Na_xCoO_2 also provides a new venue to study the spin and electronic frustrations on the triangular lattice. The interest has been further heated since the discovery of superconductivity in $Na_xCoO_2 \cdot yH_2O$ [2].

Impurity effects on T_c are known to provide indispensable information in many novel superconductors and SCES. For $Na_xCoO_2 \cdot yH_2O$, the impurities doped into the CoO_2 planes could have an influence on superconductivity, the novel quantum phase transition [1], and other properties. Knowledge of the mechanisms behind these effects would help to shed light on the mystery of $Na_xCoO_2 \cdot yH_2O$ and the related compounds. However, there are presently only limited studies of impurity effects on $Na_xCoO_2 \cdot yH_2O$ [3,4]. In particular, the Mn doping effects are studied to explore the symmetry of the superconducting order parameter in $Na_xCoO_2 \cdot yH_2O$ [4]. It is therefore desirable to characterize the doped Mn ions in detail. In this paper, the magnetic moment induced by Mn doping is investigated.

2. Experiments

Polycrystalline parent compounds of sodium cobalt oxides $\gamma - Na_{0.7}Co_{1-z}Mn_zO_2$ ($z = 0-0.03$) were prepared using a rapid heat-up procedure [4]. The resulting powders were immersed in the 3 M Br_2/CH_3CN solution for 5 days, followed by filtering and thorough washing with CH_3CN and DI water. X-ray diffraction patterns indicated that all the parent and hydrated samples were of single phase. To further 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. The magnetization $M(T)$ was measured by MPMS of quantum design.

3. Results and discussions

T_c's of $Na_xCoO_2 \cdot yH_2O$ and $Na_xCo_{0.995}Mn_{0.005}O_2 \cdot yH_2O$ are found to be 4.47 and 4.37 K by $M(T)$,

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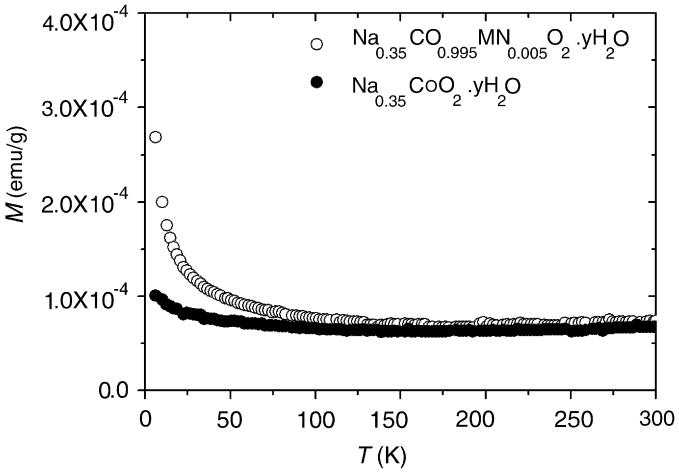

Fig. 1. $M(T)$ of $Na_xCo_{0.995}Mn_{0.005}O_2 \cdot yH_2O$ and $Na_xCoO_2 \cdot yH_2O$. The applied field $H = 20$ Oe.

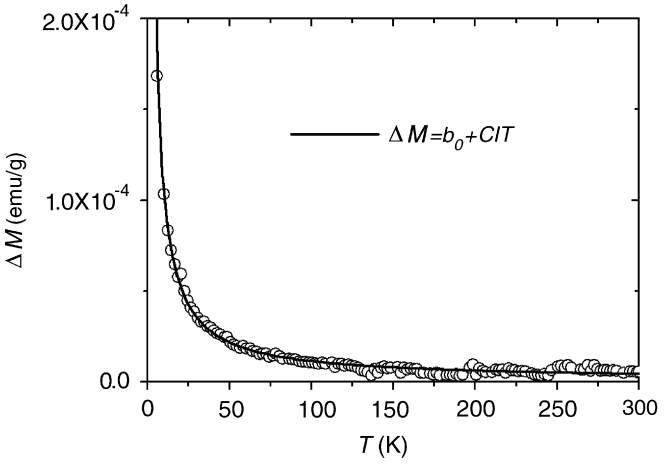

Fig. 2. $\Delta M \equiv M(T, z = 0.005) - M(T, z = 0)$. ΔM is to the induced local moment by Mn doping, and can be nicely fit by the Curie law.

respectively. Overall, T_c suppression rate $dT_c/dz = 0.64\,K/1\%$ is determined from $Na_xCo_{1-z}Mn_zO_2 \cdot yH_2O$ for $z = 0-0.02$ [4]. Mn K-edge XAS indicates that Mn ions in all the doped samples, hydrated or not, have a valance close to +4. EXAFS data at Co and Mn K-edges verify that the doped Mn ions are located on the Co sites.

$M(T)$ of $Na_xCoO_2 \cdot yH_2O$ and $Na_xCo_{0.995}Mn_{0.005}O_2 \cdot yH_2O$ is shown in Fig. 1 for $T > T_c$ to avoid the sudden drop at T_c due to the Meissner effect. At low temperatures, $M(T)$ of the Mn-doped sample is significantly larger than that of $Na_xCoO_2 \cdot yH_2O$. It is plausible that the increase in M is due to the doped Mn ions. To estimate the magnetic moment of the Mn ions, $\Delta M \equiv M(T, z = 0.005) - M(T, z = 0)$ was depicted in Fig. 2. The results can be nicely fit by the Curie law $\Delta M = b_0 + C/T$ as demonstrated in Fig. 2. The fit would lead to $b_0 = (1.3 \pm 0.2) \times 10^{-6}$ emu/g and $C = (1.03 \pm 0.01) \times 10^{-3}$ emu K/g. The small value of b_0 indicated that Mn doping at this level only slightly increase the background contribution to $M(T)$, as seen at high temperatures in Fig. 1. The increase in $M(T)$ at low temperatures mainly comes from the paramagnetic contribution of Mn ions. The effective magnet moment $\mu_{eff} = 3.20\,\mu_B$ is thus estimated from the value of C.

Spectroscopy evidence verifies that the doped Mn impurities are with a valance close to +4. Since Mn^{+4} has a d electron configuration of t_{2g}^3, the calculated $\mu_{calc} = 3.87\,\mu_B$ assuming the complete quenching of the orbital angular momentum L. It is noted that the estimate of μ_{eff} in the previous paragraph neglects the magnetic moment of the substituted Co ions and consequently underestimate μ_{eff} of the doped Mn ions. More importantly, the smaller μ_{eff} than the calculated one is likely due to the incomplete L quenching. In the absence of L quenching, $\mu_{calc} = 0.77\,\mu_B$ is expected.

Mn ions are doped into a background of Co^{3+} ($S = 1/2$)/Co^{4+} ($S = 0$) which is only weakly paramagnetic. In the case of cuprates, when the presumed nonmagnetic Zn^{2+} impurity is doped into CuO_2 planes, a local moment of $S = \frac{1}{2}$ around the Zn impurity is induced to compensate the substituted Cu $3d^{10}$ ion [5]. It is possible that the effective spin induced by Mn^{4+} in CoO_2 planes is close to $S = 1$, which leads to $\mu_{calc} = 2.83\,\mu_B$ with L quenching.

4. Conclusion

The local moment induced by Mn doping into CoO_2 planes was observed. The magnitude of μ_{eff} can be semi-quantitatively attributed to the paramagnetic contribution of the doped Mn^{4+} ions. This magnetic local moment can lead to the pair-breaking, and is likely to be responsible for the observed T_c suppression rate $dT_c/dz = 0.64\,K/1\%$ in $Na_xCo_{1-z}Mn_zO_2 \cdot yH_2O$. On the other hand, the potential pair-breaking with a sign-changing order parameter like d-or f-wave would have led to a much higher T_c suppression rate [6]. This absence of the strong impurity effects on T_c is thus difficult to reconcile with the simple picture of a sign-changing order parameter in $Na_xCoO_2 \cdot yH_2O$ [7].

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