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Specific heat of Mn-doped $Na_xCoO_2 \cdot yH_2O$

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Abstract

$C(T)$ of $Na_xCo_{0.99}Mn_{0.01}O_2 \cdot yH_2O$ is studied to reveal more details on the nature of the doped Mn ions and the T_c suppression. The extra specific heat contribution in $Na_xCo_{0.99}Mn_{0.01}O_2 \cdot yH_2O$ manifests the induced local magnetic moment due to Mn doping. The absence of the superconducting transition peak in $C(T)$ of $Na_xCo_{0.99}Mn_{0.01}O_2 \cdot yH_2O$ suggests a reduced superconducting volume fraction.

Keywords: Cobaltate; Specific heat; Magnetic moment; Impurity effect; Superconducting order parameter

The superconducting order parameter of $Na_xCoO_2 \cdot yH_2O$ has remained elusive. On the one hand, almost all the relevant experiments agree on the existence of the nodal lines in the order parameter [1] favoring p- or f-wave pairing, if the crystal and time reversal symmetries are further considered. On the other hand, the decrease in the Knight shift below T_c [2–4] is a strong advocate of s- or d-wave pairing. To gain more insights into the nature of the superconductivity in $Na_xCoO_2 \cdot yH_2O$, the impurity effects on T_c of $Na_xCoO_2 \cdot yH_2O$ has been studied [5,6]. Based on the experimental results of Mn-doped $Na_xCoO_2 \cdot yH_2O$, Ref. [6] suggests an intriguing model of coexistence of s-wave and unconventional pairing in $Na_xCoO_2 \cdot yH_2O$. Indeed, two distinct phase transition in $Na_xCo_{1-z}Mn_zO_2 \cdot yH_2O$ for $z = 0.005$ has been directly observed by the specific heat $C(T)$ experiments. In this paper, $C(T)$ of the $z = 0.01$ is studied to reveal more details on the nature of the doped Mn ions and the T_c suppression.

Polycrystalline parent compounds of sodium cobalt oxides γ-$Na_{0.7}Co_{1-z}Mn_zO_2$ ($z = 0$–0.03) were prepared using a rapid heat-up procedure [4]. The resulting powders were immersed in the 3M 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 (not shown) and hydrated samples were of single phase as in Fig. 1. $M(T)$ was measured in MPMS of Quantum Design. $C(T)$ was measured by the heat pulse relaxation method.

Fig. 2 shows $M(T)$ below 6 K for $Na_xCo_{1-z}Mn_zO_2 \cdot yH_2O$. The inset demonstrates the Meissner effect of the undoped $Na_xCoO_2 \cdot yH_2O$, as pronounced as those of the best polycrystalline samples in the literature. T_c is defined as the onset of the Meissner effect. T_c suppression rate is determined to be $dT_c/dz = 0.64$ K/1% [6]. This suppression rate is one order of magnitude slower than that of the cuprate superconductors with the line nodal order parameter.

$C(T)$ of $Na_xCoO_2 \cdot yH_2O$ and $Na_xCo_{0.99}Mn_{0.01}O_2 \cdot yH_2O$ is shown in Fig. 3. At temperatures above 8 K, both sample have almost identical $C(T)$. This indicates that Mn doping changes neither of the lattice contribution and the normal electronic linear term in $C(T)$. However, $C(T)$ of $Na_xCo_{0.995}Mn_{0.01}O_2 \cdot yH_2O$ is significantly larger than that of $Na_xCoO_2 \cdot yH_2O$ below 8 K, especially at very low temperatures. This extra contribution to $C(T)$ is magnetic, and comes from the local magnetic moment of the doped Mn

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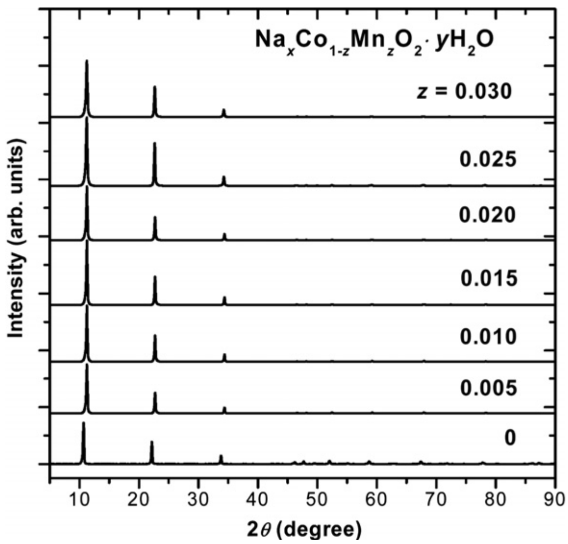

Fig. 1. X-ray diffraction patterns of $Na_xCo_{1-z}Mn_zO_2 \cdot yH_2O$ using Fe $K\alpha$ radiation.

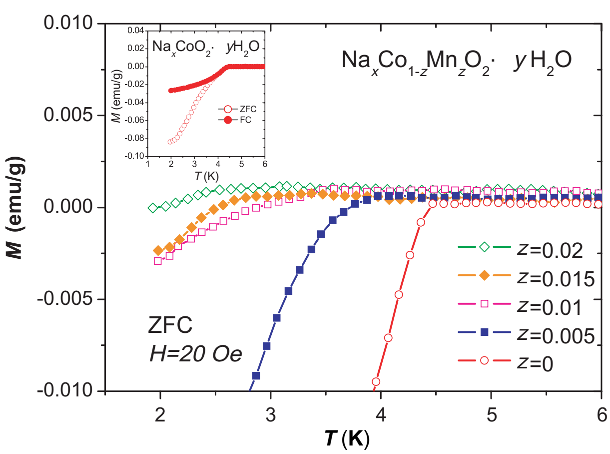

Fig. 2. M vs. T of $Na_xCo_{1-z}Mn_zO_2 \cdot yH_2O$ samples. Inset shows ZFC and FC data of undoped $Na_xCoO_2 \cdot yH_2O$.

ions. This assignment is in qualitative agreement with $M(T)$ of $Na_xCo_{0.99}Mn_{0.01}O_2 \cdot yH_2O$ which shows a paramagnetic contribution from Mn^{4+} ions [6]. Mn K-edge XAS also indicates that Mn ions in the doped samples have a valance close to +4 [6]. A quantitative analysis of the magnetic contribution to $C(T)$ of $Na_xCo_{0.99}Mn_{0.01}O_2 \cdot yH_2O$ is difficult due to, for example, the unknown crystal field of Mn^{4+} ions in the triangular CoO_2 planes. A Schottky anomaly was tried to fit the magnetic contribution to $C(T)$ at low T, but the fitting results were far from satisfactory.

Partly due to the large magnetic background, the superconducting phase transition peak was not observed in $C(T)$ of $Na_xCo_{0.99}Mn_{0.01}O_2 \cdot yH_2O$ as in that of $Na_xCoO_2 \cdot yH_2O$ (Fig. 3). Another reason could be the reduced superconducting volume in the Mn-doped sample.

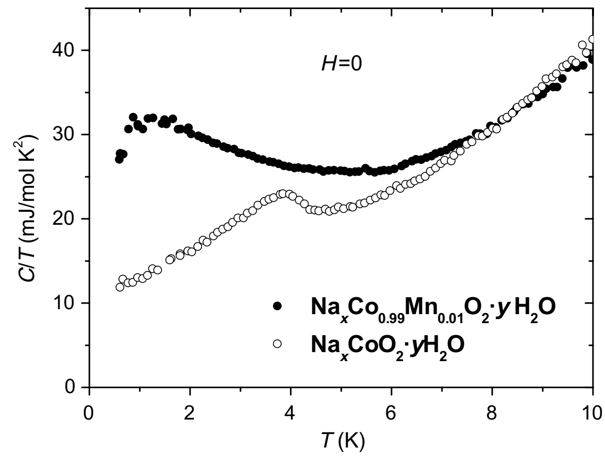

Fig. 3. $C(T)/T$ of (○) $Na_xCoO_2 \cdot yH_2O$ and (●) $Na_xCo_{0.99}Mn_{0.01}O_2 \cdot yH_2O$.

As seen in Fig. 2, though with $T_c = 3.97$ K, the Meissner diamagnetic signal is much smaller than that of $Na_xCoO_2 \cdot yH_2O$. Therefore, the results of $C(T)$ and $M(T)$ are consistent with each other. The reduced superconducting signal could be partly due to the suppression of superconductivity in part of the volume with the nodal order parameter. Moreover, impurities may perturb and remove the energy degeneracy of the two order parameters, and the system with increasing z becomes favoring the one with nodal lines [6].

In conclusion, the extra specific heat contribution in $Na_xCo_{0.99}Mn_{0.01}O_2 \cdot yH_2O$ manifests the induced local magnetic moment due to Mn doping. The absence of the superconducting transition peak in $C(T)$ of $Na_xCo_{0.99}Mn_{0.01}O_2 \cdot yH_2O$ is probably due to the large magnetic background, and could also suggest a reduced superconducting volume fraction.

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