Magnetic Properties of Al-Doped Na$_{0.7}$Co$_{1-x}$Al$_x$O$_2$

Yong Zhang, Zhi-Huan Wu, Cui-Hua Cheng, Yong Zhao

Abstract—Single phase polycrystalline samples Na$_{0.7}$Co$_{1-x}$Al$_x$O$_2$ ($x = 0$, 0.05, 0.10, 0.15, 0.20, 0.25, 0.30) were prepared by solid state reaction. The magnetic properties from 5 K to 300 K have been studied by dc and ac magnetic susceptibility measurements. Samples with lower doping quantity ($x = 0$, 0.05, 0.10) showed paramagnetic behaviors, but those with higher doping quantity ($x = 0.20$, 0.25, 0.30) showed spin-glass behaviors with a freezing temperature ($T_f$) of about 13 K.

Index Terms—ac susceptibility, Al-doped Na$_{0.7}$CoO$_2$, field-cooled magnetization, spin-glass state, zero-field-cooled magnetization.

1. Introduction

The recent discovery of superconducting system$^{[1][2]}$ in hexagonal cobalt oxyhydrates Na$_3$Co$_2$H$_2$O (y=0.3 and y=1.3) with $T_c = 4$ K to 5 K has attracted much attention because it is unique with water molecule intercalated into the parent structure of Na$_3$CoO$_2$ which is crucial for the occurrence of superconductivity. In order to obtain deeper insight into physical mechanism, investigations on the magnetic properties of this new superconducting system are highly desirable. Among many efforts towards this goal, much attention has been paid to the effects of the element doping on superconducting transition temperature and transport properties of the system. Up to now, Li$^{[3]}$ and K$^{[4]}$, or Sr and Ca$^{[5][6]}$ have been used to substitute for Na, and Cu$^{[7]}$, Ir or Ga$^{[8]}$, Mn$^{[9]}$ or Ti$^{[10]}$ used to substitute for Co. Because Na$_3$CoO$_2$ has triangle lattice in which the valence of Co ion is variable, and the electrons in the system are considered to be strongly correlated and frustrated, leading to rich phenomena in magnetism and superconductivity properties$^{[11]}$ since the spin correlation between the layers is anti-ferromagnetic correlation but inside the layer is ferromagnetic$^{[12]}$.

In this paper, the polycrystalline Na$_{0.7}$Co$_{1-x}$Al$_x$O$_2$ ($x = 0$, 0.05, 0.25, 0.4, 0.6, 0.7) were synthesized and the structural magnetic properties were studied. It is observed that the lattice parameters of Na$_{0.7}$CoO$_2$ were not significantly influenced by doping Al ions, but the magnetism was affected by such a doping. A spin-glass transition at about 13 K was detected in the samples with the doping levels $x = 0.05$ and 0.25.

2. Experimental Details

Polycrystalline Na$_{0.7}$Co$_{1-x}$Al$_x$O$_2$ ($x = 0$, 0.05, 0.25, 0.4, 0.6, 0.7) were synthesized by a solid-state chemical reaction method. A stoichiometric mixture of Na$_2$CO$_3$ (99.99%), Co$_3$O$_4$ (99.99%) and Al$_2$O$_3$ (99.99%) was ground, and heated in O$_2$ at 750 °C for 12 h. The powders were then reground, pressed into pellets and sintered at 750 °C in flow O$_2$ for 24 h. Powder X-ray diffraction (XRD) was carried out by using an X’Pert MRD diffractometer with Cu K$_α$ radiation. The ac susceptibility was measured with a physical property measurement system (quantum design PPMS 6000). The dc magnetization was measured by SQUID magnetometer (QD MPMS) with the magnetic field $H$ of 100 Oe in both zero field cooled (ZFC) and field cooled (FC) process.

3. Results and Discussion

Fig. 1 shows the XRD patterns of Na$_{0.7}$Co$_{1-x}$Al$_x$O$_2$. The observed reflections for the samples of low dopant contents ($x = 0$, 0.05, 0.25) were very narrow and no diffusion back-ground was observed, indicating a high quality of the samples. All of these samples were of a hexagonal crystal structure. The data with a chemical composition of Na$_{0.71}$Co$_{0.96}$O$_2$ matched very well with the standard data (Reference code: 00-030-1182)$^{[13]}$. No secondary phase was detected. This allows us to deduce that the sample’s composite is very close to its nominal composite. Within the limit of calculation error, the lattice parameters obtained from Rietveld refinements do not exhibit a significant change with the doping level. This is consistent with the observation of Yokoi et al.$^{[8]}$. Actually, in this system, the radius of Al$^{3+}$ (53.5 pm) was very close to that
of Co$^{4+}$ (53.0 pm), which may be the cause that the substitution of Al for Co did not significantly influence the size of unit cell. However, as the dopant content increased to $x=0.4$, the second phase occurred, indicating that the limit of the solid solubility of Al in Na$_{0.7}$Co$_1$Al$_x$O$_2$ was around $x=0.4$. In addition, there was no structural transition including superlattice formation observed, indicating that the Co$^{4+}$ ions were randomly replaced by Al$^{3+}$. This introduced disorder into the system.

Fig. 1. XRD patterns for polycrystalline Na$_{0.7}$Co$_1$Al$_x$O$_2$ samples: (a) a full scan between 10° and 70° and (b) enlarged part between 32° and 52°.

The temperature dependence of dc magnetization measured in the ZFC for the undoped and Al-doped Na$_{0.7}$Co$_x$O$_2$ samples. A paramagnetic behavior was observed for all these samples above 20 K. However, a sharp peak at about 13 K was observed for the Al-doped samples with doping level $x=0.05$ and 0.25, which suggests an antiferromagnetic-like transition. As mentioned above, Na$_{0.7}$Co$_{1-x}$Al$_x$O$_2$ has the same crystal structure as Na$_{0.7}$CoO$_2$ and Al is a nonmagnetic element, the appearance of an antiferromagnetic-like transition in such a system is quite unusual and hard to understand since the parent material Na$_{0.7}$CoO$_2$ is paramagnetic.

In order to clarify the nature of such a magnetic transition, dc magnetization was performed in both zero-field-cooling (ZFC) and field-cooling (FC) processes and the results are shown in Fig. 3. The measured ZFC curves exhibited sharp cusps in some samples ($x=0.05$, and $x=0.25$), therefore, when considered alone, the curves shape might be taken to indicate the onset of long-range antiferromagnetic ordering. However, as the ZFC and FC susceptibilities of the low-temperature region under 100 Oe are expanded in Fig. 3, the splitting of the ZFC and FC data suggests that the low temperature phases of these samples are not classical antiferromagnets. The appearance of the cusp and the irreversible behavior in the susceptibility versus temperature curves shown in Fig. 2 and Fig. 3 suggest that a spin glass transition may occur in the system.

Fig. 2 shows the temperature dependence of the dc magnetization measured in the ZFC for the undoped and Al-doped Na$_{0.7}$Co$_x$O$_2$ samples. A paramagnetic behavior was observed for all these samples above 20 K. However, a sharp peak at about 13 K was observed for the Al-doped samples with doping level $x=0.05$ and 0.25, which suggests an antiferromagnetic-like transition. As mentioned above, Na$_{0.7}$Co$_{1-x}$Al$_x$O$_2$ has the same crystal structure as Na$_{0.7}$CoO$_2$ and Al is a nonmagnetic element, the appearance of an antiferromagnetic-like transition in such a system is quite unusual and hard to understand since the parent material Na$_{0.7}$CoO$_2$ is paramagnetic.

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Fig. 3. Temperature dependence of dc magnetization measured at 100 Oe in ZFC and FC processes: (a) Na$_{0.7}$Co$_{0.95}$Al$_{0.05}$O$_2$ and (b) Na$_{0.7}$Co$_{0.75}$Al$_{0.25}$O$_2$. 
Experimentally, spin glass behavior is usually identified by the observation of a few typical features—a cusp in the temperature dependence of ac susceptibility, an irreversible behavior of magnetization versus temperature below the freezing temperature, $T_f$, and an appearance of coercivity in the spin glass state—even though the nature of the magnetic state is still controversial. The peak of the cusp determines the transition temperature $T_f$, usually referred to as the freezing temperature, from the paramagnetic state to the spin glass state. For the present system, the freezing transition temperature $T_f$ was about 13 K.

A distinct feature of a spin-glass state is that the peak in the curve of the ac susceptibility versus temperature shifts upwards with increasing frequency. As shown in Fig. 4, there was a maximum at freezing temperature $T_f$ in ac susceptibility-temperature curve, and the peak shifted towards higher temperature with increasing frequency. In the meantime the amplitude of the peak decreases. These unique frequency-dependent behaviors further confirmed that the magnetic transition in the present system was a spin-glass transition rather than antiferromagnetic ordering transition.

![Graph](image)

Fig. 4. Temperature dependence of ac magnetization measured at different frequencies (from top to bottom $f = 307$ Hz, 777 Hz, 1117 Hz, and 9999 Hz).

The results shown above confirmed that a spin glass transition took place at about 13 K in Na$_x$Co$_{1-x}$Al$_2$O$_4$ with a higher Al doping level. As we have known, both disorder and competing magnetic interactions are required for the spin-glass formation. In Na$_x$Co$_{1-x}$Al$_2$O$_4$, the disorder was provided by the random occupation of Al in Co sites. In addition, both Co$^{3+}$ and Co$^{4+}$ ions co-existed in Na$_x$Co$_2$O$_4$ compounds. In Na$_x$Co$_2$O$_4$, the CoO$_2$ layers had a hexagonal 2D crystal structure with a trigonal distortion yielding a large crystal field and a low spin configuration for the Co ions. Those can be stabilized in 3+ or 4+ charged states which corresponded to spin $S = 0$ and $S = 1/2$, respectively. The Co charge order is an intrinsic property of the CoO$_2$ planes which governs the ground state properties. In Co$^{3+}$/Co$^{4+}$-ionic model, Co$^{3+}$ ions take nominally 3d$^8$ configuration and can exist also in low-spin ($S = 1/2$; $t_{2g}^6$), intermediate-spin ($S = 3/2$; $t_{2g}^3 e_g^1$) or high-spin ($S = 2$; $t_{2g}^3 e_g^3$) states. Co$^{4+}$ ions take 3d$^4$ configuration and can exist also in low-spin ($S = 1/2$; $t_{2g}^5$), intermediate-spin ($S = 3/2$; $t_{2g}^e g^1$) or high-spin ($S = 5/2$; $t_{2g}^e g^3$) states. This variety of possible spin states was a consequence of the interplay between the intra-atomic exchange and the crystal-field interactions, which were of comparable magnitudes in Na$_x$Co$_2$O$_4$. The paramagnetic insulator behavior of the parent compound Na$_3$Co$_2$O$_5$ is attributed to the thermal population of the excited IS state. Although Al doping does not considerably change lattice constants, it may lead to a transformation of most LS Co$^{3+}$ ions into the IS state. For all level doping studied in this work, a small part of Co$^{3+}$ ions remained in the LS state. Valence states analyses showed that the Co ions had valence states of +3.3 in Na$_x$Co$_{1-x}$Al$_2$O$_4$ and +3.4 in Na$_x$Co$_{1-x}$Al$_2$O$_4$. In this system, Al$^{3+}$ radius (53.5 pm) was close to that of Co$^{4+}$ (53.0 pm), so the substitution took place between Al$^{3+}$ and Co$^{4+}$. After substituting, the Co ions valence states being higher indicates some Co$^{3+}$ change into Co$^{4+}$ in Na$_x$Co$_{1-x}$Al$_2$O$_4$. In other words, in Na$_x$Co$_{1-x}$Al$_2$O$_4$, the ratio of the number of Co$^{3+}$ vs. the number of Co$^{4+}$ ions increased with increasing Al doping level, thus tuned the spin states for Co ions in the system.

On the other hand, in Na$_x$Co$_{1-x}$Al$_2$O$_4$, depending on the spin states of considered ions, the Co$^{3+}$–Co$^{4+}$ pairs can interact ferromagnetically due to the double-exchange interaction, while the Co$^{3+}$–Co$^{3+}$ and Co$^{4+}$–Co$^{4+}$ pairs can be coupled antiferromagnetically due to the superexchange interaction. The coexistence and competition of antiferromagnetic and ferromagnetic interactions can lead to the frustration, which is responsible for spin-glass ordering observed in Na$_x$Co$_{1-x}$Al$_2$O$_4$.

Although the appearance of such a ferromagnetic metallic state can be explained based on the physical picture described above, the real physical mechanism underpinning the behavior of Na$_x$Co$_{1-x}$Al$_2$O$_4$ may be more complicated. More efforts should be made to obtain a full understanding of the mechanism behind.

### 4. Conclusions

Polycrystalline samples Na$_{x}$Co$_{1-x}$Al$_2$O$_4$ ($x = 0, 0.05, 0.10, 0.15, 0.20, 0.25, 0.30$) were prepared by solid state reaction. The dc and ac magnetic susceptibility measured between 5 K and 300 K showed rich phenomena in magnetism, including paramagnetism, spin-glass state and/or antiferromagnetism under different conditions. The samples with lower doping quantity ($x = 0, 0.05, 0.10$) were paramagnetic, but the samples with higher doping quantity ($x = 0.20, 0.25, 0.30$) were spin-glass state at lower temperatures and became antiferromagnetism at higher temperatures. The spin-glass transition temperature $T_f$ was about 13 K. Such a coexistence of both spin-glass and antiferromagnetic states reported here has not been observed in other Na$_x$Co$_2$O$_4$-related systems.
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References

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