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Effect of Ga and Mn doping on structural, electrical transport and magnetic properties of $Na_{0.75}CoO_2$

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Abstract

The effects of doping with magnetic Mn ions or nonmagnetic Ga ions on the structural, electrical transport and magnetic properties of $Na_{0.75}CoO_2$ have been investigated. It has been found that the lattice parameter c of the samples increases with Ga or Mn ion doping. Ga doping raises the electrical resistivity of $Na_{0.75}CoO_2$, but the metallic conducting behaviour of the compound has not been influenced. In contrast, 5% Mn doping leads to a metal–insulator transition at low temperatures in $Na_{0.75}Co_{1-y}Mn_yO_2$. The susceptibility of the Ga doped sample shows strong magnetic field dependence, while the susceptibility of the Mn doped samples is not very sensitive to the magnetic field. This work implies that magnetic interaction plays an important role in Na_xCoO_2.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The sodium–cobalt oxide Na_xCoO_2 system, because of its particular properties of large thermoelectric power coexisting with low electrical resistivity, has attracted much attention in recent years [1–4]. In particular, the discovery of superconductivity in the water-intercalated Na_xCoO_2 compound is a breakthrough in the search for new layered transition metal oxide superconductors [5, 6]. Now in-depth study has given evidence of strong electron–electron correlation in Na_xCoO_2, [5–8] and demonstrated that the physical properties of Na_xCoO_2 compounds are very sensitive to doping [9–12].

Terasaki *et al* studied the effect of Cu doping on $NaCo_2O_4$ [9]. They measured the specific heat, susceptibility, Hall coefficient and transverse magnetoresistance for $NaCo_{2-x}Cu_xO_4$ polycrystalline samples, and argued that the Cu substitution induces a phase transition at 22 K. Yokoi *et al* found that the superconducting transition temperature of water-intercalated Na_xCoO_2 can be affected by Ir or Ga substitution for Co, and also reported that an

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$Na_{0.75}Co_{1-x}Ir_xO_2$ sample becomes insulating for Ir content as small as 0.02 [10]. In our previous papers, we studied the structural, electrical transport and magnetic properties of $NaCo_{1-x}Mn_xO_2$ and $Na_{0.8}Co_{1-x}Ti_xO_2$, and found that a low doping with 3% Mn or Ti replacing Co leads to a metal–insulator (M–I) transition [11, 12]. A fundamental question is whether there is a distinct difference between magnetic and nonmagnetic impurity doping on the physical properties of Na_xCoO_2. This will be helpful to get some insight into the role of the magnetic interaction in this system.

In this paper, we report the effects of magnetic Mn and nonmagnetic Ga ion doping on the structural, electrical transport and magnetic properties of $Na_{0.75}CoO_2$ samples. With the increase of Mn doping, both the lattice parameter c and a of the samples increase. The lattice parameter a of Ga doped samples remains unchanged within the experimental error while the lattice parameter c increases with doping. Substitution of Ga for Co does not change the metallic behaviour of the samples. In contrast, substitution of 5% Mn for Co results in an M–I transition at low temperatures. The susceptibility of Ga doped samples shows strong magnetic field dependence, while the susceptibility of the Mn doped samples is not very sensitive to the magnetic field. Possible doping mechanisms in Na_xCoO_2 were discussed.

2. Experimental details

Polycrystalline samples of $Na_{0.8}Co_{1-z}Ga_zO_2$ ($z = 0, 0.04, 0.08, 0.12, 0.2$) and $Na_{0.8}Co_{1-y}Mn_yO_2$ ($y = 0, 0.03, 0.04, 0.05, 0.06, 0.07, 0.1$) were prepared by the conventional solid state reaction method. The raw materials (Na_2CO_3, Co_3O_4 and Ga_2O_3 or MnO_2) were weighed according to the chemical ratios to produce the mixtures of different compositions. The mixed powders were ground and calcined within the temperature range from 800 to 850 °C for 14 h in air. The product was then finely ground, pressed into pellets, and sintered at 860 °C for 12 h in air. Since sodium tends to evaporate during calcination, the composition of the samples after calcination is $Na_{0.75}Co_{1-x}M_xO_2$ (M = Ga, Mn) as determined by inductive-coupled plasma atomic emission spectroscopy analysis.

The x-ray diffraction was performed using a *Rigaku D/max-RB* x-ray diffractometer with Cu Kα radiation as the x-ray source in the θ–2θ scan mode. The electrical resistivity $\rho(T)$ was measured using the four probe method within the temperature range of 5–300 K. Indium was used for the electrical contact. The dc magnetic susceptibilities of the samples were measured using a superconducting quantum interference device (SQUID) within the temperature range of 5–120 K.

3. Results and discussions

Figures 1 and 2 show the x-ray diffraction patterns of $Na_{0.75}Co_{1-z}Ga_zO_2$ ($z = 0, 0.04, 0.08, 0.12, 0.15$) and $Na_{0.75}Co_{1-y}Mn_yO_2$ ($y = 0, 0.05, 0.1$), respectively. Most of the diffraction peaks can be indexed according to the γ phase of Na_xCoO_2 [13]. There are some minor peaks which are related to some impurity phases as indicated in the figures with *. Since the impurity phase is minor, it is unlikely that it will have remarkable influence on the properties of the doped samples. When Ga doping reaches 0.15, like Cu doping [9], a higher background noise emerges, indicating that the crystal quality of the sample becomes worse, possibly owing to the limit of solid solution of Ga, while for Mn doped samples they are single phase. This is consistent with the results of our previous paper, which showed that single phase samples can be obtained in $NaCo_{1-x}Mn_xO_2$ with the maximum doping of $x = 0.5$ used in that work.

The lattice parameters a and c of the samples are shown in figures 3 and 4. They are close to the standard values of $a = 2.833$ Å and $c = 10.88$ Å obtained by Fouassier *et al* [13]. For

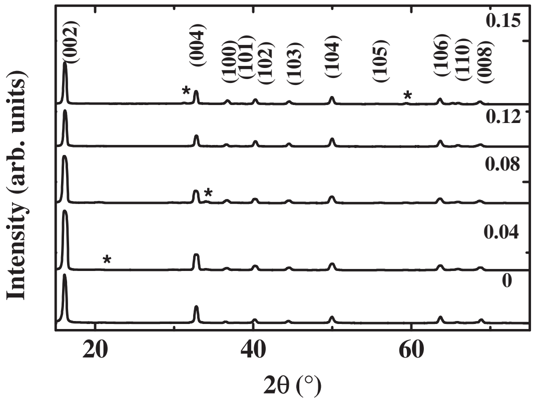

Figure 1. X-ray diffraction patterns of $Na_{0.75}Co_{1-z}Ga_zO_2$. * indicates the peaks related to the impurity phase.

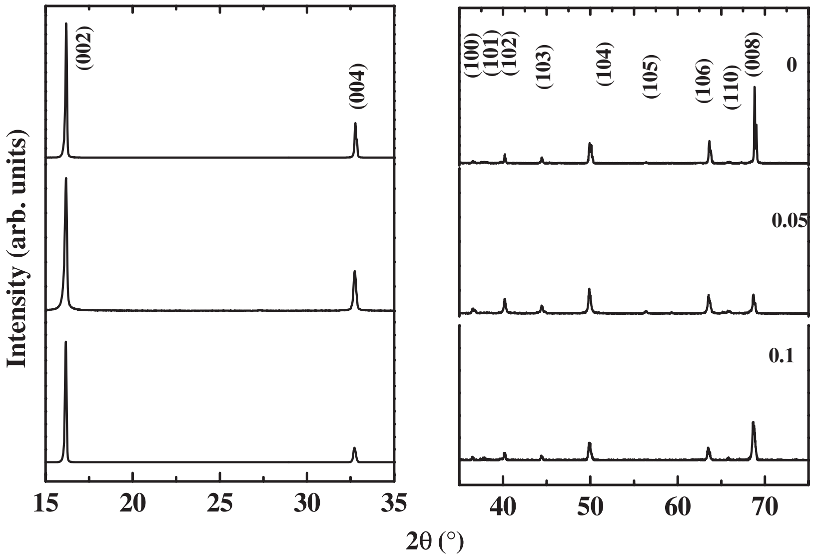

Figure 2. X-ray diffraction patterns of $Na_{0.75}Co_{1-y}Mn_yO_2$.

Mn doping, both the lattice parameters c and a increase monotonically with doping. However, for Ga doping, the lattice parameter c increases with doping, while the lattice parameter a remains unchanged within the experimental error, which implies that the in-plane chemical bond is much stronger than the out-of-plane bond for Na_xCoO_2.

The temperature dependence of resistivity for the Ga doped samples is shown in figure 5. All these samples show metallic conduction behaviour. The value of the resistivity increases gradually with Ga doping for $z < 12\%$, within a wide temperature range (5–300 K). It has been noted that the resistivity of the sample with $z = 0.15$ is smaller than that of $z = 0.08$ and 0.12 samples. The reason is not clear yet. These results indicate that the electrical transport behaviour of $Na_{0.75}CoO_2$ is not very sensitive to the nonmagnetic Ga ion doping.

Figure 6 shows the variation of resistivity with temperature for Mn doped samples. When Mn doping reaches 5%, an M–I transition occurs at low temperatures. It is noted that the

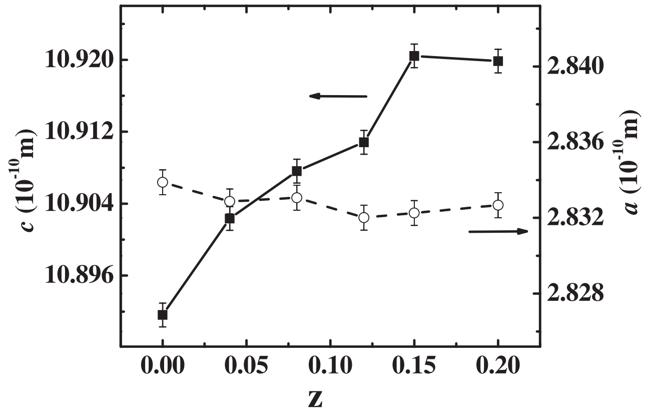

Figure 3. Variation of the lattice parameters a and c with z for $Na_{0.75}Co_{1-z}Ga_zO_2$.

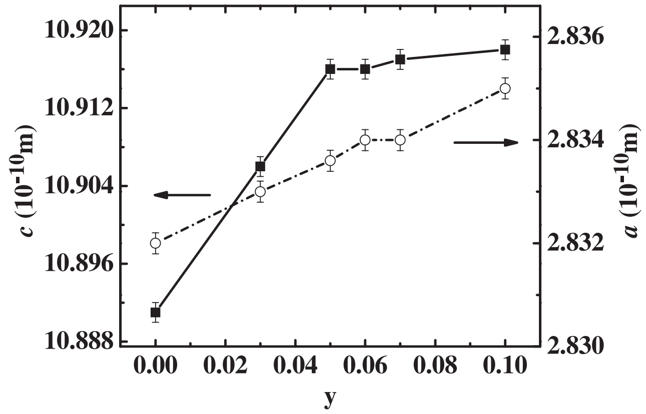

Figure 4. Lattice parameters a and c versus y for $Na_{0.75}Co_{1-y}Mn_yO_2$.

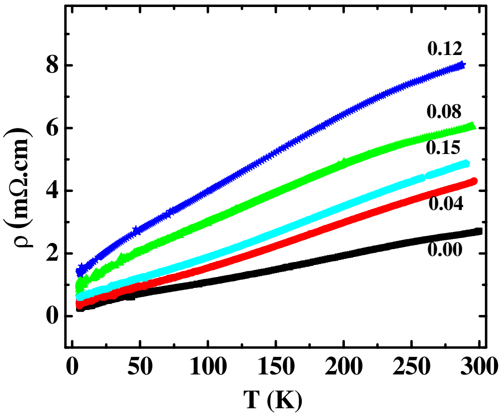

Figure 5. Temperature dependence of resistivity for $Na_{0.75}Co_{1-z}Ga_zO_2$.

resistivity of the 5% doped sample is much larger than that of the undoped sample and the samples with larger doping amounts. This result is repeatable. This behaviour is very

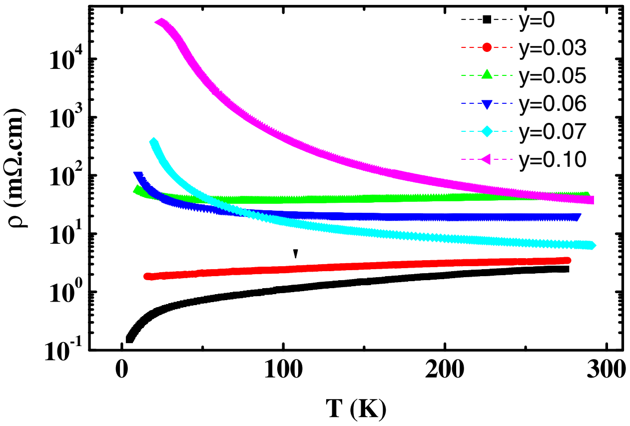

Figure 6. Temperature dependence of resistivity for $Na_{0.75}Co_{1-y}Mn_yO_2$.

unusual and deserves further study. It is possible that the electronic transport of Mn doped samples is determined by a few factors, so the resistivity of the doped samples does not change monotonically with doping. Here we focus on the M–I transition in the doped samples. It has been proposed that the conducting behaviour of the transition-metal oxides can be estimated by the value of $\Delta R = R_c - R_{m-m}$ [12, 14, 15]. R_c is the critical distance between the transition-metal atoms. R_{m-m} is the real distance between the transition-metal atoms. If $\Delta R > 0$, the oxide exhibits a metallic character. While $\Delta R < 0$, it shows an insulating behaviour. In fact, for Na_xCoO_2 with $0.7 \leqslant x \leqslant 0.85$, the real Co–Co distance is smaller than R_c [15], so Na_xCoO_2 is a metal. Mn doping increases the real Co–Co distance; this will drive the system to become an insulator. This scenario may apply to the Mn doped samples with larger doping amount because they show semiconductor-like behaviour from room temperature to low temperatures. However, this scenario may not apply to samples with low doping amounts, because these samples show metallic conducting behaviour at high temperatures instead of semiconductor-like behaviour. Other mechanisms should be considered. It should be pointed out that all the Ga doped samples show metallic conducting behaviour, while Mn doped samples with low doping amount show an M–I transition at low temperatures. Since Ga ions are nonmagnetic and Mn ions are magnetic, it is likely that the scattering of the magnetic ions with carriers plays an important role in the M–I transition of the Mn doped samples. We argued that the M–I transition is due to the enhanced magnetic fluctuation in the Mn doped samples, and this magnetic fluctuation has strong scattering to the carriers. The enhancement of magnetic fluctuation in the Mn doped samples is also indicated by the magnetic susceptibility results as shown later. It is known that in Na_xCoO_2 the cobalt ions form a layered triangular lattice, and the sodium ions are sandwiched between CoO_2 layers. The triangular lattice is also expected to result in magnetic frustration, namely strong magnetic fluctuations. This magnetic fluctuation is enhanced by Mn doping. It is interesting to know why the scattering does not arise in the undoped samples, which also contain magnetic ions (Co^{4+}). One of the possible answers may lie in the itinerant property of the magnetic moments in the Na_xCoO_2 system and the local magnetic moments induced by Mn doping. A key ingredient from previous measurements by Wang *et al* [7] is that the motion of charges in Na_xCoO_2 is tied to the local moments of spin 1/2 in a background of Co^{3+} ions that are magnetically inert. In the parent samples, the carriers contribute both the magnetic moment and the charge, so the scattering is not detected. When some of the cobalt ions are replaced by magnetic Mn ions, the carriers will be scattered

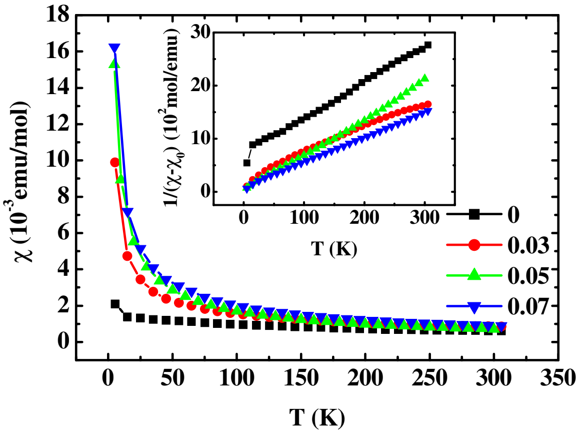

Figure 7. Temperature dependence of the zero-field cooling (ZFC) magnetic susceptibility for $Na_{0.75}Co_{1-y}Mn_yO_2$ ($y = 0$, 0.03, 0.05, 0.07). The inset shows the temperature dependence of the inverse susceptibility. The applied magnetic field is 500 Oe.

Table 1. The parameters fitting to the χ–T curves for $Na_{0.75}Co_{1-y}Mn_yO_2$.

y	C (emu K mol^{-1})	μ_{eff} (μ_B)	Θ (K)	χ_0 (emu mol^{-1})
0	0.1421	1.066	−94.3	0.000 24
0.03	0.1556	1.116	−32.1	0.000 38
0.05	0.1929	1.242	−21.0	0.000 11
0.07	0.2351	1.371	−29.7	0.000 19

near Mn ions because of the existence of the local magnetic ions and the enhanced magnetic frustration.

Figure 7 shows the temperature dependence of magnetic susceptibility for Mn doped samples. The susceptibility of these samples obeys the Curie–Weiss law from 50 to 300 K (for the undoped sample, the starting temperature is a little bit lower), and the susceptibility increases dramatically with Mn doping. By using $\chi = \chi_0 + C/(T - \Theta)$ to fit the χ–T curves [16] with the least square fitting method, we obtained the values of the Curie constant C, the effective magnetic moment, the paramagnetic Curie–Weiss temperature Θ, and the temperature-independent terms χ_0, which are displayed in table 1 for $Na_{0.75}Co_{1-y}Mn_yO_2$. Here $C = N\mu_{eff}^2/3k_B$ (μ_{eff} is the effective moment of magnetic ions, k_B is the Boltzmann constant and N is the number of magnetic ions per unit volume). The effective magnetic moment of the undoped sample is consistent with the previous reports [17, 18]. As expected, Mn ions with larger magnetic moment have a dramatic influence on the magnetic property of Na_xCoO_2 and the effective magnetic moment of $Na_{0.75}Co_{1-y}Mn_yO_2$ increases with Mn doping. The value of Θ is negative and is larger in the Mn doped samples, indicating that the antiferromagnetic correlations are weakened due to Mn doping. So Mn doping also affects the magnetic interaction in $Na_{0.75}Co_{1-y}Mn_yO_2$. For the $Na_{0.75}Co_{0.92}Ga_{0.08}O_2$ sample, the temperature and magnetic field dependence of magnetic susceptibility was measured and the result is shown in figure 8. Low-field $\chi(T)$ shows a large enhancement below 10 K. With increasing magnetic field, the amplitude of the magnetic susceptibility is strongly suppressed. This behaviour is similar to that of the undoped Na_xCoO_2 samples, which has been attributed to the suppression of the spin fluctuation by magnetic field in the Na_xCoO_2 system [19, 20]. The

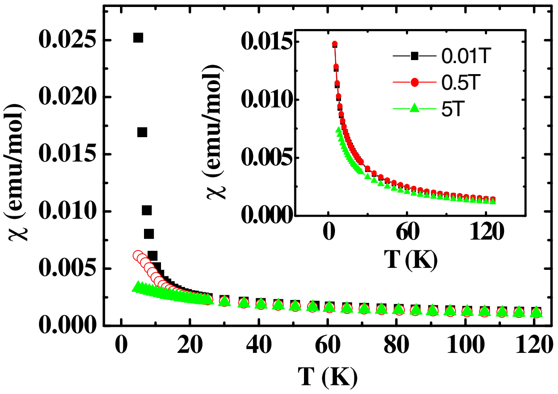

Figure 8. Temperature and field dependence of the zero-field cooling (ZFC) magnetic susceptibility for $Na_{0.75}Co_{0.92}Ga_{0.08}O_2$. The inset shows the temperature dependence of the susceptibility for $Na_{0.75}Co_{0.95}Mn_{0.05}O_2$ under different magnetic fields.

inset of figure 8 shows the temperature dependence of magnetic susceptibility for an Mn doped sample ($y = 0.05$) under different magnetic fields. For Mn doped samples the susceptibility is not very sensitive to magnetic filed, indicating that the magnetic fluctuations in Na_xCoO_2 are enhanced by Mn doping. The magnetic susceptibility of the Ga doped Na_xCoO_2 samples shows strong magnetic field dependence, just as in $Na_{0.69}CoO_2$ [19], $Na_{0.75}CoO_2$ [21] and $Na_{0.85}CoO_2$ [22]. So Ga doping does not change the magnetic property of Na_xCoO_2. This can be understood if one considers the substitution of nonmagnetic Co^{3+} ions by nonmagnetic Ga^{3+} ions, since, in Na_xCoO_2, Co^{3+} and Co^{4+} ions are in the low spin state with $S = 0$ and $S = 1/2$ [7, 16], respectively. On the other hand, as expected, Mn ions with larger magnetic moment have dramatic influence on the triangular lattice of Na_xCoO_2 and the magnetic fluctuation in $Na_{0.75}Co_{1-y}Mn_yO_2$ is enhanced by Mn doping.

4. Summary

$Na_{0.75}Co_{1-z}Ga_zO_2$ ($z = 0, 0.04, 0.08, 0.12, 0.2$) and $Na_{0.75}Co_{1-y}Mn_yO_2$ ($y = 0, 0.03, 0.04, 0.05, 0.06, 0.07, 0.1$) samples were prepared by solid-state reaction. The lattice parameter c and the electrical resistivity increase with Ga or Mn ion doping, and the specimens exceeding 5% Mn ion doping exhibit insulating behaviour at low temperatures, which was attributed to the strong scattering of carriers with the magnetic fluctuation, which was enhanced by Mn doping. Mn substitution also results in the increase of the lattice parameter a, which will drive the system to become an insulator if the Co–Co distance is larger than the critical distance R_c. The Ga ion doped samples show a metallic transport behaviour and strong magnetic field dependence of susceptibility, similar to the undoped samples. This work shows that the magnetic interaction and the spin fluctuations play important roles in Na_xCoO_2.

Acknowledgments

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