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Abstract

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Keywords

Magnetic, anisotropy, NaxCoO2, single, crystals

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Magnetic anisotropy of Na_xCoO_2 single crystals

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We report the magnetic properties of single crystals of Na_xCoO_2 (x=0.42, 0.82, and 0.87). The magnetic susceptibility measurements revealed considerable anisotropy along H$\parallel ab$ and H$\parallel c$ for the as-grown single crystals. It was found that an antiferromagnetic transition with a Neel temperature T_N=21 K occurred for the x=0.82 sample, and there was a paramagnetic phase for the x=0.87 sample over a wide temperature range from 2 to 300 K, but the sample with x=0.42 shows a monotonic increase of χ with increasing temperature above ~100 K. In addition, the x=0.82 sample has the largest derived anisotropic g-factor ratio ($g_{ab}/g_c \sim 1.30$), whereas the sample with x=0.42 is nearly isotropic ($g_{ab}/g_c \sim 0.96$). © *2008 American Institute of Physics*. [DOI: 10.1063/1.2828595]

I. INTRODUCTION

Layered cobaltite Na_xCoO_2 has received much attention because of its potential as a battery electrode material and in thermoelectric devices.[1,2] The bulk superconductivity induced by water insertion in $Na_{0.33}CoO_2$ has increased investigations into the physical properties of Na_xCoO_2 compounds,[3–6] which have remained largely unexplored so far. One of the outstanding puzzles is the nature of the magnetic interactions. In the large x region of Na_xCoO_2 ($x > 0.75$), the research has been hampered by difficulties in growing single crystals, as well as by phase separation effects, which appear above a threshold doping known as x_p.[4] So far, most studies have been carried out on polycrystalline samples or poor quality crystals. Studies using high quality single crystals will give more accurate results on the structure and physical properties of this frustrating material. In this work, we report on the anisotropic magnetic properties of large single crystals of Na_xCoO_2 with x=0.42, 0.82, and 0.87.

II. EXPERIMENT

Crystals of $Na_{0.82}CoO_2$ and $Na_{0.87}CoO_2$ were prepared by the traveling solvent floating zone (TSFZ) method.[7] The $Na_{0.42}CoO_2$ sample was obtained by deintercalation of $Na_{0.82}CoO_2$ as-grown single crystal, as previously described.[8] The composition of the samples for measurements was determined using energy dispersive x-ray analysis. Single crystal x-ray diffraction (XRD) was carried out on mechanically cleaved faces of the crystals along the growth direction to examine the crystalline quality and orientation of the crystal growth. Cu Kα radiation was used as the x-ray source. The magnetic susceptibility measurements were carried out using a superconducting quantum interference device magnetometer (Quantum Design, model MPMS 7.0) over a wide range of temperatures from 2 to 300 K under a magnetic field of 1 T.

III. RESULTS AND DISCUSSION

Single crystals of Na_xCoO_2 were obtained with a growth rate of 1.5 mm/h in flowing oxygen atmosphere. The typical as-grown cylindrical crystal ingot size is 6.5 mm in diameter and 10 cm in length. When conditions were close to optimum, very clear facets appeared on opposite sides of the crystal rod. These facets were found to be perpendicular to the c axis. The rest of the measurements were performed on crystal samples cleaved from the top ends of the crystal rods, which are normally of higher quality without any detectable Co_3O_4 impurity present.

Single crystal XRD measurements were made on crystal samples. Typical XRD patterns are shown in Fig. 1. All the peaks were indexed as the (00l) peaks of Na_xCoO_2. Using a fitting method with the Nelson-Riley function, the c-axis lattice constants are estimated to be 11.116, 10.808, and 10.806 Å for $Na_{0.42}CoO_2$, $Na_{0.82}CoO_2$, and $Na_{0.87}CoO_2$, respectively. The c parameter decreased as the Na content increased. No traces of impurities or inclusions were observed in our samples for magnetic measurements.

The as-grown crystal quality was determined to be high, with the mosaic structure of the full width at half maximum (FWHM) <0.133°. A typical x-ray (Mo $K\alpha$ radiation) rocking curve measured on $Na_{0.82}CoO_2$ crystal is depicted in Fig. 2. The profiles of the (300) and (001 0) Bragg-reflections have FWHM values of 0.042° and 0.133°, respectively, indicating the excellent quality of the crystal.

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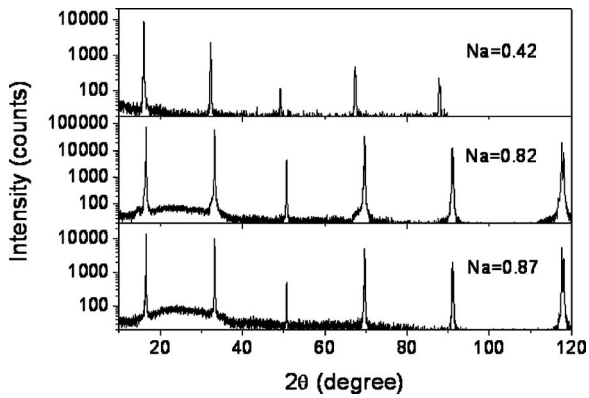

FIG. 1. X-ray diffraction patterns for Na_xCoO_2 single crystals cleaved along the growth direction. All the peaks can be attributed to the (00l) orientation.

The temperature dependence of the susceptibility for the $Na_{0.82}CoO_2$ and $Na_{0.87}CoO_2$, as measured in a field of 1 T oriented either along or perpendicular to the (001) direction is shown in Fig. 3. Upon cooling, a broad peak develops around 21 K for the $Na_{0.82}CoO_2$ sample. Below 20 K, the susceptibility drops down sharply for H∥*c* but goes up for H∥*ab*. Similar behaviors were observed in other single crystal samples in a region with sodium contents ranging from 0.78 to 0.85.[9–11] The upturn of the curves below 14 K appears to be due to paramagnetic contributions from impurities; this upturn is suppressed in a field of 5 T.[10]

The broad maximum at ~40 K for H∥*ab* is characteristic of low-dimensional short-range magnetic ordering.

The susceptibility of the $Na_{0.87}CoO_2$ sample shows a paramagnetic behavior over a wide temperature range from 2 to 300 K. Two tiny kinks can be observed at about 19 and 13 K in a field of 1 T parallel to (001), but are absent for the perpendicular direction.

The magnetization is very sensitive to the presence of Co_3O_4 and CoO, which are antiferromagnets with T_N=35 and 292 K, respectively. No other transitions in the susceptibility have been found from 20 K to room temperature for any of the as-grown crystals, indicating high quality of the samples. This is consistent with x-ray diffraction measurements, which exhibit no traces of impurities.

The magnetic susceptibility data for $Na_{0.42}CoO_2$ are

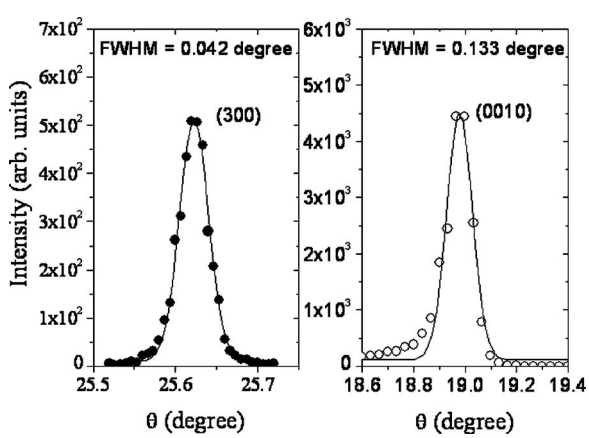

FIG. 2. X-ray rocking curves for the as-grown $Na_{0.82}CoO_2$ crystal (Mo $K\alpha$ radiation).

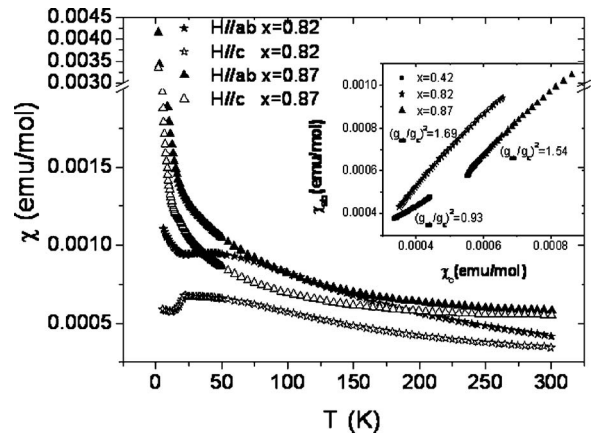

FIG. 3. Temperature dependence of the susceptibility of $Na_{0.82}CoO_2$ and $Na_{0.87}CoO_2$ measured in a field of 1 T. The open and closed symbols are for the magnetic fields applied parallel and perpendicular to the (001) direction, respectively. The inset shows $\chi_{ab}(T)$ vs $\chi_c(T)$.

shown in Fig. 4, where a magnetic field of 1 T was applied parallel to the *ab* plane and to the *c* direction. χ decreases from 300 to 86 K and sharply increases after 33 K. Two small anomalies develop at 51 and 86 K along the *c* direction. The susceptibility cusp at 51 K is isotropic, whereas the one near 86 K is anisotropic, which is consistent with the reports for $x \leqslant 0.5$ single crystals.[12,13] We note that the 287 K anomaly does not exist in the parent x=0.82 crystal sample. It is therefore tempting to assign the 287 K anomaly to the existence of CoO (T_N=292 K) impurity which appears during the deintercalation. It can be seen that the susceptibility increases as the sodium content x changes from 0.42 to 0.87.

In order to analyze the temperature dependence of the anisotropic susceptibility quantitatively, we plotted χ_{ab} (T) versus χ_c (T) with an implicit parameter T for the sample as shown in the inset of Fig. 3. The analysis mentioned in Ref. 12 leads to the relation between χ_{ab} (T) and χ_c (T),

$$\chi_{ab}(T) = (g_{ab}/g_c)^2\chi_c(T) + (\chi^{ab}{}_0 - (g_{ab}/g_c)^2\chi^c{}_0).$$

The fitted slope of the data corresponds to the ratio $(g_{ab}/g_c)^2$. The samples with x=0.42, 0.82, and 0.87 have $g_{ab}/g_c \approx 0.96$, 1.30, and 1.24, respectively. The sample with x

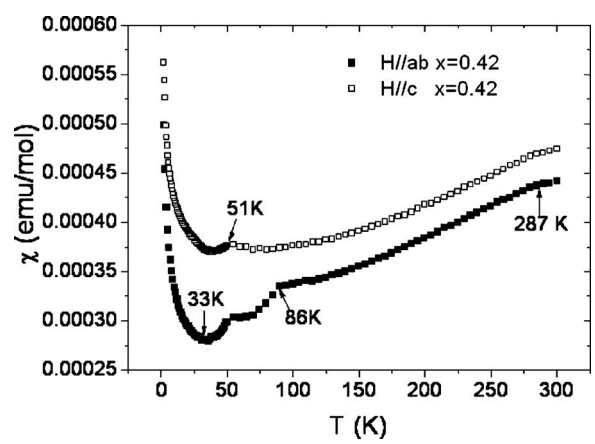

FIG. 4. Temperature dependences of the susceptibility for $Na_{0.42}CoO_2$ sample measured with the field parallel and perpendicular to the (001) direction.

TABLE I. Summary of magnetic data for $Na_{0.82}CoO_2$ and $Na_{0.87}CoO_2$.

Sample	Field orientation	C (cm^3 K/mole)	θ (K)	χ_0 (emu/$mole_{Co}$ Oe)
$Na_{0.82}CoO_2$	$//ab$	0.36(2)	−243(10)	−0.000 27(3)
	$//c$	0.135(7)	−159(8)	0.000 04(1)
	Powder	0.29(2)	−215(10)	−0.000 19(3)
$Na_{0.87}CoO_2$	$//ab$	0.054 (2)	−33(2)	0.000 41(1)
	$//c$	0.0262(9)	−14(2)	0.000 46(1)
	Powder	0.045(2)	−27(2)	0.000 43(1)

$=0.82$ has the largest anisotropy, whereas the sample with $x=0.42$ is near to isotropic. These results agree with the tendency reported by Chou *et al.*[12]

We fitted the temperature dependence of the susceptibility under a 1 T field for the $x=0.82$ and 0.87 single crystals to a modified Curie-Weiss law, $\chi=\chi_0+C/(T\text{-}\theta)$, by a least-squares calculation, where χ_0, C, and θ are the temperature independent susceptibility, the Curie constant, and the asymptotic Curie temperature, respectively. The fitting parameters for both field orientations in the range $T=70-300$ K are given in Table I. The fitted values for the powder average are also listed. As expected, we find that the Curie constants for $H\|ab$ and $H\|c$ are significantly different for these single crystal samples, which may arise from an anisotropic g-factor. The negative θ suggests antiferromagnetically interacting spins. The powder averaged Curie constant gives effective magnetic moments of $\mu_{exp}=1.52\mu_B$ and $0.60\mu_B$ for the single crystal with $x=0.82$ and 0.87, respectively, where μ_B is the Bohr magneton.

Since Na^+ is nonmagnetic, the Curie-Weiss behavior of $\chi(T)$ is attributed to the distinct Co^{3+} and Co^{4+} ions arranged at the cobalt ion sites. In the localized spin approximation, there are three kinds of possible spin states for each cobalt ion, i.e., Co^{3+}: $s=0,1,2$, and Co4+: $s=1/2,3/2,5/2$, respectively. In this study, the effective magnetic moment was calculated using the formula, $\mu_{calc}=\{x\times 4S(Co^{3+})[S(Co^{3+})+1]+(1-x)\times 4S(Co^{4+})[S(Co^{4+})+1]\}^{1/2}$, where the ratio $[Co^{3+}]:[Co^{4+}]=x:1-x$, was assumed. The experimental value ($0.60\mu_B$) of $x=0.87$ single crystal is close to the value of $\mu_{calc}=0.62\mu_B$, which is the spin-only value of Co^{4+} in $S=1/2$. When assuming $S(Co^{3+})=0$ and $S(Co^{4+})=1/2$, the value obtained for $x=0.82$ crystal is $\mu_{calc}=0.73\mu_B$. The closest value obtained for $x=0.82$ crystal is $\mu_{calc}=1.64\mu_B$, assuming $S(Co^{3+})=0$ and $S(Co^{4+})=3/2$. Another possible explanation for the larger experimental value for the $x=0.82$ crystal is the spin state transition of the Co ions,[14,15] which implies that the actual mole fraction of the anisotropic spin sites in Na_xCoO_2 can be considerably larger than $1-x$ because of the presence of nearest-neighbor Co^{3+} ions. Further study is needed to understand the spin states of the mixed valence cobalt ions in the present compounds.

IV. CONCLUSION

High quality single crystals of Na_xCoO_2 ($x=0.82$ and $x=0.87$) have been successfully prepared by the TSFZ method. A $Na_{0.42}CoO_2$ sample was obtained by deintercalation of an as-grown single crystal. The magnetic susceptibility measurements revealed considerable anisotropy along $H\|ab$ and $H\|c$ for the as-grown single crystals. The $x=0.82$ sample had the largest derived anisotropic g-factor ratio of $g_{ab}/g_c\sim 1.30$, whereas the sample with $x=0.42$ was nearly isotropic ($g_{ab}/g_c\sim 0.96$). The magnetic susceptibility for the as-grown crystals was fitted by a modified Curie-Weiss law, and the results were discussed.

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