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Abstract
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Magnetic anisotropy of Na$_x$CoO$_2$ single crystals

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We report the magnetic properties of single crystals of Na$_x$CoO$_2$ ($x$=0.42, 0.82, and 0.87). The magnetic susceptibility measurements revealed considerable anisotropy along H//ab and H//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 $\chi$ with increasing temperature above $\sim$100 K. In addition, the $x$=0.82 sample has the largest derived anisotropic g-factor ratio ($g_{ab}/g_c$~1.30), whereas the sample with $x$=0.42 is nearly isotropic ($g_{ab}/g_c$~0.96). © 2008 American Institute of Physics. [DOI: 10.1063/1.2828595]

I. INTRODUCTION

Layered cobaltite Na$_x$CoO$_2$ has received much attention because of its potential as a battery electrode material and in thermoelectric devices. The bulk superconductivity induced by water insertion in Na$_{0.33}$CoO$_2$ has increased investigations into the physical properties of Na$_x$CoO$_2$ compounds, 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$_x$CoO$_2$ ($x$ >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 $x_p$. 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$_x$CoO$_2$ 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. The Na$_{0.42}$CoO$_2$ sample was obtained by deintercalation of Na$_{0.82}$CoO$_2$ as-grown single crystal, as previously described. 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

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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. 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.

The broad maximum at $T=40$ 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$_3$O$_4$ 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 shown in Fig. 4, where a magnetic field of 1 T was applied parallel to the $ab$ plane and to the $c$ direction. $\chi$ 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 $x=0.5$ single crystals. 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 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 $\chi_{ab}(T)$ versus $\chi_c(T)$ 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 $\chi_{ab}(T)$ and $\chi_c(T)$,

$$\chi_{ab}(T) = (g_{ab}/g_c)^2 \chi_c(T) + (\chi_{ab}^{0} - (g_{ab}/g_c)^2 \chi_{c}^{0})$$

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 $g_{ab}/g_c = 1.96, 1.30, \text{ and } 1.24$, respectively. The sample with $x$
TABLE I. Summary of magnetic data for Na_{0.82}CoO_2 and Na_{0.42}CoO_2.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Field orientation</th>
<th>C (cm^3 K/mole)</th>
<th>( \theta ) (K)</th>
<th>( \chi_0 ) (emu/moleCo Oe)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na_{0.82}CoO_2</td>
<td>//ab</td>
<td>0.36(2)</td>
<td>-243(10)</td>
<td>-0.000 27(3)</td>
</tr>
<tr>
<td></td>
<td>//c</td>
<td>0.135(7)</td>
<td>-159(8)</td>
<td>0.000 04(1)</td>
</tr>
<tr>
<td></td>
<td>Powder</td>
<td>0.29(2)</td>
<td>-215(10)</td>
<td>-0.000 19(3)</td>
</tr>
<tr>
<td>Na_{0.42}CoO_2</td>
<td>//ab</td>
<td>0.054 (2)</td>
<td>-33(2)</td>
<td>0.000 41(1)</td>
</tr>
<tr>
<td></td>
<td>//c</td>
<td>0.0262(9)</td>
<td>-14(2)</td>
<td>0.000 46(1)</td>
</tr>
<tr>
<td></td>
<td>Powder</td>
<td>0.045(2)</td>
<td>-27(2)</td>
<td>0.000 43(1)</td>
</tr>
</tbody>
</table>

=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.\(^1\).

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, \( \chi=\chi_0+C/(T-\theta) \), by a least-squares calculation, where \( \chi_0 \), \( C \), and \( \theta \) 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 \( \theta \) suggests antiferromagnetically interacting spins. The powder averaged Curie constant gives effective magnetic moments of \( \mu_{\text{exp}}=1.52 \mu_B \) and 0.60\( \mu_B \) for the single crystal with \( x=0.82 \) and 0.87, respectively, where \( \mu_B \) 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 Co\(^{4+}\): \( s=1/2, 3/2, 5/2 \), respectively. In this study, the effective magnetic moment was calculated using the formula, \( \mu_{\text{calc}}=\{x \times 4S(\text{Co}^{3+})[S(\text{Co}^{3+})+1] +(1-x) \times 4S(\text{Co}^{4+})[S(\text{Co}^{4+})+1]\}^{1/2} \), where the ratio [Co\(^{3+}\):[Co\(^{4+}\)]=1:x, was assumed. The experimental value (0.60\( \mu_B \)) of \( x=0.87 \) single crystal is close to the value of \( \mu_{\text{calc}}=0.62 \mu_B \), which is the spin-only value of Co\(^{4+}\) in \( S=1/2 \). When assuming \( S(\text{Co}^{3+})=0 \) and \( S(\text{Co}^{4+})=1/2 \), the value obtained for \( x=0.82 \) crystal is \( \mu_{\text{calc}}=0.73 \mu_B \). The closest value obtained for \( x=0.82 \) crystal is \( \mu_{\text{calc}}=1.64 \mu_B \), assuming \( S(\text{Co}^{3+})=0 \) and \( S(\text{Co}^{4+})=3/2 \). 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\(_8\)CoO\(_2\) 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\(_{0.82}\)CoO\(_2\) (\( x=0.82 \) 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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