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Electrochemical synthesis and properties of Co O 2 , the x = 0 phase of the A x Co O 2 systems ( A = Li , Na )

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Electrochemical synthesis and properties of CoO$_2$, the $x=0$ phase of the $A_x$CoO$_2$ systems ($A=$Li,Na)

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Single-phase bulk samples of the “exotic” CoO$_2$, the $x=0$ phase of the $A_x$CoO$_2$ systems ($A=$Li,Na), were successfully synthesized through electrochemical deintercalation of Li from pristine LiCoO$_2$ samples. The samples of pure CoO$_2$ were found to be essentially oxygen stoichiometric and possess a hexagonal structure consisting of stacked triangular-lattice CoO$_2$ layers only. The magnetism of CoO$_2$ is featured with a temperature-independent susceptibility of the magnitude of 10$^{-3}$ emu/mol Oe, being essentially identical to that of a Li-doped phase, Li$_{0.12}$CoO$_2$. It is most likely that the CoO$_2$ phase is a Pauli-paramagnetic metal with itinerant electrons. © 2008 American Institute of Physics. [DOI: 10.1063/1.2828525]

The layered cobalt oxide systems, $A_x$CoO$_2$ ($A=$Li,Na), have attracted increased attention due to recent discoveries of various unconventional transport and magnetic properties. Namely, among the members of the systems, Na$_x$CoO$_2$ exhibits a superb thermoelectric property about $x=0.7$, a spin-density-wave excitation at $x=0.75$, a charge ordering at $x=0.50$, and superconductivity about $x=0.35$ with a hydrated form. The crystals of $A_x$CoO$_2$ consist of alternate stacking of a CoO$_2$ layer and a single atomic layer of $A$ ions. The CoO$_2$ layer contains a two-dimensional triangular cobalt lattice with possible magnetic frustrations (due to the geometry) that may be underlying aforementioned unconventional electronic states.

As mentioned above, the physical properties sensitively depend on the concentration of $A$ ions. It is thus important to establish the electronic phase diagrams for the $A_x$CoO$_2$ systems with respect to $x$. Nevertheless, properties have remained unclear in the low $x$ regime, i.e., $x<0.25$, due to the difficulty in sample syntheses. In particular, it is worth synthesizing the $x=0$ phase of the $A_x$CoO$_2$ systems, i.e., pure CoO$_2$, since it can be regarded as the parent of these systems.

Synthesis of CoO$_2$ samples was previously reported, but the sample purity was insufficient for the accurate determination of physical properties. Here we report the synthesis and the properties of pure CoO$_2$ bulk samples.

Bulk samples of pure CoO$_2$ phase were synthesized through electrochemical deintercalation of Li from pristine LiCoO$_2$ samples. The LiCoO$_2$ samples were prepared by a conventional solid-state reaction technique. A mixture of Li$_2$CO$_3$ and Co$_3$O$_4$ with the ratio of Li/Co=1:1 was calcined (600 °C) and then sintered (900 °C) in flowing O$_2$ gas. Electrochemical oxidation was carried out with a constant current (i.e., galvanometric) setup utilizing an airtight flat cell filled with a nonaqueous electrolyte. The electrochemical cell consisted of an as-synthesized LiCoO$_2$ pellet and an aluminum metal disk as the cathode and anode, respectively. No auxiliary agents (e.g., acetylene black and Teflon powder) were added to the bulk pellet to avoid any magnetic noise sources. Since high-valent cobalt oxides tend to experience chemical instability when exposed to atmospheric moisture, sample handling and characterization were carefully made in an inert gas atmosphere. Details of experimental procedures are given elsewhere.

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Single-phase CoO$_2$ samples were successfully obtained through the aforementioned electrochemical synthesis technique. Figure 1 shows a typical voltage versus $x$ plot for the Li$_x$CoO$_2$/Al cell. The $x$ values were estimated through theoretical calculations based on Faraday’s law with an assumption that the full amount of electricity was used for the Li deintercalation reaction. The cell voltage gradually increased with decreasing $x$ in Li$_x$CoO$_2$ and finally reached +4.78 V at $x=0.0$. As $x$ decreased below $=0.1$, the cell voltage increased rapidly to indicate the completion of lithium extraction.$^6$ The actual Li content ($x$) of the resultant CoO$_2$ sample was determined by means of inductively coupled plasma atomic emission spectroscopy to be below the detection limit of the apparatus, i.e., smaller than 0.01. This ensures that our CoO$_2$ samples are indeed the $x=0$ end member of the Li$_x$CoO$_2$ system.

In Fig. 2, x-ray powder diffraction patterns for the pristine Li$_x$CoO$_2$ and the CoO$_2$ samples are shown. The pattern for Li$_x$CoO$_2$ was readily refined based on space group $R-3m$ with the lattice parameters $a=2.814$ Å and $c=14.05$ Å, being in good agreement with those previously reported.$^6,9$ For CoO$_2$, on the other hand, diffraction peaks were indexed based on space group $P-3m1$ with the lattice parameters $a$

\[ a=2.82 \text{ Å} \] and $c=4.238$ Å. The LiCoO$_2$ phase crystallizes in the so-called O3-type structure, in which Li ions occupy the octahedral site with three CoO$_2$ layers per unit cell, while the CoO$_2$ phase possesses an O1-type structure consisting of a single CoO$_2$ layer only per unit cell. Oxygen-content analysis was performed based on hydrogen reduction experiments in a 5% H$_2$/Ar gas flow with a thermobalance. The oxygen content of the sample was determined to be CoO$_{1.98 \pm 0.02}$. Thus, the resultant CoO$_2$ sample is essentially oxygen stoichiometric, implying that the highest formal valence of cobalt is realized, i.e., $V_{Co}^{\text{III}}=+4.0$.

In the cell voltage versus $x$ curve shown in Fig. 1, one may notice that there appears a narrow plateau at about $x=0.12$ prior to the rapid increase in voltage, suggesting the existence of another stable phase neighboring on the $x=0$ end member. We thus synthesized a Li$_{0.12}$CoO$_2$ sample precisely controlling the electric charge setting at $x=0.12$. It is found that the $x=0.12$ sample is indeed of single phase possessing a hexagonal structure with the lattice parameters $a=2.821$ Å and $c=27.13$ Å (Fig. 2). The crystal of the $x=0.12$ phase is reported to consist of alternate stacking of a Li-deintercalated O3-type block (as in LiCoO$_2$) and a Li-free O1-type block (as in CoO$_2$), leading to a six-CoO$_2$-layer unit cell that is called “H1-3.”$^{10,11}$ Note that Li$_{0.12}$CoO$_2$ ($V_{Co}^{\text{III}}=+3.88$) may correspond to an electron-doped phase of CoO$_2$ ($V_{Co}^{\text{III}}=+4$).

Magnetic susceptibility ($\chi$) measurements were performed with a superconducting quantum interference device magnetometer (MPMS-XL, Quantum Design). The $\chi$ vs $T$ plots for the LiCoO$_2$ (pristine), Li$_{0.12}$CoO$_2$, and CoO$_2$ samples are given in Fig. 3. The $\chi$ value for the LiCoO$_2$ sample is small in magnitude and little dependent on temperature due to the nonmagnetic nature of low-spin Co$^{\text{III}}$. Surprisingly, the CoO$_2$ and Li$_{0.12}$CoO$_2$ samples also exhibit temperature-independent susceptibility in the temperature range between 50 and 300 K. The susceptibility data for CoO$_2$ are in good agreement with those reported by de Vaulx et al.,$^7$ although their sample contains a large amount of secondary phases. The $\chi$ vs $T$ plots were fitted with the following formula: $\chi=\chi_0+C/(T-\Theta)$, where $\chi_0$, $C$, and $\Theta$ denote the constant susceptibility, the Curie constant, and the Weiss temperature, respectively. Fitted values for $\chi_0$, $C$, and $\Theta$ are

\[ \chi_0=14 \text{ emu/kmol} \]

\[ C=4 \text{ emu/kmol} \]

\[ \Theta=20 \text{ K} \]
summarized in Table I. The $C$ value for the CoO$_2$ sample yields an effective magnetic moment ($\mu_{\text{eff}}$) of 0.18$\mu_B$/Co site, being much smaller than the theoretical spin-only value of low-spin Co$^{III}$ ($S=1/2$), i.e., 1.73$\mu_B$/Co site. Thus, any localized spin model is unlikely.

We conclude that (1) the magnetism of CoO$_2$ is featured with a temperature-independent susceptibility with a relatively large value for $\chi_0$ and that (2) the upturn behavior at low temperatures likely originates from an extrinsic cause, e.g., lattice defects. A possible (and the most conservative) explanation for this is that the CoO$_2$ phase is a Pauli-paramagnetic metal with itinerant electrons. Assuming that the difference in magnitude of $\chi_0$ between CoO$_2$ and LiCoO$_2$ corresponds to the Pauli-paramagnetic contribution, the density of states at the Fermi level, $D(e_F)$, is calculated at 13 electrons/eV. This value is three times larger than the theoretical value: $D(e_F) \approx 4$ electrons/eV for nonmagnetic CoO$_2$ according to local density approximation calculations.\(^\text{12}\)

It is worthwhile to compare the magnetic properties of “electron-doped” Li$_{0.12}$CoO$_2$ to that of the parent phase, CoO$_2$. Our magnetic data (Fig. 3) demonstrate that the $\chi$-$T$ curve for Li$_{0.12}$CoO$_2$ is essentially identical to that for CoO$_2$, indicating that Li$_{0.12}$CoO$_2$ is also a Pauli paramagnet of the same magnetic origin as CoO$_2$. Thus, the $x=0$ composition is not a singular point in the electronic phase diagram of the $A_x$CoO$_2$ systems. The situation is in sharp contrast to the case of high-$T_c$ superconductive copper oxides in which the parent material is a Mott insulator. The present study implies that any theoretical approaches starting from a Mott insulator may not be appropriate for discussion of the metallic state in $A_x$CoO$_2$.

In summary, synthesis and properties of CoO$_2$, the $x=0$ phase of the $A_x$CoO$_2$ systems ($A=$Li,Na), were reported. Single-phase bulk samples of CoO$_2$ were successfully obtained through electrochemical deintercalation of Li from pristine LiCoO$_2$. The magnetism of CoO$_2$ is featured with a temperature-independent susceptibility with a relatively large value, being essentially identical to that of a Li-doped phase, Li$_{0.12}$CoO$_2$. This suggests that the CoO$_2$ phase is a Pauli-paramagnetic metal with itinerant electrons.

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TABLE I. The $\chi_0$, $C$, and $\Theta$ values for the LiCoO$_2$, Li$_{0.12}$CoO$_2$, and CoO$_2$ samples. These values were determined based on least-squares calculations for the $\chi$ vs $T$ plots (Fig. 3).

<table>
<thead>
<tr>
<th>$x$ in Li$_x$CoO$_2$</th>
<th>$\chi_0$ ($10^{-8}$ emu/mol Oe)</th>
<th>$C$ ($10^{-3}$ emu K/mol Oe)</th>
<th>$\Theta$ (K)</th>
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<tbody>
<tr>
<td>0.0</td>
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<td>−3.3</td>
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<td>1.34</td>
<td>0.89</td>
<td>−1.6</td>
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