

Deintercalated NaCoO₂ and LiCoO₂

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Na_{0.5}CoO₂ and Na_{0.6}CoO₂ were obtained by chemical deintercalations of NaCoO₂ using bromine and iodine as oxidizing agents, respectively. The magnetic susceptibility of Na_{0.6}CoO₂ obeyed a Curie-Weiss law with $T_\theta = -550$ K, $\mu_{\text{eff}} = 1.9 \mu_B$. This compound had a resistivity of about 1 Ωcm at room temperature with an activation energy of 0.01 eV. Na_{0.5}CoO₂ revealed an almost temperature-independent paramagnetism above 270 K. The susceptibility anomalously decreased below 270 K. Electrochemically prepared Li_{0.5}CoO₂ showed similar behavior in its magnetic property. Na_{0.5}CoO₂ had a resistivity of about $10^{-1} \Omega\text{cm}$ at room temperature and an activation energy less than 0.01 eV. © 1986

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Introduction

A series of alkali transition metal oxides, AMO_2 , have α -NaFeO₂-type layered structure, which can be described as an ordered rock salt structure (1). Transition metals are octahedrally surrounded by oxygens forming an $(MO_2)_n$ infinite sheet by edge-sharing. The M - M distance in the MO_2 layers is relatively short, and is one of the determining factors of the electronic properties of AMO_2 compounds. NaCoO₂ and LiCoO₂ have been expected to show metallic behavior because the Co-Co distances (2.88 Å and 2.82 Å, respectively) in CoO₂ layers are shorter than Goodenough's critical distance $R_c = 2.90$ Å for Co³⁺ ions (2). There have been no previous reports on the electron transport properties of these compounds.

The interlayered alkali ions can be partly removed from the interlayer region of AMO_2 compounds. Electrochemical deintercalation was first reported on LiCoO₂ by

Mizushima *et al.* (3, 4) and then several electrochemical investigations were performed on NaMO₂ where $M = \text{Ti, Cr, Co, Ni}$ in relation to battery applications (5-7). Powder X-ray diffraction results were reported on the deintercalated products, but other characterizations have not yet been made. This is probably because the amount of material available from the electrochemical deintercalations was insufficient for other physical measurements. We have shown that it is possible to deintercalate sodium partly from NaMO₂ where $M = \text{Cr, Fe, Co, or Ni}$ using iodine and bromine as oxidizing agents in acetonitrile (CH₃CN) (8). The chemical deintercalation yields sufficient amounts of homogeneous samples to investigate some properties. Drastic changes of electronic properties were observed after deintercalations of NaCrO₂ and α -NaFeO₂ (9, 10). On deintercalation the distances between transition metals within the MO_2 layers decrease and the interlayer distances slightly expand. Thus en-

hancement of direct bonding between transition metal ions within a layer and also two-dimensional behavior upon deintercalation might be expected.

In the present paper, results of the electrical resistivity and magnetic susceptibility of NaCoO_2 , LiCoO_2 , and their chemically and electrochemically deintercalated products are reported.

Experimental

NaCoO_2 was prepared by the reaction of Co_3O_4 with a small excess of Na_2O_2 in air at 500°C for 2 days (11). LiCoO_2 was synthesized by heating the mixture of Co_3O_4 and Li_2CO_3 in air at 900°C for 2 days (3). NaCoO_2 and LiCoO_2 were oxidized with $\text{I}_2/\text{CH}_3\text{CN}$ and $\text{Br}_2/\text{CH}_3\text{CN}$ in a Teflon bottle for 1 day. $\text{Li}_{0.5}\text{CoO}_2$ was prepared electrochemically in the cell $\text{Li}/1\text{ M LiClO}_4$ in propylene carbonate/ LiCoO_2 using a $200\text{-}\mu\text{A}/\text{cm}^2$ constant current. The chemical compositions of the products were determined using atomic absorption for alkali and cobalt ions. Magnetic susceptibility measurements were carried out using Faraday's method from 77 to 400 K. Electrical resistivities were measured in helium down to 77 K on the sample compacted at 3 GPa. A two-probe d.c. method was used for the measurements. Seebeck effects were measured at room temperature on the sample bars having dimensions of $5 \times 5 \times 20$ mm.

Results and Discussion

Na_xCoO_2

The deintercalation products of NaCoO_2 in $\text{I}_2/\text{CH}_3\text{CN}$ and $\text{Br}_2/\text{CH}_3\text{CN}$ had approximate compositions of $\text{Na}_{0.6}\text{CoO}_2$ and $\text{Na}_{0.5}\text{CoO}_2$, respectively. NaCoO_2 has a hexagonal lattice with $a = 2.880 \text{ \AA}$ and $c = 15.58 \text{ \AA}$. Powder X-ray diffraction data of the two deintercalated products were similar and could be indexed with monoclinic cell pa-

rameters: $a = 4.899 \text{ \AA}$, $b = 2.829 \text{ \AA}$, $c = 16.53 \text{ \AA}$, $\beta = 90.58^\circ$ for $\text{Na}_{0.6}\text{CoO}_2$ and $a = 4.878 \text{ \AA}$, $b = 2.816 \text{ \AA}$, $c = 16.68 \text{ \AA}$, $\beta = 90.82^\circ$ for $\text{Na}_{0.5}\text{CoO}_2$. These two phases probably belong to the nonstoichiometric compositional range of $\text{Na}_{0.6}\text{CoO}_2\beta$ which were prepared at high temperature and reported to have a definite composition (11). The small difference in composition between these deintercalated products can be well explained by their open circuit voltages in relation to the oxidation potentials of iodine and bromine (8). There was some confusion as to the nature of these products in a previous report due to the close similarity of their composition and X-ray data (8).

Figure 1 shows the temperature variation of magnetic susceptibility for NaCoO_2 , $\text{Na}_{0.6}\text{CoO}_2$, and $\text{Na}_{0.5}\text{CoO}_2$. NaCoO_2 showed a weak and temperature-independent paramagnetic susceptibility, which was attributed to Van Vleck paramagnetism for the Co^{3+} ion in a low spin state of $3d^6$ configuration (12, 13). Logarithmical resistivities were plotted against temperature as indicated in Fig. 2. NaCoO_2 shows semiconducting behavior with an activation energy of 0.02 eV, although it can be expected to be a metallic conductor on the basis of Co-Co distance (2).

The magnetic susceptibility results showed an effective spin consistent with the formation of Co^{4+} upon deintercalation. The susceptibility of $\text{Na}_{0.6}\text{CoO}_2$ obeyed a Curie-Weiss law with $T_\theta = -550 \text{ K}$, $\mu_{\text{eff}} = 1.9 \mu_{\text{B}}$ in the temperature range 200 to 400 K (Fig. 1). The calculated effective moment is $1.1 \mu_{\text{B}}$ using spin-only values for Co^{3+} ($t_{2g}^6 e_g^0$) and Co^{4+} ($t_{2g}^5 e_g^0$). This result suggests that $\text{Na}_{0.6}\text{CoO}_2$ has localized d electrons. The conductivity of $\text{Na}_{0.6}\text{CoO}_2$ was higher than that of NaCoO_2 , but the temperature dependence of conductivity indicated semiconducting behavior with the very small activation energy of 0.01 eV as shown in Fig. 2. $\text{Na}_{0.5}\text{CoO}_2$ revealed an almost temperature-independent paramagnetism above 270

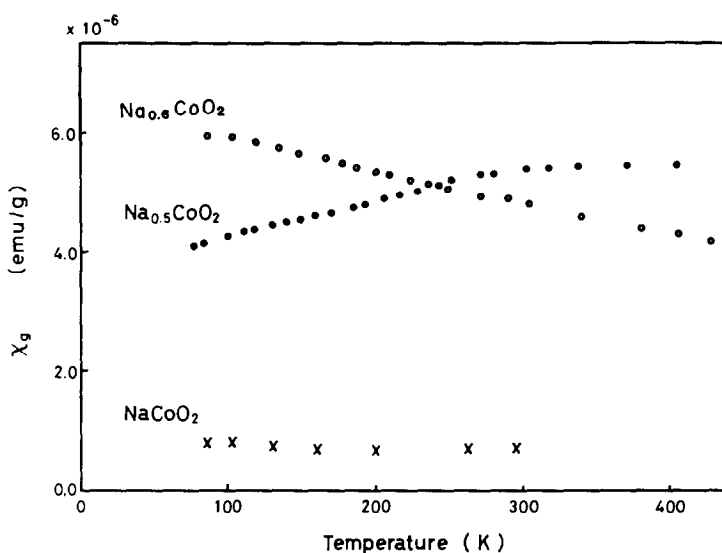


FIG. 1. Temperature variation of the magnetic susceptibilities of Na_xCoO₂ ($x = 1, 0.6, 0.5$).

K. The susceptibility decreased anomalously below 270 K. This behavior in susceptibility is quite similar to that of NaVS₂ (metallic type 1) (14). In the case of NaVS₂, the slightly temperature-dependent paramagnetism at high temperatures was attributed to Pauli paramagnetism of conduction electrons. The anomalous behavior below 250 K in NaVS₂ was related to a lattice dis-

tortion due to the formation of a charge density wave (CDW). Electrical resistivity of Na_{0.5}CoO₂ slightly decreased with increasing temperature having an activation energy less than 0.01 eV as shown in Fig. 2. A small anomaly is suggested around 260 K in the electrical resistivity corresponding to the change in magnetic susceptibility. The resistivity was $\sim 10^{-1} \Omega\text{cm}$ and significantly

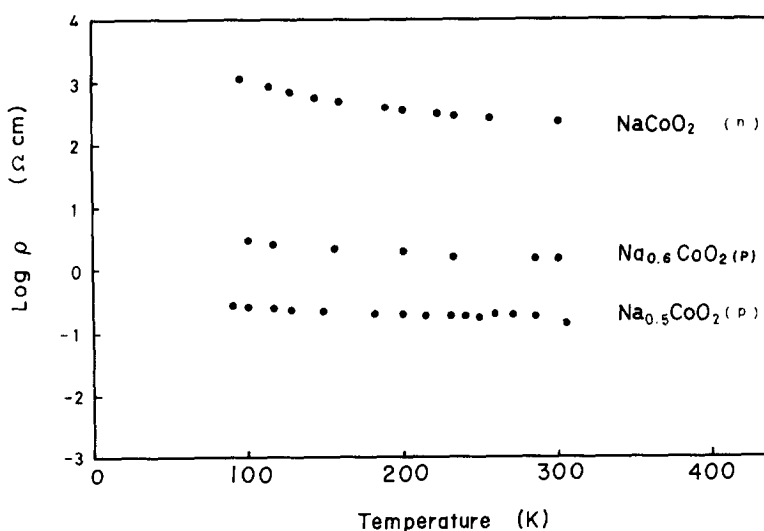


FIG. 2. Temperature variation of the electrical resistivities of Na_xCoO₂ ($x = 1, 0.6, 0.5$).

larger than the expected value for a metallic conductor. The sample might be essentially metallic above 260 K. The negative temperature dependence of resistivity might be due to the scattering of carriers at grain boundaries in the compacted sample.

In NaCoO_2 , the Co^{3+} ion is in the low spin state ($t_{2g}^6 e_g^0$). The t_{2g} orbital of NaCoO_2 is filled. NaCoO_2 was found to be a n -type semiconductor. The positive hole is made in the filled band by deintercalation. $\text{Na}_{0.6}\text{CoO}_2$ was a p -type semiconductor with a small activation energy and localized d electrons. It is possible to form a partly filled d band in $\text{Na}_{0.5}\text{CoO}_2$ at high temperatures. The anomaly around 260 K in the resistivity and the susceptibility may be due to some phase transition or possibly to an opening of a gap at the Fermi surface due to the onset of a CDW. However, this must be confirmed by diffraction measurements of superlattice lines.

Li_xCoO_2

LiCoO_2 had a hexagonal crystal lattice having lattice parameters $a = 2.817 \text{ \AA}$ and c

$= 14.05 \text{ \AA}$. Lithium could not be removed using oxidizing agents as previously described because the open circuit voltage of LiCoO_2 was above the oxidation potential of bromine (8). An X-ray diffraction pattern of the electrochemically prepared $\text{Li}_{0.5}\text{CoO}_2$ could be indexed with hexagonal lattice parameters of $a = 2.810 \text{ \AA}$ and $c = 14.41 \text{ \AA}$, which agree quite well with previous results (3).

The magnetic susceptibility of LiCoO_2 (Fig. 3) showed a weak and practically temperature independent paramagnetism which can be attributed to Van Vleck paramagnetism for the Co^{3+} ion in a low spin state as in NaCoO_2 . LiCoO_2 showed a semiconducting behavior with a large activation energy of about 0.5 eV. $\text{Li}_{0.5}\text{CoO}_2$ revealed a slightly temperature-dependent paramagnetism above 180 K and an anomalous change was observed at 180 K in the susceptibility (Fig. 3). The results are quite similar to those of Na_xCoO_2 .

In summary chemical and electrochemical deintercalations were performed on LiCoO_2 and NaCoO_2 . Using bromine and io-

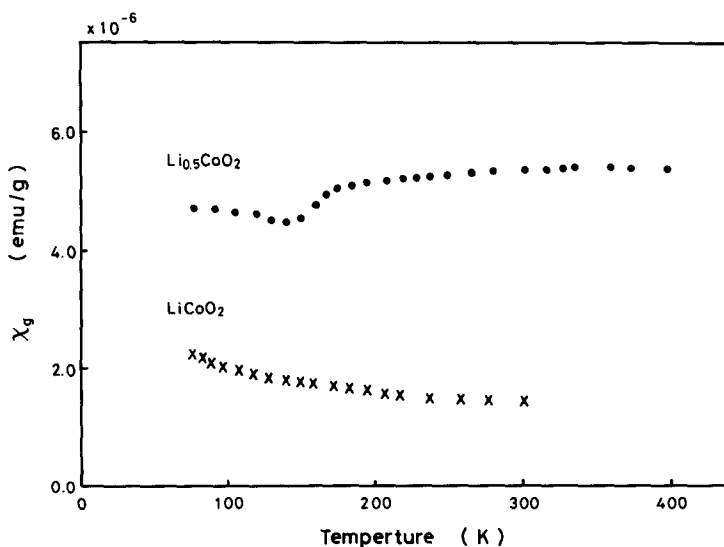


FIG. 3. Temperature variation of the magnetic susceptibilities of LiCoO_2 and $\text{Li}_{0.5}\text{CoO}_2$.

dine as oxidizing agents, Na_{0.5}CoO₂ and Na_{0.6}CoO₂, respectively, were obtained. These reagents did not work on LiCoO₂ because their oxidizing potentials are too low. LiCoO₂ and NaCoO₂ are semiconductors having activation energies of ≈ 0.5 eV and ≈ 0.02 eV, respectively. The compounds showed weak paramagnetisms, which can be attributed to Van Vleck paramagnetism and/or a small amount of Co²⁺ impurity. Temperature dependences of magnetic susceptibility of Li_{0.5}CoO₂ and Na_{0.5}CoO₂ revealed a slightly temperature-dependent paramagnetism at high temperatures. At lower temperatures the susceptibilities of both materials showed anomalous behavior which might be attributed to the formation of a CDW. The electrical resistivity decreased by an order of 10⁴ Ω cm upon the deintercalation of NaCoO₂. Critical distances can be estimated as 2.90 Å for Co³⁺ and 2.82 Å for Co⁴⁺ in low spin state in oxides (2). The observed Co–Co distances are 2.81 Å for Li_{0.5}CoO₂ and 2.82 Å for Na_{0.5}CoO₂. They are much shorter than $R_c(\text{Co}^{3+})$ and are close to $R_c(\text{Co}^{4+})$. Thus delocalization of *d* electron might be expected for the deintercalated products. The metallic properties of K_{0.50}CoO₂ and K_{0.67}CoO₂ which were prepared by calcinations KO₂ and Co₃O₄ were accounted for by similar arguments (15).

The interlayer distances between CoO₂ layers expanded from 4.68 to 4.77 Å in LiCoO₂ and from 5.19 to 5.56 Å in NaCoO₂ as a result of deintercalation. The expansions might enhance two-dimensional behavior in A_xCoO₂ compounds. Thus, a charge density wave might be induced in the deintercalated products. Measurements of electrical resistivity on single crystal and

electron diffraction studies are required for further investigation.

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