

## Observation of Distinct Metallic Conductivity in $\text{NaCo}_2\text{O}_4$

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Electrical conductivity and powder X-ray studies have been made on  $(\text{Sr}_{1-\alpha}\text{Na}_{[\alpha]})\text{CoO}_x$  after firing at  $980^\circ\text{C}$  in air. The data are explainable in terms of the mixed phase of  $\text{SrCoO}_x$  ( $x \sim 2.5$ ) and  $\text{NaCo}_2\text{O}_4$ . We found a distinct metallic conductivity in  $\text{NaCo}_2\text{O}_4$ ; the resistivity decreases linearly to 12 K from room temperature. This compound may be another candidate mother oxide for future study of high-temperature superconductivity.

KEYWORDS:  $\text{NaCo}_2\text{O}_4$ ,  $\text{Sr}_{1-\alpha}\text{Na}_{[\alpha]}\text{CoO}_x$ ,  $\text{SrCoO}_x$ , metallic conductivity, magnetic susceptibility, superconductivity of oxides

We have observed metallic conductivity in  $\text{NaCo}_2\text{O}_4$ , i.e., an end compound of the  $(\text{Sr}_{1-\alpha}\text{Na}_{[\alpha]})\text{CoO}_x$  system, and in this paper we report the brief outline of the results hitherto obtained. Here we have used  $[\alpha]$  for the  $\alpha$  of Na, because Na ions are volatile during the firings. In Fig. 1, we show our initial data of the electrical resistivity-temperature curve obtained for impure  $[\text{SrCoO}_x$  ( $x \sim 2.5$ )] in which sodium ions are present as contaminants, because  $[\text{CoCO}_3$  basic] is used as a starting material. Here we have observed a broad maximum of the resistivity, which is quite similar to the behavior reported by Watanabe and Takeda<sup>1)</sup> for their low-temperature phase of  $\text{SrCoO}_x$  (hexagonal), which was prepared below  $850^\circ\text{C}$  in air similarly using  $[\text{CoCO}_3]$ . These results motivated us to conduct more detailed study in this area, as to the possibility and mechanism of high-temperature superconductivity of oxides.

In our study, the specimens were prepared by the standard technique for oxide ceramics, in which the raw materials were  $\text{Na}_2\text{CO}_3$  (99.5%),  $\text{SrCO}_3$  (99.9%), and  $\text{Co}_3\text{O}_4$  (99.9%). The mixed powders were calcined at  $850^\circ\text{C}$  for 6 hours in air, pressed into disks, and sintered at  $980^\circ\text{C}$  in air for 8 hours, followed by subsequent cooling in the furnace. The results for  $(\text{Sr}_{1-\alpha}\text{Na}_{[\alpha]})\text{CoO}_x$  with  $\alpha = 0, 0.2$  or  $0.24, 0.3, 0.4, 0.6, 0.8$  and  $1.0$  are shown in Figs. 2 and 3. The resistivity-

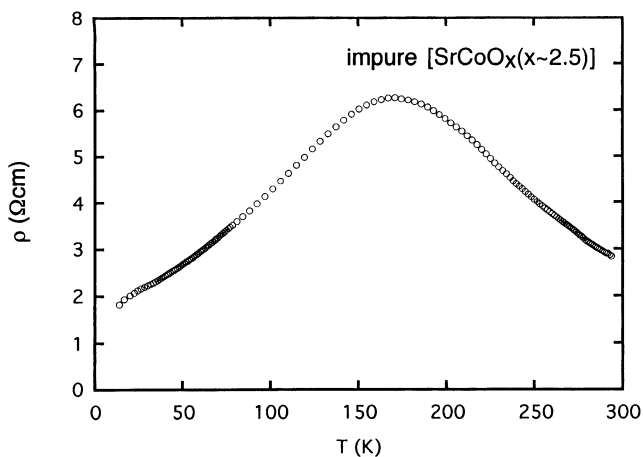


Fig. 1. Electrical resistivity versus temperature curve for impure  $[\text{SrCoO}_x$  ( $x \sim 2.5$ )] in which sodium ions are assumed to be present as contaminants.

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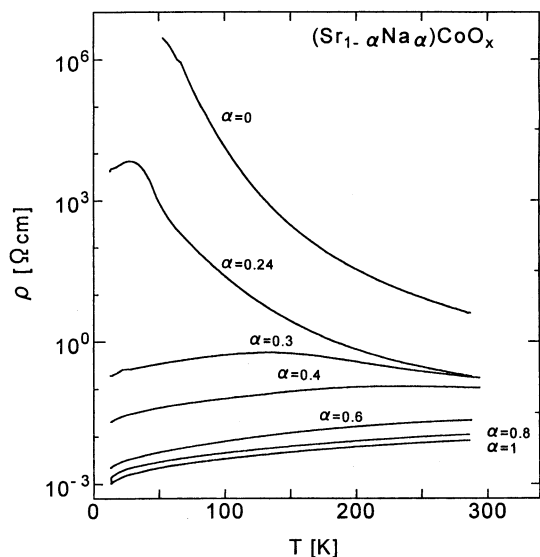


Fig. 2. Electrical resistivity versus temperature curves for  $(\text{Sr}_{1-\alpha}\text{Na}_{[\alpha]})\text{CoO}_x$  with  $\alpha = 0.0, 0.24, 0.3, 0.4, 0.6, 0.8,$  and  $1.0$ , indicating the monotonous transition from semiconductive to metallic phases. Final firing was in air at  $980^\circ\text{C}$  with cooling in furnace.

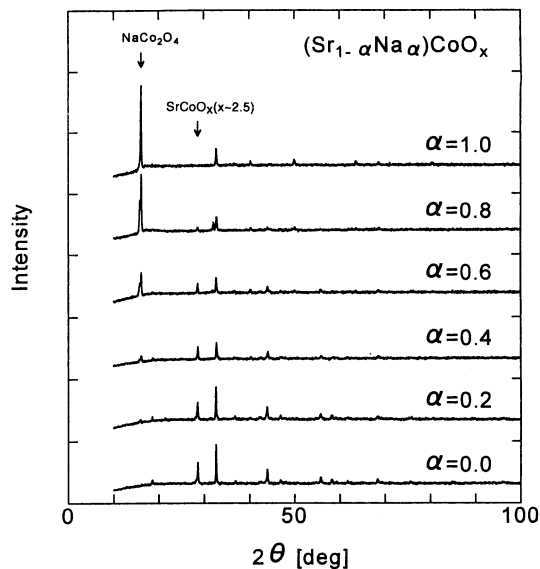


Fig. 3. X-ray ( $\text{Cu K}\alpha$ ) powder diffraction profiles of  $(\text{Sr}_{1-\alpha}\text{Na}_{[\alpha]})\text{CoO}_x$  with  $\alpha = 0.0, 0.2, 0.4, 0.6, 0.8,$  and  $1.0$ . The strongest lines of  $\text{NaCo}_2\text{O}_4$  and  $\text{SrCoO}_x$  ( $x \sim 2.5$ ) are indicated by arrows. Final firing was in air at  $980^\circ\text{C}$  with cooling in furnace.

temperature curves in Fig. 2 were obtained by a conventional four-terminal method in a closed-cycle refrigerator, and the powder X-ray diffraction patterns of Fig. 3 were obtained using an X-ray diffractometer with Cu K $\alpha$  radiation.

In Fig. 2, we can clearly see the transition of the character of the conductivity from semiconductive to metallic with the increase of  $\alpha$ . The curve in Fig. 1 is similar to the curve of  $\alpha=0.3$  in Fig. 2. Figure 3 indicates that the intermediate specimens are explainable by presuming that the  $(\text{Sr}_{1-\alpha}\text{Na}_{\alpha})\text{CoO}_x$  are the so-called mixed phase of the two end compounds. The uncertainty of the solubilities of the two compounds is within a few percent. We assume at present that the same explanation holds for the resistivity-temperature curves in Fig. 2.

We know from the data of the previous studies<sup>1-4)</sup> and our own data that the  $\text{SrCoO}_x$  prepared in air has the high-temperature phase (orthorhombic, Brownmillerite structure) and low-temperature phase (hexagonal), of which the separation temperature seems to be in the range of 850 $^{\circ}$ ~900 $^{\circ}$ C.<sup>2)</sup> Our X-ray data for  $\alpha=0$  correspond to the low-temperature phase and are similar to the data for  $\text{SrCoO}_{2.52}$  of Takeda *et al.*<sup>2)</sup> We know further from experiments that the  $\text{SrCoO}_x$  prepared in air at 800 $^{\circ}$ ~1000 $^{\circ}$ C followed by furnace cooling has  $x\sim 2.5$ , so that we designate this phase as  $\text{SrCoO}_x$  ( $x\sim 2.5$ ).

In 1973, Fouassier *et al.*<sup>5)</sup> conducted an extensive study on the  $\text{Na}_x\text{Co}_2\text{O}_4$  ( $x\leq 2$ ) system in the temperature range of 600~750 $^{\circ}$ C, and reported four phases with  $\alpha$ - $\text{Na}_x\text{Co}_2\text{O}_4$  ( $0.90\leq x\leq 1$ ),  $\alpha'$ - $\text{Na}_{0.75}\text{Co}_2\text{O}_4$ ,  $\beta$ - $\text{Na}_x\text{Co}_2\text{O}_4$  ( $0.55\leq x\leq 0.60$ ), and  $\gamma$ - $\text{Na}_x\text{Co}_y\text{O}_2$  ( $x<1$ ,  $y\leq 1$ ,  $0.55\leq x/y\leq 0.74$ ). In 1974, Von Jansen and Hoppe<sup>6)</sup> showed that the compound  $\text{NaCo}_2\text{O}_4$ , whose crystal structure is hexagonal with the space group of  $D_6^h\text{-P6}_3\text{22}$ , is isostructural with  $\text{KCo}_2\text{O}_4$  and has the lattice constants of  $a=2.843$  Å and  $c=10.81$  Å. Their specimen was obtained after firing in a Ag container at 700 $^{\circ}$ C for 7 days with  $\text{Na}_2\text{O}_2$  and  $\text{Co}_3\text{O}_4$  at the ratio of Na:Co=1.1:2.0. The structure is close to that of  $\gamma$ - $\text{Na}_x\text{Co}_y\text{O}_2$  of the former study. Since our data for  $\alpha=1$  are similar to those of Von Jansen and Hoppe, we have assumed that this end structure is identical to their  $\text{NaCo}_2\text{O}_4$ . Our lattice constants are  $a=2.888$  Å and  $c=10.906$  Å, which are slightly different from those of Jansen and Hoppe.

In Figs. 4 and 5, we show, for  $\text{NaCo}_2\text{O}_4$ , the variations of the resistivity in a linear scale, and the magnetic susceptibility  $\chi$  and its inverse,  $\chi^{-1}$ , against temperature  $T$ , respectively. The magnetic susceptibilities were measured by a vibrating sample magnetometer (VSM) in a closed-cycle refrigerator. The decrease of the resistivity from room temperature is linear down to 12 K. We have not yet confirmed whether  $\text{NaCo}_2\text{O}_4$  becomes superconductive at low temperatures, but the tendency seems clearly against the presence of residual resistivity. Delmas *et al.*<sup>7)</sup> reported that  $\text{KCo}_2\text{O}_4$ , which is isostructural to  $\text{NaCo}_2\text{O}_4$ , showed metallic conduc-

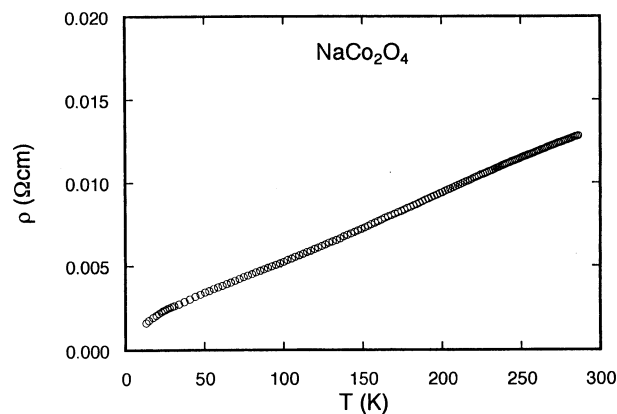


Fig. 4. Variation of the electrical resistivity of  $\text{NaCo}_2\text{O}_4$  in linear scale against the temperature.

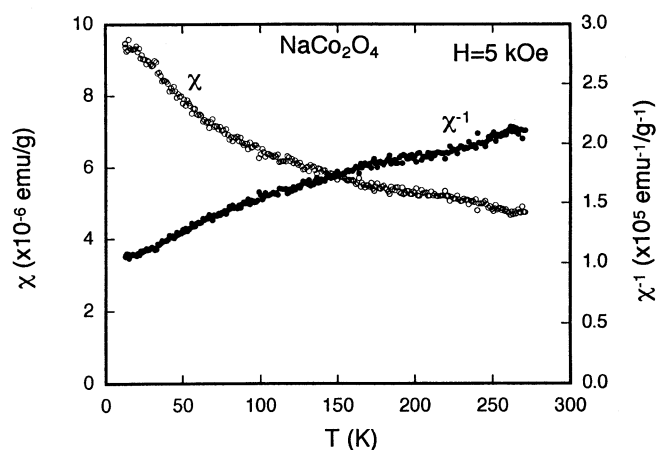


Fig. 5. Magnetic susceptibility,  $\chi$ , and its inverse,  $\chi^{-1}$ , of  $\text{NaCo}_2\text{O}_4$  as functions of temperature.

tion. Our results for  $\text{NaCo}_2\text{O}_4$  are quite consistent to their data, but, they did not find any sharp decrease of the resistivity below 50 K. The magnetic susceptibility,  $\chi$ , is small, at least one order of magnitude smaller than, *e.g.*, that of  $[\text{SrCoO}_x$  ( $x\sim 2.5$ )] in Fig. 1, and the temperature variation is even smaller. This indicates that the spin magnetic moments of the cobalt ions do not survive at 0 K. A similar tendency is also reported for  $\text{KCo}_2\text{O}_4$ .<sup>7)</sup> At present, no further comments can be made regarding these magnetic and electronic characteristics.

- 1) H. Watanabe and T. Takeda: *Proc. Int. Conf. Ferrites, 1970* (Univ. Tokyo Press, Tokyo, 1971) p. 588.
- 2) Y. Takeda, R. Kanno, T. Takada, O. Yamamoto, M. Takano and Y. Bando: *Z. Anorg. Allg. Chem.* **540/541** (1986) 259.
- 3) JCPDS Card No. 40-1018.
- 4) JCPDS Card No. 34-1475.
- 5) C. Fouassier, G. Matejka, J.-M. Reau and P. Hagenmuller: *J. Solid State Chem.* **6** (1973) 532.
- 6) M. Von Jansen and R. Hoppe: *Z. Anorg. Allg. Chem.* **408** (1974) 104.
- 7) C. Delmas, C. Fouassier and P. Hagenmuller: *J. Solid State Chem.* **13** (1975) 165.