Thermal and Electrical Properties of γ-Na$_x$CoO$_2$ ($0.70 \leq x \leq 0.78$)

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We have performed specific heat and electric resistivity measurements of Na$_x$CoO$_2$ ($x = 0.70$-$0.78$). Two anomalies have been observed in the specific heat data for $x = 0.78$, corresponding to magnetic transitions at $T_c = 22$ K and $T_K \simeq 9$ K reported previously. In the electrical resistivity, a steep decrease at $T_c$ and a bending-like variation at $T_K (=120$ K for $x = 0.78$) have been observed. Moreover, we have investigated the $x$-dependence of these parameters in detail. The physical properties of this system are very sensitive to $x$, and the inconsistent results of previous reports can be explained by a small difference in $x$. Furthermore, for a higher $x$ value, a phase separation into Na-rich and Na-poor domains occurs as we previously proposed, while for a lower $x$ value, characteristic behaviors of the specific heat and the electrical resistivity at the low-temperature region, the system is expected to be in the vicinity of the magnetic instability which virtually exists below $x = 0.70$.

KEYWORDS: Na$_x$CoO$_2$, specific heat, electrical resistivity, spin fluctuation, nearly ferromagnetic

Na$_x$CoO$_2$ is a quite attractive compound for condensed matter physicists and chemists because of its rich physical properties. For instance, Na$_{0.5}$CoO$_2$ shows unusually high thermoelectrical performance.$^{1,2}$ In the case of $x = 0.35$, superconductivity below $\sim 5$ K is induced by water insertion.$^3$ Na$_{0.75}$CoO$_2$ shows a magnetic transition at $T_c = 22$ K, which is believed to be caused by spin density wave (SDW) formation.$^{4,5}$ Moreover, for Na$_x$CoO$_2$ ($x = 0.7 - 0.75$), Sommerfeld constant, $\gamma$, has been estimated from the specific heat to be $\sim 24$-$30$ mJ/Co mol-K$^2$,$^{4,6-9}$ and the heavy fermion behavior has been observed.$^8$

Despite intensive studies, there are still serious discrepancies in physical property data of Na$_x$CoO$_2$. The reports on the specific heat are inconsistent with each other, particularly those on low-temperature data: the $C/T-T^2$ curve (C: specific heat, $T$: temperature) in the low-temperature region has been reported to show an upturn$^6,7,10$ linear dependence$^8,11$ or a downturn.$^9$

As regards the electrical resistivity, the variation of the data is less than that of the specific heat. When the transition at $T_c$ is magnetically observed, the resistivity shows a drop at $T_c$, while no anomaly at $T_c$ in a transition-free sample is observed. A slight bend in the resistivity around 100 K is seen clearly in the data reported by Shi et al.$^{12}$ and is observed in most cases,$^7,9,13$ the origin of which is left unclarified.

The discrepancies in the physical properties including magnetic properties seem to be mainly caused by their strong dependencies on the Na content $x$. Very recently, we prepared γ-Na$_x$CoO$_2$ samples by varying $x$ minutely and measured their magnetic properties. We found that the solid-solution range of the system is quite narrow with $0.70 \leq x \leq 0.78$, and moreover, its magnetic properties are very sensitive to $x$.$^{14}$ Most previous studies were carried out only for one of the two end members with $x \sim 0.7$ and $\sim 0.78$. In the present study, we measured the specific heats and the electrical resistivities for the same sets of samples used in the previous magnetic measurements, in order to elucidate their dependences on $x$ and to clarify the origin of the above-mentioned discrepancies.

The powder samples of Na$_x$CoO$_2$ ($x = 0.70$, 0.72, 0.74, 0.76, 0.78, 0.80, and 0.82) were synthesized by the conventional solid state reaction from the stoichiometric mixtures of Na$_2$CO$_3$ (99.99%) and Co$_3$O$_4$ (99.9%). The detailed preparation method and the results of chemical analyses of the samples are described elsewhere.$^{14}$ The specific heat data were collected using a commercial physical property measurement system (PPMS, Quantum Design) for the sintered samples with weights of 14-27 mg. The measurements were usually carried out with decreasing temperature, and the magnetic field ($H$) was applied before cooling. The electrical resistivity ($\rho$) was also measured using PPMS by the conventional four-probe method for the sintered samples with typical dimensions of $8 \times 3 \times 1$ mm$^3$ (1-2 mm distance between adjacent probes) with increasing temperature at a rate of 1 K/min, after the samples were cooled down to 1.8 K at the same rate.

The $C/T-T^2$ curves of Na$_{0.78}$CoO$_2$ are shown in Fig. 1(a). Two anomalies are seen: (i) a sharp peak at $T_c = 22$ K and (ii) a dull downward bend at $T_K \simeq 9$ K. These anomalies correspond to the magnetic transitions.$^{14}$ The latter transition will be discussed later. The $C/T-T^2$ curves of Na$_x$CoO$_2$ with various $x$ values are shown in Fig. 1(b).

The peak position and shape at $T_c$ measured with increasing temperature were completely the same as those measured with decreasing temperature, and, as seen in Fig. 1(a), $T_c$ is also independent of $H$. Moreover, it does not depend on $x$ as shown in Fig. 1(b). Only the jump
in $C/T$ at $T_C$, $\Delta C/T$, decreases with decreasing $x$ below 0.78 as seen in the inset of Fig. 1(b). These strongly suggest that the phase responsible for the transition in question does not change but only its fraction varies with $x$, which is consistent with the magnetic measurements. Namely, for the samples with $x$ above 0.74, a phase separation into Na-rich and Na-poor domains occurs. In addition, as seen in the inset of Fig. 1(b), the independent behavior of $\Delta C/T$ on $x$ for $x > 0.78$ supports the higher limit of the solid-solution range of $x = 0.78$.\(^{14}\)

The Sommerfeld constants $\gamma$ and Debye temperatures $\Theta$ were first estimated by the function of

$$C/T = \gamma + AT^2$$  \hspace{1cm} (1)

($A = \frac{12\pi^4 Nk_B}{5\Theta}$; $N$, the number of the atom and $k_B$, Boltzmann constant) using the data between 26 and 36 K ($700 \leq T^2 \leq 1300$ K\(^2\)). The parameters obtained are shown in Fig. 2 by circular markers. Since the temperature range seems to be high, the same parameters were estimated from the same data by a different function:

$$C = \gamma T + 9Nk_B\left(\frac{T}{\Theta}\right)^3 \int_0^{\Theta/T} dx \frac{x^4e^x}{(e^x - 1)^2}$$  \hspace{1cm} (Debye model),

where the fitting parameters are only $\gamma$ and $\Theta$. As shown in Fig. 2, the $\gamma$ and $\Theta$ values obtained from the two different equations are in good agreement with each other, which means that eq. 1 is applicable to this temperature range of these compounds. These $\gamma$ values agree well with those reported previously,$^{4,6-9}$ and lie on the line of $\gamma = 74.6 - 62.4x$. This $x$-dependence of $\gamma$ indicates that the density of states (DOS) decreases with increasing Fermi energy, although it is difficult to estimate the influence of the phase separation of the samples with higher $x$ on the $\gamma$ values; it is confirmed that this negative inclination corresponds to that of the energy dependence of DOS above the Fermi energy of Na\(_{0.5}\)CoO\(_2\).\(^{15}\)

Below about 15 K, the line of eq. 1 is located above the experimental data (see the inset of Fig. 1(a)), which implies that some part of DOS is lost due to the transition at $T_C$. This fact seems to be in favor of the SDW formation at $T_C$ rather than the typical second-order transition suggested previously.\(^4\) However, it should be noted that the SDW state is realized only in a part of a sample as mentioned above and suggested previously.\(^{14}\)

The dull anomaly at $T_K$, which has been observed by a single crystal,\(^9\) is likely due to another weak ferromagnetic transition.\(^{14}\) The transition temperature $T_K$ is independent of $H$ as in the case of $T_C$. Since the degree of the anomaly seems to change synchronically with $\Delta C/T$ at $T_C$, it seems that the domain which undergoes the transition at $T_C$ is followed by the transition at $T_K$. The transition at $T_K$ may be caused by the change in the magnetic structure formed in the first transition at $T_C$ with additional lost of DOS. It is, however, necessary to perform microscopic experiments, such as nuclear magnetic resonance (NMR), to elucidate details of the transition.

The $T$-dependence of $\rho$ for $x = 0.78$ is shown in Fig. 3(a). Three characteristic features are seen in this log-log plot: (i) a metallic behavior in the entire $T$-range, (ii) a steep decrease in $\rho$ below $T_C$, and (iii) bending of the curve at $T_b = 120$ K. The metallic behavior even below $T_C$ and $T_K$ is consistent with the existence of the residual $\gamma$ of approximately 10 mJ/Co mol-K\(^2\) for $x = 0.78$ at 0 K.

The steep decrease in $\rho$ below $T_C$ is, of course, related to the magnetic transition seen in the specific heat and the magnetic susceptibility.\(^{14}\) Indeed, as shown in Fig.
In the specific heat for $x = 0.70$, two anomalies were seen, corresponding to magnetic transitions at $T_C = 22$ K and $T_K \approx 9$ K. Both anomalies become less pronounced simultaneously with decreasing $x$, while keeping $T_C$ and $T_K$ unchanged, and disappear below $x = 0.72$. This behavior is consistent with our phase separation model proposed previously. The Sommerfeld constant was estimated to be $\gamma = 26.31 \text{ mJ/mol} \cdot \text{K}^2$, which is consistent with the previous reports. The resistivity measurements showed that this system is metallic for both the entire $x$ and $T$ ranges. The steep decrease at $T_C$ and
the bending-like variation at $T_b (=120K)$ were found in the resistivity for $x = 0.78$. $T_b$ increased slightly with $x$, the origin of which is unclear. From these results, for a higher $x$ value, a phase separation into Na-rich and Na-poor domains occurs as we previously proposed, while, for a lower $x$ value, the system is expected to be in the vicinity of the magnetic instability which virtually exists below $x = 0.70$.

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