Mass-enhanced Fermi-liquid ground state in Na$_{1.5}$Co$_2$O$_4$

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Magnetic, transport, and specific-heat measurements have been performed on layered metallic oxide Na$_{1.5}$Co$_2$O$_4$ as a function of temperature T. Below a characteristic temperature $T^* = 30 - 40$ K, electrical resistivity shows a metallic conductivity with a T^2 behavior and magnetic susceptibility deviates from the Curie-Weiss behavior showing a broad peak at ~ 14 K. The electronic specific-heat coefficient γ is ~ 60 mJ/mol K^2 at 2 K. No evidence for magnetic ordering is found. These behaviors suggest the formation of mass-enhanced Fermi-liquid ground state analogous to that in d-electron heavy fermion compound LiV$_2$O$_4$.

There has been a great deal of interest in the physics of geometrically frustrated spin systems, in which the long-range magnetic order tends to be suppressed and novel types of phase transitions or ground states are expected. In particular, the recent discovery of the heavy fermion (HF) behavior in LiV$_2$O$_4$ has stimulated new interest in the geometrically frustrated systems, where the HF behavior is demonstrated by the d electrons on the spinel B lattice.[1] One of the most exciting scenario is the generation of the d-electron heavy fermions through the effect coming from the geometrical frustration, which is possibly inherent due to the geometry of V atoms and the negative Weiss temperature of -40 K.[1]

The low-T properties of LiV$_2$O$_4$ are apparently of intermetallic dense Kondo systems, showing a fairly large electronic specific-heat coefficient $\gamma \sim 420$ mJ/mol K^2,[1,2] a broad maximum of magnetic susceptibility,[1,3] and a metallic conductivity with a T^2 behavior below a coherence temperature $T^* = 20 - 30$ K.[4] Indeed, the origin of the HF behavior has been considered from various angles, but a uniform understanding remains to be achieved. Urano *et al.* suggest the importance of the geometrical frustration,[4] which is inferred from the occurrence of spin-glass order by the slight substitution for the Li or V sites.[5–7] A recent inelastic neutron-scattering study has revealed a feature of frustrated magnetism in LiV$_2$O$_4$.[8] On the other hand, a broad maximum of ^{7}Li $1/T_1(T)$ at $30 - 50$ K and a constant $(T_1 T)^{-1}$ at low T have been found, suggesting a dense Kondo picture.[9] ^{7}Li $1/T_1(T)$ has also been interpreted from the viewpoint of the ferromagnetic instability predicted in the spin fluctuation theory.[10] From the theoretical side, various approaches have been introduced and several groups focus on the geometrical frustration.[11–13]

To gain more insight into this problem, the discovery of other examples of d-electron material to exhibit HF behavior is of significant importance. From this viewpoint, it is interesting to note the low-T properties of the metallic oxide γ-Na$_x$Co$_2$O$_4$ ($1 \leqslant x \leqslant 1.5$), which is well known as a large thermoelectric material.[14] This compound has been found to exhibit a large γ of ~ 80 mJ/mol K^2 at 2 K and a Curie-Weiss behavior of magnetic susceptibility with a Weiss temperature $\Theta \sim -120$ K showing no sign of magnetic order.[15–17] Na$_x$Co$_2$O$_4$ has a layered structure consisting of CoO$_2$ layers in which the Co atoms form a two-dimensional regular triangular lattice with interlayers of Na atoms alternatively stacked along the c axis.[18] In addition to the large γ value and the metallic conductivity, the absence of magnetic order and the arrangement of the magnetic ions sitting on a geometrically frustrated lattice are characteristic features in common with LiV$_2$O$_4$. Also, the C15 Laves phase compound (Y$_{0.95}$Sc$_{0.05}$)Mn$_2$, in which the arrangement of the Mn atoms is equivalent to B sites on spinel lattice, has been found to show no magnetic order and HF behavior with $\gamma = 150$ mJ/mol K^2.[19]

In the present work, the intrinsic low-T properties of Na$_{1.5}$Co$_2$O$_4$ have been investigated through the measurements of dc magnetic susceptibility (χ), electrical resistivity (ρ), and specific heat (C). For the precise investigations, high-purity specimens which were melted and grown in a floating-zone furnace were prepared. The crystal growth was performed in a high-pressure oxygen atmosphere of $0.5 - 1.0$ MPa. The final products were not single crystals but multiple crystals. All the peaks observed in the powder x-ray diffraction were indexed as γ-Na$_x$Co$_2$O$_4$. The lattice constants were estimated to be $a = 2.84(5)$ Å and $c = 10.85(2)$ Å, similar to those reported in the previous work.[20] The chemical composition of Na$_x$Co$_2$O$_4$ was determined to be $x \sim 1.5$ by inductively coupled plasma analysis. dc magnetic susceptibility was measured by a superconducting quantum interference device magnetometer. Specific heat was measured by a thermal relaxation method. Electrical resistivity was measured using a standard four-probe technique.

Figure 1 shows the $\chi(T)$ data for the melt-grown crystal of Na$_{1.5}$Co$_2$O$_4$ in a magnetic field of $H = 1$ T. A remarkable feature is a broad peak of $\chi(T)$ at $10 - 20$ K, which is similar to that observed in LiV$_2$O$_4$.[1] No indication of magnetic order above 2 K was found in our field-cooled and zero-field-cooled $\chi(T)$ measurements. While for the sintered sample of Na$_{1.5}$Co$_2$O$_4$, the $\chi(T)$ curve has been reported to show a monotonic increase as temperature decreases.[17] This is probably because the low-T peak is masked by a Curie-like behavior of magnetic impurities or defects contained in the sintered sample. Also for LiV$_2$O$_4$, a broad peak of $\chi(T)$ is often masked by a Curie-like behavior depending on the sample quality.[3] The $\chi(T)$ curve for the melt-grown crystal
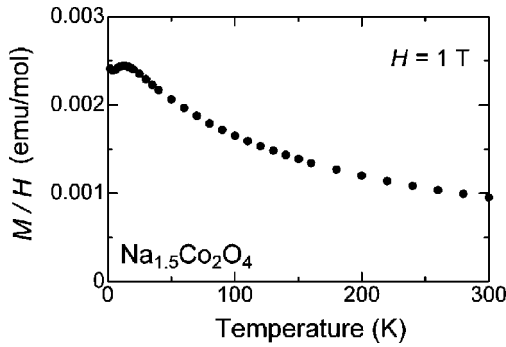
FIG. 1. Plots of magnetic susceptibility vs temperature data for $Na_{1.5}Co_2O_4$ at $H = 1$ T.

was fitted by the expression $\chi(T) = \chi_0 + C/(T - \Theta)$ for $50 \leqslant T \leqslant 300$ K, yielding a Curie constant $C = 0.369$ emu/mol K, a Weiss temperature $\Theta = -139$ K, and a T-independent susceptibility $\chi_0 = 1.12 \times 10^{-4}$ emu/mol. For $NaCo_2O_4$, Co ion has a mixed valence between Co^{3+} ($3d^6$) and Co^{4+} ($3d^5$) ($Co^{3+}/Co^{4+} = 1$), which are presumably in the low spin state with $S = 0$ and $S = 1/2$, respectively. The value of C corresponds to an effective magnetic moment $\mu_{eff} \sim 1.22\mu_B$ per Co site.

Next, we show the $\chi(T)$ data for $Na_{1.5}Co_2O_4$ at various magnetic fields up to 7 T in Fig. 2. The inset of Fig. 2 shows the $\chi(T)$ data for LiV_2O_4, which were collected using the specimen used in the previous work.[7] In the $\chi(T)$ curves both for $Na_{1.5}Co_2O_4$ and LiV_2O_4, a broad peak is observed at $10-20$ K, and a low-T upturn seen at $H = 0.1$ T vanishes at $H = 7$ T. This is due to the saturation of the moments of the magnetic impurities in the high magnetic field, indicating that the intrinsic $\chi(T)$ behavior is observed at $H = 7$ T. A remarkable feature is that the height and position of the peak commonly appear to be almost unchanged by the application of high magnetic field. Moreover, the peak temperature of $\chi(T)$ at $H = 7$ T for $Na_{1.5}Co_2O_4$ is identified as $T_p \sim 14$ K, similar to that for LiV_2O_4 ($T_p = 15-16$ K). The broad peak behavior in $\chi(T)$ is similarly observed in intermetallic dense
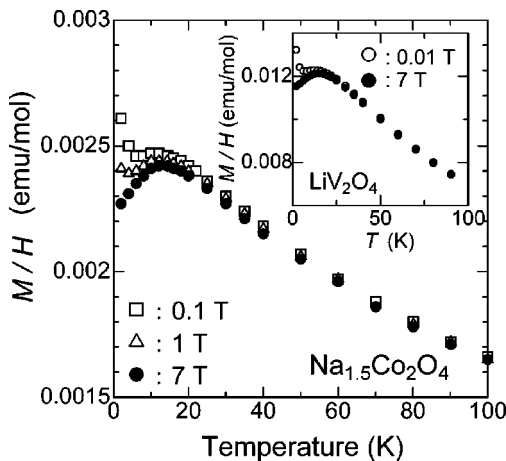

FIG. 2. Plots of magnetic susceptibility vs temperature data for the melt-grown crystal of $Na_{1.5}Co_2O_4$ in various magnetic fields up to 7 T. The inset shows those for LiV_2O_4.
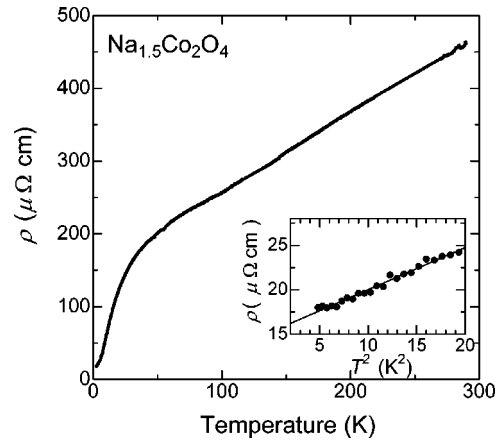

FIG. 3. Temperature dependence of electrical resistivity for the melt-grown crystal of $Na_{1.5}Co_2O_4$. The inset shows the data of electrical resistivity plotted against T^2.

Kondo systems, which are thought to become Pauli paramagnetic below the peak temperature. The broad peak behavior, however, does not agree with $S = 1/2$ Kondo model predictions,[3] since the behavior is limited to the model with $J \geqslant 3/2$.[21]

For LiV_2O_4, a metallic behavior with $\rho(T) \propto T^2$ has been observed below $T^* = 20-30$ K, indicating the formation of heavy-mass Fermi liquid (FL) below T^*.[4] The results of the $\rho(T)$ measurements for the melt-grown crystal of $Na_{1.5}Co_2O_4$ are displayed in Fig. 3. $\rho(T)$ was measured along the cleaved (001) surface of the melt-grown crystal. The sample was not a single crystal but we think that the data roughly represent the in-plane resistivity due to the crystal orientation. In Fig. 3, the $\rho(T)$ curve decreases as the temperature is lowered below 300 K and shows a higher rate of decrease below $30-40$ K. The inset of Fig. 3 shows a plot of ρ vs T^2 at low T, clearly indicating a T^2 behavior in $\rho(T)$. Thus, the $\rho(T)$ data suggest the FL behavior below $T^* = 30-40$ K. T^* was found to nearly correspond to the temperature below which the deviation from the Curie-Weiss behavior in $\chi(T)$ is apparent, as in LiV_2O_4.[4] We obtain a coefficient of the T^2 term, $A = 0.48$ $\mu\Omega$ cm/K^2, which yields $A/\gamma^2 \sim 1.3 \times 10^{-4}$ $\mu\Omega$ cm/K^2/(mJ/mol K^{-2})^2. The value of A/γ^2 is fairly larger than that for the Kadowaki-Woods relation, i.e., $A/\gamma^2 \sim 10^{-5}$ $\mu\Omega$ cm/K^2/(mJ/mol K^{-2})^2, but the value would be reduced if we used a single-crystal specimen for the $\rho(T)$ measurement.

The $\rho(T)$ data in Fig. 3 is inconsistent with that measured using a single-crystal specimen of $NaCo_2O_4$ prepared by NaCl-flux technique in the previous work,[14] where $\rho(T)$ along the (001) plane decreases monotonously as temperature decreases even at low T. The origin of the discrepancy is unclear but a similar discrepancy has also been observed between sintered samples,[22,23] one of which shows a metallic behavior with a marked decrease in $\rho(T)$ below ~ 40 K, similar to $\rho(T)$ in Fig. 3, and is prepared by "rapid heat-up technique."[23] One may consider that the $\rho(T)$ data in Fig. 3 reflect not only in-plane resistivity but also out-of-plane resistivity, which has been reported to show a maximum at ~ 200 K.[14] However, we note that $\rho(T)$ in Fig. 3 shows no tendency to make a maximum at ~ 200 K and out-of-plane
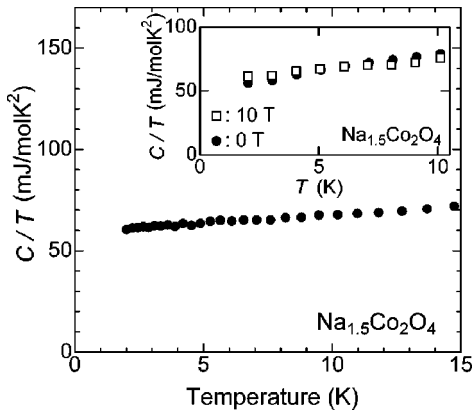
FIG. 4. Plots of specific heat divided by temperature C/T vs temperature T for the melt-grown crystal of $Na_{1.5}Co_2O_4$. The inset shows plots of C/T vs T in a magnetic field of 10 T (open squares) and in zero field (closed circles).

resistivity reported previously does not show a marked decrease below 40 K.[14]

Next, we investigate the behavior of C/T vs T for the melt-grown crystal of $Na_{1.5}Co_2O_4$. The result is shown in Fig. 4, where C/T shows a gradual decrease with decreasing temperature. The behavior is inconsistent with that for the sintered sample of $NaCo_2O_4$ in the previous work, where C/T increases with decreasing temperature below 5 K and reaches 80 mJ/mol K^2 at 2 K.[15] For a sintered sample, the contribution of the magnetic impurities, associated with the release of the magnetic entropy $S = \int C/T dT$ at low T, could not be excluded. In Fig. 4, $\gamma(2$ K$)$ $(\equiv C/T$ at 2 K) for $Na_{1.5}Co_2O_4$ is estimated to be ~ 60 mJ/mol K^2, which is three times larger than the value obtained from a recent band calculation.[24] The $C/T - T$ curve is qualitatively similar to that for UGa_3 $(\gamma = 43$ mJ/mol K$^2)$.[25] Using $\chi(2$ K$)$ $= 22$ mJ/mol T^2 and $\gamma(2$ K$) = 60$ mJ/mol K^2, we obtain a Wilson ratio $R_w \sim 2.7$. No indication of magnetic order was found for both samples in the measurements for $2 \leqslant T \leqslant 100$ K.

For LiV_2O_4, $\gamma(T)$ is fitted by the prediction for the $S = 1/2$ Kondo model, yielding a Kondo temperature $T_K = 27.5$ K.[1] Assuming one spin ($S = 1/2$) per formula unit, the $C/T - T$ curve for the melt-grown crystal of $Na_{1.5}Co_2O_4$ was also reproduced by the prediction for an $S = 1/2$ Kondo model (Ref. 26) with $T_K = 140$ K at least in the limited temperature range $2 \leqslant T \leqslant 15$ K. However, T_K is fairly higher than T_p $(\sim 14$ K$)$ for $\chi(T)$ and T^* $(= 30 - 40$ K$)$ for $\rho(T)$, inconsistent with a dense Kondo picture. In the inset of Fig.

4, the $C/T - T$ curve for the melt-grown crystal of $Na_{1.5}Co_2O_4$ in a magnetic field of $H = 10$ T, together with the zero-field data, is shown. $\gamma(2$ K$)$ for $H = 10$ T was estimated to be about 10% larger than that for zero field. This is contrary to that expected in conventional dense Kondo systems, where the value of γ tends to decrease with applied magnetic field and the field dependence is explained by the broadening of the Kondo resonance with applied field.[27,28] $Na_{1.5}Co_2O_4$ is unlike dense Kondo systems.

It should be noted that, in both of $Na_{1.5}Co_2O_4$ and LiV_2O_4, below T^*, the system shows FL behavior accompanied by a large mass enhancement and $\chi(T)$ deviates from the Curie-Weiss behavior showing a broad peak at 14 $- 16$ K. These behaviors suggest that the mass-enhanced FL ground states in these compounds are analogous to each other. A Kondo lattice model has been proposed for LiV_2O_4,[29] but is not adequate as a unified description for these compounds because $Na_{1.5}Co_2O_4$ is unlike dense Kondo systems as mentioned above. Moreover, it is not obvious how the localized moments and itinerant carriers as in f-electron HF compounds originate from the same $3d$ shell. A common feature between $Na_{1.5}Co_2O_4$ and LiV_2O_4 is the geometry of magnetic ions possibly giving rise to the spin frustration. Furthermore, HF behavior has been found in $(Y_{0.95}Sc_{0.05})Mn_2$ $(\gamma = 150$ mJ/mol K$^2)$ (Ref. 19) and β-Mn $(\gamma = 70$ mJ/mol K$^2)$,[30] both of which have magnetic ions sitting on a geometrically frustrated lattice and do not show any magnetic order. It is hard to imagine that the common structural feature possibly leading to the spin frustration in the mass-enhanced FL compounds noted above is accidental.

In summary, our measurements for the melt-grown crystal of $Na_{1.5}Co_2O_4$ have revealed a large γ value of ~ 60 mJ/mol K^2 at 2 K, a T^2 behavior of $\rho(T)$, and a characteristic broad peak behavior of $\chi(T)$ at ~ 14 K, suggesting the formation of mass-enhanced FL analogous to that in LiV_2O_4 below $T^* = 30 - 40$ K. Absence of magnetic order and mass-enhanced FL behavior are common features among $Na_{1.5}Co_2O_4$, LiV_2O_4, $(Y_{0.95}Sc_{0.05})Mn_2$, and β-Mn, all of which have a magnetic sublattice identical to that in geometrically frustrated systems. To advance towards further understanding for what happens in these systems, the theoretical explanation is desirable for the origin of the broad peak behavior in $\chi(T)$ and the role of the geometrically frustrated lattice in the ground state.

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