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Specific-heat evidence for strong electron correlations in the thermoelectric material $(\mathrm{Na,Ca})\mathrm{Co}_2\mathrm{O}_4$

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The specific heat of (Na,Ca)$\mathrm{Co}_2\mathrm{O}_4$ is measured at low-temperatures to determine the magnitude of the electronic specific-heat coefficient γ, in an attempt to gain an insight into the origin of the unusually large thermoelectric power of this compound. It is found that γ is as large as ~ 48 mJ/molK^2, which is an order of magnitude larger than γ of simple metals. This indicates that (Na,Ca)$\mathrm{Co}_2\mathrm{O}_4$ is a strongly-correlated electron system, where the strong correlation probably comes from the low-dimensionality and the frustrated spin structure. We discuss how the large thermopower and its dependence on Ca doping can be understood with the strong electron correlations. [S0163-1829(99)01036-X]

Recently, coexistence of a large thermopower (~ 100 μV/K at 300 K) and a low resistivity was found in a transition-metal oxide $\mathrm{NaCo}_2\mathrm{O}_4$,[1] which made this compound an attractive candidate for thermoelectric (TE) applications. Normally, large thermopower is associated with materials with low carrier densities and the thermoelectric properties are optimized for systems with typical carrier concentration of 10^{19} cm^{-3};[2] on the other hand, $\mathrm{NaCo}_2\mathrm{O}_4$ has two-orders-of-magnitude larger carrier density ($\sim 10^{21}$ cm^{-3}) and yet shows a thermopower comparable to that of the usual low-carrier-density TE materials.[1] The origin of the large thermopower in $\mathrm{NaCo}_2\mathrm{O}_4$ is yet to be understood.

In $\mathrm{NaCo}_2\mathrm{O}_4$, Co ion has a mixed valence between 3+ and 4+. Since $\mathrm{NaCo}_2\mathrm{O}_4$ is a layered system with a triangular lattice and Co^{4+} has spins,[1] it is expected that the interplay between charges and spins is playing a major role in producing the peculiar electronic properties of this compound, as in the case of high-T_c cuprates. In those systems where Coulomb interactions or spin fluctuations are important, it is often found that the electrons become strongly correlated and thus the simple band picture is not well applicable. In fact, magnetotransport studies of $\mathrm{NaCo}_2\mathrm{O}_4$ found that the Hall coefficient has an opposite sign to the thermopower and is strongly temperature dependent,[3] which suggests the presence of a strong correlation in this system. Therefore, to elucidate the origin of the large thermopower in $\mathrm{NaCo}_2\mathrm{O}_4$, it would be illuminating to determine the strength of the electron correlations in $\mathrm{NaCo}_2\mathrm{O}_4$ by measuring the electronic specific heat.

In this paper, we report our specific-heat measurement of $\mathrm{NaCo}_2\mathrm{O}_4$ at low temperatures, which determines the electronic specific-heat coefficient γ of this system. Since it has been reported that partial replacement of Na with Ca systematically increases the thermopower,[4] we measured a series of $(\mathrm{Na}_{1-x}\mathrm{Ca}_x)\mathrm{Co}_2\mathrm{O}_4$ samples and investigated the change of γ with Ca substitution. Our results show that this system is indeed a strongly-correlated system with $\gamma \simeq 48$ mJ/molK^2. It is also found that the Ca substitution does not change the γ value appreciably, while the Ca substitution reduces carrier concentration and increases the thermopower. Based on these observations and by invoking a simple Drude picture, we discuss that the large thermopower of $\mathrm{NaCo}_2\mathrm{O}_4$ is a result of a large electronic specific heat.

The samples used in this study are polycrystals prepared with a conventional solid-state reaction. Starting powders of NaCO_3, CaCO_3, and $\mathrm{Co}_3\mathrm{O}_4$ are mixed and calcined first at 860 °C for 12 h, and then at 800 °C for 6 h. Since it is known that Na tends to evaporate during the calcination, which produces impurity phases in samples with (nominally) stoichio-

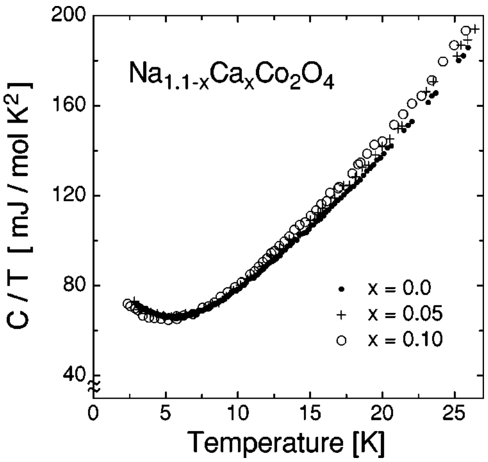

FIG. 1. Plot of C/T vs T of the $\mathrm{Na}_{1.1-x}\mathrm{Ca}_x\mathrm{Co}_2\mathrm{O}_4$ samples with $x = 0.0$, 0.05, and 0.10.

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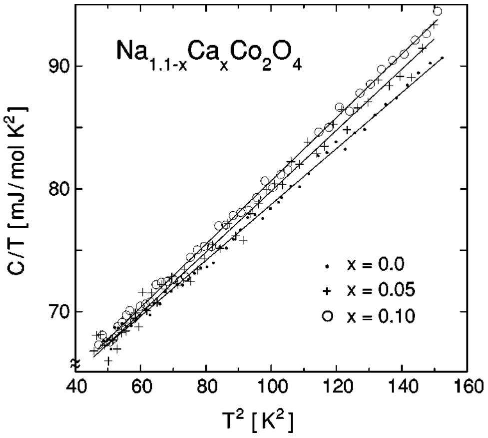

FIG. 2. Plot of C/T vs T^2 in the temperature range 7 - 12 K. The solid lines are the straight-line fits to the data.

metric composition, we used samples with the composition of $Na_{1.1-x}Ca_xCo_2O_4$.[4] The measurements were done on samples with three different Ca contents, $x=0.0$, 0.05, and 0.10. The specific heat is measured using a standard quasi-adiabatic method with a mechanical heat switch. The mass of the samples used for the measurement is typically 1000 mg and the heat capacity of the samples is always more than two orders of magnitude larger than the addenda heat capacity.

Figure 1 shows the specific heat C of $Na_{1.1-x}Ca_xCo_2O_4$ in one decade of temperature range, from 2 to 26 K. One may immediately notice two features: (i) The magnitude of C/T, about 80 mJ/molK^2 at 10 K, is large compared to simple metals (for example, pure Cu has $C/T \simeq 6$ mJ/molK^2 at 10 K). (ii) An unusual increase is observed at low temperatures for all x values.

As the first approximation, let us neglect the low-temperature increase in C for the moment and analyze the data for $T > 7$ K with the Debye formula. Since the temperature range to be analyzed is not quite low enough, we should include higher-order terms for the phonon specific heat and use the formula

$$C/T = \gamma + \beta T^2 + \beta_5 T^4 + \beta_7 T^6. \tag{1}$$

Figure 2 shows the result of the analysis that neglects β_5 and β_7 (thereby the fit becomes a straight line in the plot of C/T vs T^2) to show that the simple Debye formula without the higher-order lattice terms is moderately good to describe the data in the temperature region 7 - 12 K. It is clear from Fig. 2 that γ does not change appreciably with x. The values of γ and β obtained from the straight-line fits in Fig. 2 are listed in Table I. The result of the analysis that uses the full formula of Eq. (1) is shown in Fig. 3. Clearly, Eq. (1) describes the data above 7 K very well and we obtained good fits in the temperature range 7 - 26 K for all three data sets. The values of γ, β, β_5, and β_7 obtained from the fits in Fig. 3 are also listed in Table I. The electronic specific-heat coefficient γ obtained from this analysis is relatively large, 52–54 mJ/molK^2, compared to simple metals where γ is usually a few mJ/molK^2. Interestingly, γ does not change appreciably with x within our range of resolution.

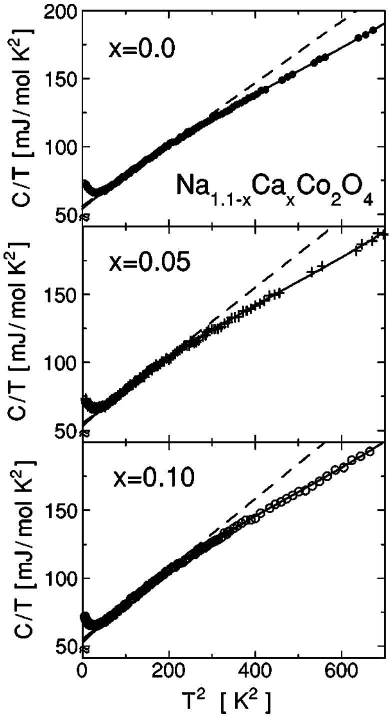

FIG. 3. Plots of C/T vs T^2 for $x=0.0$, 0.05, and 0.10. The data from 7 to 26 K are fitted with Eq. (1) (solid lines). The straight-line fits to the data in a narrower range (7 - 12 K) are also shown (dashed lines).

Perhaps as a better approximation, we next analyze our data using the formula that includes the Schottky term:

$$C/T = \gamma + \beta T^2 + \beta_5 T^4 + \beta_7 T^6 + c_0 (T_0/T)^2 \frac{\exp(T_0/T)}{(\exp(T_0/T)+1)^2}, \tag{2}$$

where T_0 is the characteristic temperature for the Schottky anomaly. Figure 4 shows the result of the fit of the data to

TABLE I. Parameters obtained from the fit to Eq. (1) and the Debye temperature Θ_D.

x	γ(mJ/molK^2)	β(mJ/molK^4)	β_5(mJ/molK^6)	β_7(mJ/molK^8)	Θ_D(K)
0.0	56.0 ± 0.2	0.227			393
0.0	54.0 ± 0.2	0.268	-1.95×10^{-4}	1.31×10^{-7}	372
0.05	54.7 ± 0.3	0.250			381
0.05	52.8 ± 0.4	0.296	-2.54×10^{-4}	1.77×10^{-7}	360
0.10	54.8 ± 0.2	0.259			376
0.10	52.3 ± 0.3	0.313	-2.75×10^{-4}	1.86×10^{-7}	353

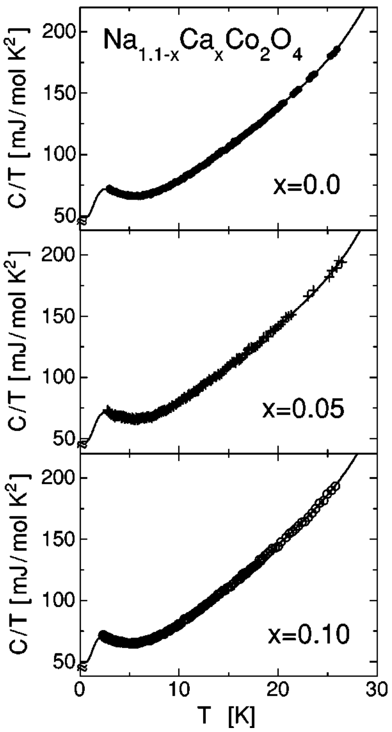

FIG. 4. Plots of C/T vs T together with the fits (solid lines) to Eq. (2), which includes the Schottky term.

Eq. (2). Apparently, the data in the whole temperature range measured (2–26 K) are well fitted with Eq. (2). The fitting parameters are listed in Table II. In both Tables I and II, the Debye temperatures calculated from β are also listed. Although the γ values obtained with Eq. (2) tend to be smaller compared to the result of the simpler analysis using Eq. (1), the changes are only about 10%. The values of γ with this analysis are about 48 mJ/molK^2 and, again, do not seem to be systematically correlated with x. We note that the low temperature limit used for fitting the Schottky term is 2 K; extending the measurement to lower temperature is desirable for a better determination of both the Schottky anomaly and the γ value. It is possible that γ becomes smaller than $\sim$48 mJ/molK^2 when the temperature range is extended.

The above results indicate that the magnitude of the enhancement of the density of states, which is represented in the magnitude of γ, does not show a clear change with Ca substitution. This is not a trivial result, because Ca substitution is expected to reduce carrier density n.[4] As mentioned in the introduction, the origin of the strong correlation in this system is probably the frustration of the antiferromagnetically interacting spins in the two-dimensional triangular lattice.[1] The magnetic susceptibility of $NaCo_2O_4$ shows a Curie-Weiss-like temperature dependence,[5] which suggests that spin fluctuations are actually appreciable in the magnetic properties. Also, a negative magnetoresistance has been observed in the temperature region where the resistivity does not show any localization behavior,[3] suggesting that the scattering from spin fluctuations is playing a major role in the charge transport. If the spin fluctuations are indeed the source of the strong correlation, one would expect the electron correlation to become stronger as the carrier concentration n is decreased, because mobile carriers tend to destroy spin correlations. Since we expect Ca doping to reduce the free-electron density of states (DOS) through the reduction in n, the effect of increasing correlation and the decreasing free-electron DOS upon Ca doping would tend to cancel with each other in determining the electronic specific heat. This might explain the apparent insensitivity of the observed γ to the Ca doping.

Now, let us briefly discuss the inference of our specific-heat result to the large thermopower by employing the Drude picture for the thermoelectric transport. Although the simple Drude picture cannot explain all the aspects of the complicated charge transport in $NaCo_2O_4$, it may help us to capture the basic physics for the enhancement of the thermopower. The Seebeck coefficient S of $NaCo_2O_4$ monotonically increases with T,[1] which suggests that the charge transport is Fermi-liquid like and the Drude model is expected to be used as the first approximation (as opposed to many other strongly-correlated systems, which show non-Fermi-liquid behavior). In the simple Drude picture, the Seebeck coefficient S is proportional to c_e/n, where c_e is the electronic specific heat.[6] Thus, when the strong correlation enhances c_e, the Drude picture predicts a large thermopower. More interestingly, the increase in S of $Na_{1.1-x}Ca_xCo_2O_4$ with the Ca concentration x is in qualitative agreement with the Drude picture, because our result shows γ (and thus c_e) to be almost unchanged upon Ca doping while n decreases with increasing x. This suggests that the simple Drude picture captures the basic physics of the thermoelectric transport in $NaCo_2O_4$ and thus the large thermopower is actually a result of the strong electron correlation. We note that an enhancement of the thermopower due to the large effective mass has recently been discussed theoretically for strongly-correlated systems.[7]

It should be mentioned that the rather large change in S with Ca doping (S increases by about 20% upon 0.1 of Ca substitution[4]) cannot be quantitatively explained by the simple Drude picture; apparently, a more sophisticated model should be employed for the full understanding of the large thermopower. A semiclassical Boltzmann approach gives a formula for S, which includes the energy dependence of the scattering time τ, $d\tau/d\varepsilon$.[8] Since the temperature dependence of S changes with Ca doping in $Na_{1.1-x}Ca_xCo_2O_4$,[4]

TABLE II. Parameters obtained from the fit to Eq. (2) and the Debye temperature Θ_D.

x	γ(mJ/molK^2)	β(mJ/molK^4)	β_5(mJ/molK^6)	β_7(mJ/molK^8)	c_0(mJ/molK^2)	T_0(K)	Θ_D(K)
0.0	48.4 ± 0.3	0.311	-3.06×10^{-4}	2.19×10^{-7}	16.9	8.14	354
0.05	47.5 ± 0.8	0.334	-3.48×10^{-4}	2.49×10^{-7}	17.4	8.13	346
0.10	49.0 ± 0.3	0.336	-3.29×10^{-4}	2.27×10^{-7}	14.0	7.24	345

one can expect that $d\tau/d\varepsilon$ is actually changing with Ca doping, which introduces an additional factor in determining the Ca-doping dependence of S.

In summary, we found that the electronic specific-heat coefficient γ of $NaCo_2O_4$ is about 48 mJ/molK^2, which indicates that $NaCo_2O_4$ is a strongly-correlated system. No apparent correlation was found between γ and the x value in $Na_{1.1-x}Ca_xCo_2O_4$, in which increasing x reduces the carrier concentration n. The increase in the Seebeck coefficient S with increasing x and the apparent insensitivity of γ to the change in x together suggest that the simple Drude picture, which gives $S \sim c_e/n$, captures the basic physics for the enhancement of the thermopower, although quantitatively the simple Drude picture is insufficient. Therefore, it may be concluded that the larger thermopower of $NaCo_2O_4$ is a result of the strong electron correlation.

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