Dependence of the specific heat of Na$_x$CoO$_2$·$y$H$_2$O/D$_2$O on sodium and water concentrations

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(Received 1 June 2005; published 26 August 2005)

We report specific heat measurements down to 0.4 K on the layered oxide Na$_x$CoO$_2$·$y$H$_2$O/D$_2$O with 0 ≤ $x$ ≤ 0.74 and $y$ = 0 and 1.4. For the nonhydrated system ($y$ = 0), the electronic specific heat coefficient $\gamma_e$ and the Debye temperature $\Theta_D$ vary nonmonotonically with $x$, both displaying minima when $x$ is close to 0.5. This indicates a systematic change of the electronic and vibrational structures with Na content. For both hydrated and deuterated systems ($x$ = 0.35 and $y$ = 1.4), the specific heat reveals a sharp peak with $\Delta C_p \sim 45.5$ mJ/mol K at $T_c$ ~ 4.7 K and an anomaly at $T_s$ ~ 0.8 K. While the origin of the latter is not clear, the former corresponds to the superconducting transition. With the application of magnetic fields up to 14 Tesla, $T_c$ decreases gradually but $T_s$ remains more or less unchanged. The implication of these results is discussed.

DOI: 10.1103/PhysRevB.72.060512

PACS number(s): 74.25.Bt, 74.20.Rp, 74.25.Jb, 74.90.+n

There is growing evidence that the strong electron-electron correlation in layered Na$_x$CoO$_2$ is responsible for some of its anomalous physical properties such as its “colossal” thermopower,$^{1,2}$ and possibly superconductivity in its hydrated form.$^3$ Although it is a good metal with high electrical conductivity for a wide Na-doping range except for $x$ = 0.5, both local-density approximation (LDA) calculations$^4$ and experimental work$^3$ indicate that the itinerant bands of Na$_x$CoO$_2$ are very narrow with $W \ll U$, where $W$ is the bandwidth and $U$ is the effective on-site Coulomb interaction. This implies a high value of the density of states (DOS) at the Fermi level. However, all specific heat data reported so far reveal a weak or moderate enhancement of electronic specific heat coefficient $\gamma_e$ for both hydrated and nonhydrated cases compared to the value from the LDA band structure.$^{4,6-9}$ In these reports, the $\gamma_e$ value was obtained by analyzing specific heat data above 2 K for $x$ in the range of 0.3–0.8. It is possible that the extracted $\gamma_e$ value does not represent that for $T$ = 0 K. On the other hand, recent calculations, using the LDA+U method, suggest that the strength and effect of Coulomb interactions are reduced with decreasing $x$.$^{10}$ One would thus expect a variation of $\gamma_e$ with $x$.

On the experimental side, the electronic properties of hydrated and nonhydrated Na$_x$CoO$_2$ have not been systematically studied as a function of composition. While the phase diagram shown in Ref. 11 is constructed from electrical transport and magnetic measurements for 1/3 ≤ $x$ ≤ 3/4 and water content $y$ = 1.4, little is known about how the thermodynamic properties vary with both $x$ and $y$. Of particular importance is the specific heat behavior in the superconducting state of the system, which can provide key information about the superconducting pairing symmetry. In this paper, we report the low-temperature specific heat of Na$_x$CoO$_2$·$y$H$_2$O/D$_2$O with 0 ≤ $x$ ≤ 0.74 and $y$ = 0 and 1.4.

Single crystals of Na$_x$CoO$_2$ were used for specific heat measurements. Starting with Na$_{0.74}$CoO$_2$ single crystals grown using a flux method,$^{12}$ crystals with smaller $x$ were obtained by chemical deintercalation as described in Ref. 6. By controlling the deintercalation time, we obtain single crystals with $x$ = 0.72 and 0.48, as determined from measurements of the $c$-axis lattice parameter using the calibration curve in Ref. 11. However, it is known that the above technique cannot extract all Na from Na$_x$CoO$_2$. In order to obtain CoO$_2$ ($x$ = 0) with the hexagonal structure, we extract all Li from LiCoO$_2$ powders using NO$_3$BF$_3$ as described in Ref. 13. Polycrystalline samples of Na$_{0.35}$CoO$_2$ and superconducting Na$_{0.35}$CoO$_2$·1.4H$_2$O/D$_2$O were prepared following a procedure similar to that described in Ref. 14. Specific heat measurements were carried out using a physical property measurement system (PPMS) from Quantum Design.

In Fig. 1, we present the temperature ($T$) dependence of the specific heat ($C_p$) for Na$_x$CoO$_2$ with $x$ ~ 0.74, 0.72, 0.48, 0.35, 0. Note that $C_p$ varies monotonically with $T$ between 0.4 and 10 K and the curve tends to move upward with increasing $x$. For easy analysis, we replot the data as $C_p/T$ vs $T^2$ as shown in Fig. 1(b). If the specific heat is due to electrons and phonons only, it is expected that $C_p/T$ will be a linear function of $T^2$ at low $T$. While this is true for CoO$_2$ ($x$ ~ 0) between 0.4 and 10 K, $C_p/T$ clearly deviates from linearity below ~ 2 K for samples with $x$ ≠ 0. The low-$T$ upturn indicates that an additional contribution sets in that increases with decreasing $T$. Similar behavior was reported previously and was attributed to a Schottky effect.$^7$ Thus, for

![FIG. 1. (a) Temperature dependence of the specific heat $C_p$ for single crystalline Na$_{0.74}$CoO$_2$ (filled circles), Na$_{0.72}$CoO$_2$ (unfilled circles), Na$_{0.48}$CoO$_2$ (crosses), polycrystalline Na$_{0.35}$CoO$_2$ (filled diamonds), and CoO$_2$ (unfilled diamonds) between 0.4 and 10 K. Shown in (b) is the replot of the data as $C_p/T$ vs $T^2$, and the solid curves are the fits of experimental data to Eq. (1).](image-url)
agreement with LDA+U calculations. The small effects not only the DOS
vary nonmonotonically with \( x \), displaying extrema for \( x \sim 0.48 \); (2) \( \alpha \) decreases with decreasing \( x \); (3) \( \Delta \) does not vary much with \( x \). Compared to the calculated band value of \( \gamma_N = 10 \text{ mJ/mol K}^2 \) for \( x > 0.5 \) (Refs. 4 and 10) and 13 mJ/mol K\(^2\) for \( x < 0.5 \), our \( \gamma_N \) values have a factor of 3 enhancement for \( x > 0.48 \) but are very close for \( x < 0.48 \).

This implies that the correlation effects are moderate for \( x > 0.48 \) and become negligible for \( x < 0.48 \), in very good agreement with LDA+U calculations. The small \( \gamma_N \) value for \( x \sim 0.48 \) is likely related to the charge ordering reported in Na\(_{0.35}\)CoO\(_2\) below 52 K. For Na\(_{0.48}\)CoO\(_2\), there may exist partial charge ordering, leading to a small \( \gamma_N \) value. It should also be mentioned that the \( \gamma_N \) for the end compound CoO\(_2\) is nonzero, consistent with the metallic behavior reported previously. Interestingly, the variation of \( x \) in Na\(_{x}\)CoO\(_2\) affects not only the DOS (reflected by \( \gamma_N \)) but also \( \Theta_D \) with a minimum occurring at the same composition (\( x \sim 0.48 \)) as that for \( \gamma_N \). This suggests strong coupling between electrons and the lattice, and the lattice tends to soften near \( x \sim 0.5 \). The monotonic decrease of \( \alpha \) with \( x \) reflects that the Schottky specific heat \( C_{p}^{Sch} \) decreases with Na content, and is almost negligible in CoO\(_2\). This is consistent with the trend that the low-\( T \) magnetic susceptibility decreases with decreasing \( x \). The almost constant \( \Delta \) value for different \( x \) strongly suggests that \( C_{p}^{Sch} \) is mainly controlled by nuclear moments.

We now focus on the specific heat of hydrated and deuterated Na\(_{0.35}\)CoO\(_2\). Shown in Fig. 2(a) is the \( T \) dependence of \( C_p \) for Na\(_{0.35}\)CoO\(_2\)-1.4H\(_2\)O/D\(_2\)O between 0.4 and 10 K. Compared to that of the parent compound, \( C_p \) of hydrated and deuterated Na\(_{0.35}\)CoO\(_2\) is larger at high \( T \) but smaller below \( \sim 2 \) K. Most prominent is the specific heat anomaly below \( T_c \sim 5 \) K in both hydrated and deuterated cases, reflecting the superconducting phase transition. To obtain superconducting-state properties, all nonelectronic contributions, which are not affected by the superconducting phase transition, should be subtracted from the total specific heat. As shown in Fig. 2(b), \( C_p/T \) reveals more or less linear dependence with \( T^2 \) above \( T_c \) for both hydrated and deuterated compounds. This suggests that the first two terms of Eq. (1) are dominating. While the low-\( T \) upturn is absent, \( C_{p}^{Sch} \) may be hidden due to sharp decrease of electronic specific heat in superconducting state. For comparison, we extract the

<table>
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<th>( x )</th>
<th>( \gamma_N ) (mJ/mol K(^2))</th>
<th>( \beta_5 ) (mJ/mol K(^4))</th>
<th>( \Theta_D ) (K)</th>
<th>( \beta_5 ) (mJ/mol K(^6))</th>
<th>( \alpha ) (mK(^2)/mol)</th>
<th>( \Delta ) (K)</th>
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<td>0.3958</td>
<td>257.4</td>
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<td>319.0</td>
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<tr>
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<td>0.0333</td>
<td>559.1</td>
<td>0.0319</td>
<td>0.5174</td>
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</table>

FIG. 2. (a) Temperature dependence of the specific heat \( C_p \) for polycrystalline Na\(_{0.35}\)CoO\(_2\)-1.4H\(_2\)O (filled circles), Na\(_{0.35}\)CoO\(_2\)-1.4D\(_2\)O (unfilled circles), and Na\(_{0.35}\)CoO\(_2\) (filled diamonds) between 0.4 and 10 K; (b) replot of the data in (a) as \( C_p/T \) vs \( T^2 \); solid curves are fits of experimental data to Eq. (1); (c) and (d) present the \( T \) dependence of \( (C_p-C_{p}^{n})/T \) and \( (C_p-C_{p}^{n})/T \) of Na\(_{0.35}\)CoO\(_2\)-1.4H\(_2\)O and Na\(_{0.35}\)CoO\(_2\)-1.4D\(_2\)O. In each case, the solid line is the linear fit of experimental data between 0.8 and 4.1 K and the broken line is the extrapolation of experimental data below 0.7 K to the origin.
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electronic specific heat with or without considering \( C_p^{Sch} \). Shown in Figs. 2(c) and 2(d) are the \( T \) dependence of the electronic specific heat assuming \( C_p^{el} = C_p - C_p^{ph} \) [Fig. 2(c)] or \( C_p^{el} = C_p - C_p^{ph} - C_p^{Sch} \) [Fig. 2(d)]. Here, parameters for \( C_p^{el} \) are assumed to be the same as that for Na0.35CoO2 (see Table I) since they cannot be determined by fitting data above \( T_c \) and \( C_p^{el}(T) \) are obtained by fitting the experimental data between 6 and 10 K without [Fig. 2(c)] or with [Fig. 2(d)] the consideration of the Schottky effect. It turns out that the results are almost the same at high \( T \) with only a slight difference at low \( T \). In both cases, note that the substitution of \( D \) for \( H \) has little effect on \( C_p^{el} \), or with

\[ T \]

measurements. This and the fact that all other \( C_p^{el} \) measurements on either powders \cite{17,18} or single crystals \cite{3} result in a large superconducting transition weakens and moves toward lower \( T \), indicating the suppression of \( T_c \) due to the dynamical instability of Na ions.\cite{24} To determine whether the anomaly at \( T_c \) is unlikely due to the small-gap contribution in the two-gap superconductivity scenario.\cite{22} Similar behavior was observed in the superconducting state of single crystalline KO\(_2\)O\(_6\)\cite{23} which was attributed to the dynamical instability of K ions.\cite{24} To determine whether the anomaly at \( T_c \) is unlikely due to the small-gap contribution in the two-gap superconductivity scenario.\cite{22}

To gain insight into the transition at \( T_c \) and anomaly at \( T_a \), we have measured the specific heat of Na0.35CoO2·1.4H\(_2\)O and Na0.35CoO2·1.4D\(_2\)O under the application of magnetic field. Shown in Fig. 3(a) is \( C_p/T \) vs \( T \) with \( H=0 \), 1, 2, 4, 7, 10, and 14 T. Interestingly, the anomaly at \( T_a \) seems to be insensitive to \( H \) and remains after subtracting \( C_p^{ph} \) and \( C_p^{Sch} \) [Fig. 3(b)]. This suggests that the anomaly at \( T_a \) is unlikely due to the small-gap contribution in the two-gap superconductivity scenario.\cite{22} Similar behavior was observed in the superconducting state of single crystalline KO\(_2\)O\(_6\)\cite{23} which was attributed to the dynamical instability of K ions.\cite{24} To determine whether the anomaly at \( T_c \) is due to the dynamical instability of Na (which is stronger than K, according to Ref. 24) in our studied superconducting systems, further theoretical investigation is necessary.

Nevertheless, the specific heat jump due to superconducting transition weakens and moves toward lower \( T \) with increasing \( H \), indicating the suppression of \( T_c \) and superconducting volume fraction. In Fig. 3(c), we plot the upper critical field \( H_c(2) \) vs \( T \) for polycrystalline Na0.35CoO2·1.4H\(_2\)O. Compared to that obtained from the electrical resistivity of single crystals\cite{3} and magnetic susceptibility measurements on powders,\cite{25} the averaged \( H_c(2)(T) \) shown in Fig. 3(c) for polycrystalline samples varies moderately with initial slope \( dH_c(2)/dT \) \( \sim -5.3 \) T/K. Using this value and the Werthamer-Helfand-Hohenberg (WHH) for-
mula for the dirty limit,\textsuperscript{26} we may estimate the $T$ dependence of $H_{c2}$ between 0 and $T_c$. Remarkably, our experimental $H_{c2}(T)$ follows very well the WHH expression represented by the dashed line in Fig. 3(c). At $T = 0$ K, the WHH formula gives $H_{c2}(0) = 17.1$ T. This allows us to estimate the coherence length $\xi(0) \sim 44 \text{Å}$ using $H_{c2} = \phi_0/2\pi\xi^2$ ($\phi_0$ is the flux quantum). As emphasized previously,\textsuperscript{3,25} the coherence length is short for a superconductor with such a low $T_c$. On the other hand, the reduction of the superconducting volume fraction due to the application of $H$ is reflected by the increase of $\gamma_{res}$ value. From linear extrapolation of $C_p/T$ in the linear regime of superconducting state to $T = 0$ K, we obtain the intercept $\gamma_{res}$ for each $H$ and plot them as $\gamma_{res}$ vs $H^{0.5}$ in Fig. 3(d) for Na$_{0.35}$CoO$_2$$\cdot$1.4H$_2$O/D$_2$O. As guided by the solid lines, $\gamma_{res}$ varies more or less linearly with $H^{0.5}$ for both systems. This is consistent with unconventional superconducting pairing symmetry with line nodes but is not a proof, since it has been seen in conventional superconductors as well.

Based on the present specific heat studies, we conclude that the electronic and vibrational properties are sensitive to $x$ but not $y$ in Na$_x$CoO$_2$$\cdot$yH$_2$O/D$_2$O. For the nonhydrated system with $y = 0$, both $\gamma_N$ and $\Theta_D$ change systematically with $x$, showing minima at $x \sim 0.48$. For the hydrated and deuterated system with $x = 0.35$, the variation of $y$ between 0 and 1.4 results in little effect on $\gamma_N$ value. There is evidence for “double transitions” with one at $T_c \sim 4.7$ K and another at $T_c \sim 0.8$ K. While the origin of the later “transition” is not very clear, our results provide important information about the mixed-state properties due to the superconducting transition at $T_c$.

We thank G. M. Veith for advice on materials preparation, and D. J. Singh for fruitful discussions. Oak Ridge National Laboratory is managed by UT-Battelle, LLC, for the U.S. Department of Energy under Contract No. DE-AC05-00OR22725.