Variation of Specific Heat with $x$ and $y$ in Na$_x$CoO$_2$·$y$H$_2$O/D$_2$O

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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 $\leq x \leq 0.74$ and $y = 0$ and 1.4. For the nonhydrated system ($y = 0$), the electronic specific heat coefficient $\gamma_N$ 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 $T_c^\text{mid}$ ~ 4.7 K and an anomaly at $T_x \sim 0.8$ K. While the origin of the later is unknown, the former corresponds to the superconducting transition. Interestingly, the electronic specific heat, after subtracting lattice and Schottky contributions, exhibits roughly $T^2$ behavior between 0.2$T_c$ and $T_c$. This can be explained by assuming an unconventional superconducting symmetry with line nodes. The results obtained under applied magnetic field further support this scenario.

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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 and possibly superconductivity in its hydrated form. 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 and experimental work indicate that the itinerant bands of Na$_x$CoO$_2$ are very narrow with $W \ll U$, where $W$ is the band width 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 $\gamma_N$ for both hydrated and nonhydrated cases compared to the value from LDA band structure. In these reports, the $\gamma_N$ value was obtained by analyzing specific heat data above 2 K for Na content $x$ in the range of 0.3 - 0.8. It is possible that the extracted $\gamma_N$ value does not represent that for $T \approx 0$ 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 $x$. One would thus expect the variation of $\gamma_N$ 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 $\leq x \leq 3/4$ and $y = 1.4$, 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 Letter, we report the low-temperature specific heat of Na$_x$CoO$_2$·$y$H$_2$O/D$_2$O with 0 $\leq x \leq 0.74$ and $y = 0$ and 1.4.

Single crystals of Na$_x$CoO$_2$ were used for specific heat measurements. Starting with Na$_{0.73}$CoO$_2$ single crystals grown using a flux method, crystals with lower Na content were obtained by chemical deintercalation as described in Ref. 7. By controlling the deintercalation time, we obtain single crystals with $x \approx 0.72$ 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$_2$BF$_4$ as described in Ref. 15. 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 PPMS (Physical Property Measurement System) from Quantum Design.

In Fig. 1a, we present the temperature dependence of the specific heat $C_p$ for single crystalline Na$_{0.73}$CoO$_2$ (filled circles), Na$_{0.75}$CoO$_2$ (unfilled circles), Na$_{0.48}$CoO$_2$ (crosses), polycrystalline Na$_{0.35}$CoO$_2$ (filled diamonds), and CoO$_2$ (unfilled diamonds). 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 replott the data as $C_p/T$ versus $T^2$ as shown in Fig. 1b. If the specific heat is due to electrons and phonons only, it is expected that $C_p/T$ will be proportional to $T^2$ at low temperatures. While this is true for CoO$_2$ ($x \sim 0$) between 0.4 and 10 K, $C_p/T$ clearly deviates from linearity below $\sim 2$ K for samples with $x \neq 0$. The low-temperature upturn indicates that an additional contribution sets in which increases with decreasing $T$. Similar behavior was reported previously and was attributed to a Schottky effect. Thus, for $T \ll \Theta_D$ (Debye temper-
from electrons, phonons (terms inside the bracket), note these terms are corresponding to contributions to the heat of \( C_p \). Figure 1: (a) Temperature dependence of the specific heat \( C_p \) for single crystal 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 \( C_p/T \) versus \( T^2 \), and solid curves are the fits of experimental data to Eq. 1.

The solid curves shown in Fig. 1b are fits of experimental data between 0.4 and 10 K to Eq. 1. Note that Eq. 1 describes our experimental data very well in the superconducting state. For comparison, we extract the electronic specific heat with/without considering the Schottky form may be subtracted from the total specific heat. As shown in Table I, the almost constant \( \Delta \) value for different \( x \) strongly suggests that Schottky effect is mainly controlled by nuclear moments.

We now focus on the specific heat of hydrated/deuturated Na\(_{0.35}\)CoO\(_2\). Shown in Fig. 2a is the temperature dependence of specific heat for Na\(_{0.35}\)CoO\(_2\)-1.4H\(_2\)O (filled circles) and Na\(_{0.35}\)CoO\(_2\)-1.4D\(_2\)O (unfilled circles) between 0.4 and 10 K. Compared to that of the parent compound (filled diamonds), the specific heat of hydrated/deuturated Na\(_{0.35}\)CoO\(_2\) is larger at high temperatures but smaller below \( \sim 2 K \). Most prominent is the specific heat anomaly below 5 K in both hydrated and deuturated cases, reflecting the superconducting phase transition at \( T_{\text{onset}} \sim 5 K \). To obtain superconducting-state properties, all non-electronic contributions, which are not affected by the superconducting phase transition, should be subtracted from the total specific heat. As shown in Fig. 2b, \( C_p/T \) reveals more or less linear dependence with \( T^2 \) above \( T_c \) for both hydrated and deuturated compounds. This suggests that the first two terms of Eq. 1 are dominating. While the low-temperature upturn is absent, the contribution from the Schottky form may be hidden due to sharp decrease of electronic specific heat in superconducting state. For comparison, we extract the electronic specific heat with/without considering the Schottky effect. Shown in Figs. 2c-2d are the temperature dependence of the electronic specific heat assuming \( C_p^{\text{el}} = C_p - C_p^{\text{Sch}} \) (Fig. 2c) or \( C_p^{\text{el}} = C_p - C_p^{\text{Sch}} - C_p^{\text{Sch}} \) (Fig. 2d).

The small \( \gamma_N \) value for \( x \sim 0.48 \) is likely related to the charge ordering reported in Na\(_{0.5}\)CoO\(_2\) at temperatures 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 \( \gamma_N \) value for the end compound CoO\(_2\) is nonzero, consistent with the metallic behavior reported previously. Interestingly, the variation of Na concentration 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 \( x \sim 0.48 \).

\[
\frac{C_p}{T} = \gamma_N + (\beta_3 T^2 + \beta_5 T^4) + \frac{e^\alpha}{T^3(1 + e^\alpha)^2} \tag{1}
\]

The small \( \Delta \) values at high temperatures may be related to the Schottky order-disorder transition reported in Na\(_x\)CoO\(_2\) and other systems.

**Table I:** Parameters obtained from the fit of experimental data between 0.4 and 10 K to Eq. 1 and the inferred Debye temperatures \( \Theta_D \) (see text) for all \( x \) values.

| \( x \) | \( \gamma_N \) (mJ/mol-K\(^2\)) | \( \beta_3 \) (mJ/mol-K\(^4\)) | \( \beta_5 \) (mJ/mol-K\(^6\)) | \( \Theta_D \) (K) | \( \Delta \) (K) |
|---|---|---|---|---|---|
| 0.74 | 34.05 | 0.2051 | 328.2 | -0.3447 | 258.1 |
| 0.72 | 32.91 | 0.0773 | 453.6 | -0.0875 | 19.44 |
| 0.48 | 8.231 | 0.3958 | 257.4 | -0.990 | 11.59 |
| 0.35 | 12.11 | 0.2002 | 319.0 | -0.2232 | 3.410 |
| 0.4 | 13.33 | 0.0333 | 559.1 | 0.0319 | 0.5174 |

Note these terms are corresponding to contributions from electrons, phonons (terms inside the bracket), and Schottky anomalies, respectively. Here, \( \beta_3 = N(\alpha \beta_3 \Theta_D^3) \) with \( R = 8.314 \) J/mol-K and \( N = \) atomic number per formula unit, \( \alpha \) is a constant describing the anharmonic coupling, \( \alpha \) is a constant proportional to number of two-level systems, and \( T \) is the energy separation between the two levels.

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between 6 and 10 K without (Fig. 2c) or with (Fig. 2d) the consideration of the Schottky effect. It turns out that the results are almost the same at high temperatures with only a slight difference at low temperatures. In both cases, note that the substitution of D for H has little effect on the specific heat as we concluded earlier in Ref. 10. As marked by the dashed line in Figs. 2c-2d, the normal-state electronic specific heat coefficient $\gamma_N$ = 13.7 mJ/mol-K² for Na₃.₃₅CoO₂·1.₄H₂O and 13.3 mJ/mol-K² for Na₀.₃₅CoO₂·1.₄D₂O, is very close to that for the parent compound Na₀.₃₅CoO₂ (see Table 1). This is in very good agreement with a theoretical prediction that the intercalation of water into Na₀.₃₅CoO₂ results in little change in the electronic structure. 10

Although the specific heat starts to depart from the high-temperature behavior at 5 K and peaks at $\sim$ 4.1 K, the thermodynamic transition temperature of Na₀.₃₅CoO₂·1.₄H₂O/D₂O is at $T_c^{mid}$ $\sim$ 4.7 K where specific heat jump reaches half of the maximum. By extrapolating the low-temperature specific heat to $T_c^{mid}$ (see Figs. 2e-2d), we obtain the specific heat jump $\Delta C_p$ $\sim$ 45.5 mJ/mol-K. It follows that $\Delta C_p/\gamma_N T_c^{mid} \sim$ 0.71 mJ/mol-K², roughly 50% of the BCS value. According to previous work, this result is compatible with (a) 50% superconducting volume fraction 17,18 or (b) 100% superconductivity if there exists line nodes in the superconducting pairing symmetry. 17,18 As the specific heat measurements are always carried out in high vacuum, it is possible that some H₂O/D₂O is pumped out of the material thus reducing the superconducting volume fraction. For this reason, samples were cooled rapidly to 20 K in helium gas before pumping. Thermogravimetric analysis indicates that the H₂O/D₂O content y remains 1.4 after the specific heat measurements. This and the fact that all other specific heat measurements on either powder 17,18 or single crystals 10 result in $\Delta C_p/\gamma_N T_c^{mid}$ up to 50% of the BCS value indicate that the small specific heat jump is unlikely due to the sample quality. In the second scenario, one would expect a $T^2$ dependence of...
the electronic specific heat in the superconducting state, i.e., \( C_p^e/T \propto T \). As may be seen in Figs. 2c-2d, \( C_p^e/T \) varies more or less linearly between 0.8 and 4.1 K. The solid lines are the linear fit to the experimental data in this region. A somewhat steeper slope is obtained when the Schottky effect is considered (see Fig. 2d). Thus, it is conceivable that there exist line nodes in superconducting pairing symmetry of \( \text{Na}_{0.35}\text{CoO}_2\cdot\text{1.4H}_2\text{O/2D}_2\text{O} \). However, \( C_p^e/T \) shows an apparent deviation from linearity with sharper decrease below \( T_x \sim 0.8 \) K. This implies that not all of the conducting electrons are involved in the superconducting phase transition at \( T_c \), leading to a small specific heat jump and a non-zero intercept \( \gamma_{res} \) when the solid lines in Fig. 2c-2d are extrapolated to \( T = 0 \) K. Residual unpaired electrons should be responsible for the anomaly at \( T_x \), below which \( C_p^e/T \) seems to approach linearly to the origin as guided by the broken lines. It should be mentioned that the entropy is well balanced and Schottky contributions. To determine whether it is unlikely due to the small-gap contribution in the two-gap specific heat of \( \text{Na}_{0.35}\text{CoO}_2\cdot\text{1.4H}_2\text{O} \). 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 DE-AC05-00OR22725.

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