Large enhancement of the thermopower in Na$_x$CoO$_2$ at high Na doping

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Research on the oxide perovskites has uncovered electronic properties that are strikingly enhanced compared with those in conventional metals. Examples are the high critical temperatures of the cuprate superconductors and the colossal magnetoresistance in the manganites. The conducting layered cobaltate Na$_x$CoO$_2$ displays several interesting electronic phases as $x$ is varied [1, 2, 3], including water-induced superconductivity [4] and an insulating state [3] that is destroyed by field [5]. Initial measurements [1] showed that, in the as-grown composition, Na$_x$CoO$_2$ displays moderately large thermopower $S$ and conductivity $\sigma$. However, the prospects for thermoelectric cooling applications faded when the figure of merit $Z$ was found to be small at this composition (0.6 < $x$ < 0.7). Here we report that, in the poorly-explored high-doping region $x$ > 0.75, S undergoes an even steeper enhancement. At the critical doping $x_p$ ~ 0.85, $Z$ (at 80 K) reaches values ~40 times larger than in the as-grown crystals. We discuss prospects for low-temperature thermoelectric applications.

In the large-$x$ region of Na$_x$CoO$_2$ ($x$ > 0.75), progress has been hampered by difficulties in growing single crystals as well as by phase-separation effects which appear above $x_p$. Powder neutron diffraction [6] has revealed subtle shifts in the Na ions as $x$ is increased above 0.75. The doping interval 0.75 < $x$ < $x_p$ is a homogeneous phase $H_2$, in which the thickness $t$ of the CoO$_2$ layers undergoes a steep increase [4]. Above $x_p$, the neutron results indicate phase separation (the mixed-phase region is labelled $H_2 + H_3$). Muon spin rotation [12], nuclear magnetic resonance (NMR) [14] and susceptibility [13, 14] experiments also suggest mixed phases in highly-doped samples. Finally, the limiting phase $H_3$ ($x$ → 1) is inferred from NMR and magnetic susceptibility to be a non-magnetic insulator with a slight admixture of a residual metallic phase [13, 14].

In a thermopower experiment, the current density $J' = \sigma E$ produced by the $E$-field is cancelled by the thermoelectric current $J = \alpha(-\nabla T)$ driven by the applied gradient $-\nabla T$ ($\alpha$ the thermoelectric or Peltier conductivity). Whereas the thermopower $S = \alpha/\sigma$ is the quantity usually reported, we have found that $\alpha$ provides a more incisive probe for sorting out the results in the region $H_2 + H_3$. Results from 10 crystals (of nominal size 400×700 $\mu$m) with $x$ ranging from 0.71 to ~1 reveal that $\alpha$ rises steeply to a peak at the threshold doping $x_p$, with $\alpha$ nearly constant (as shown in Fig. 1) at low $T$. These large $\alpha$ values far exceed any reasonable extrapolation of the Sommerfeld expression $S = (k_B/\epsilon)(k_BT/\epsilon_F)$ ($k_B$ is Boltzmann’s constant and $\epsilon$ the electron charge). To match the observed $\partial S/\partial T \simeq 3 \mu V/K^2$ at low $T$, we would need the Fermi energy $\epsilon_F$ to equal ~30 K, which is unphysically small. The unusually large $S$, coexisting with low resistivities (~100 $\mu$2cm in Samples 4–6), challenges our understanding of how strong correlation enhances the Peltier effect. Approaches include the use

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of the Heikes formula $\alpha = T^{1/2}/\rho \kappa e$, with $\kappa$ measured separately.

As $x$ increases from 0.71 (Sample 1), the peak value of $Z$ increases steeply to $1.8 \times 10^{-2} \text{ K}^{-2}$ in Sample 5. At higher $x$, the peak value of $Z$ falls rapidly because of the sharp increase in $\rho$. At 80 K, $Z$ in Sample 5 is $\sim 40$ times larger than that in Sample 1. The dashed line labeled CBT is $Z$ reported for CsBi$_4$Te$_6$. A/MK in Sample 4) are strikingly anomalous, and likely a consequence of strong correlation.

By tracking $T_{\text{max}}$ (the peak temperature of $\alpha$), we see that $\alpha$ vs. $T$ in 1–4 ($x \leq x_p$) evolves differently from $\alpha$ in 5–10* (in $H_2 + H_3$). In the first group, $T_{\text{max}}$ decreases from 110 K to 50 K (in 1 and 4, respectively). The continuous change in $T_{\text{max}}$ precludes a simple scaling analysis. By contrast, in the second group, $T_{\text{max}}$ remains fixed at $\sim 50$ K. Moreover, by multiplying each curve by a scale factor $p$, we may match it to the curve of 4 (Fig. 3b). The exception is Sample 6 which has a cusp at 36 K (of unknown origin) that ruins the scaling. Hence, as we traverse the homogeneous region $H_2$, the peak value of
\(\alpha\) increases rapidly from 20 A/mK in 2* to 135 A/mK in 4, but the form of \(\alpha\) vs. \(T\) also changes continuously. However, once we cross the threshold \(x_p\) into the mixed phase, the profile is locked to that of 4.

The simplest explanation of the scaling is that, in \(H_2 + H_3\), the carriers segregate into continuous conducting layers embedded in a nearly insulating matrix. The conducting layers correspond to doping \(x_p\) whereas the insulating matrix is at \(x = 1.0\). The mean doping \(x_m\) is then given by

\[
x_m = f x_p + (1 - f), \quad (x_p < x_m < 1)
\]

where \(f\) is the fraction of layers with doping \(x_p\). Additivity of the Peltier currents implies that the observed \(\alpha\) is given by

\[
\alpha(T) = f \alpha_p(T) + (1 - f)\alpha_1(T),
\]

where subscripts \(p\) and 1 refer to quantities evaluated at \(x = x_p\) and 1, respectively.

The scaling behavior in Fig. 3 implies that the second term in Eq. (2) is negligible if \(f\) is not too small. The Peltier conductivity \(\alpha_1(T)\), which has a maximum value of \(\sim 0.85\) A/mK, is observable only when \(f\) becomes very small, as in the case of Sample 10* (see Supplementary Information). Away from this limit, we may take \(f \approx 1/p\) throughout the mixed-phase region; this allows us to find \(x_m\) using Eq. (1). For e.g., in Sample 9*, the scaling of \(\alpha\) shows that 1 in 40 of the layers is conducting \((x_m = 0.996\) instead of 1.00), which is consistent with the observed \(\rho(300)\) in Fig. 4. In addition, we have employed other checks on the calibration. The trilayer crystals, with \(x = \frac{1}{3}\) and \(\sim 1\), provide valuable calibration points. Moreover, \(x\) in Samples 1 and 4 was determined from the \(c\)-axis lattice parameter measured by x-ray diffraction. These checks lend support for our calibration.

With the inferred values of \(x\) and \(x_m\), we next plot the variation of \(\alpha\) at 50 K (circles) and \(\sigma\) (triangles) at 300 K in the phase diagram at large doping (Fig. 4). From \(x = 0.71\) to \(x_p\), \(\alpha(50)\) rises by a factor of 14. The modest changes in \(\sigma(300)\) (triangles) and \(\kappa\) (see Supplementary Information) result in a substantial increase in \(Z\). We emphasize that these increases occur within the homogeneous phase \(H_2\) and are possibly correlated with the increase in layer thickness \(t\) (4). Clearly, they are not a consequence of the phase separation that onsets at \(x_p\). Both quantities decrease linearly above \(x_p\).

The 40-fold enhancement of \(Z\) realized at 80 K improves greatly the prospects for thermoelectric applications. The peak value in Fig. 4 (\(Z \sim 1.8 \times 10^{-3}\) K\(^{-1}\)) is among the highest known for a hole-type material below 100 K. The promising material CsBi\(_2\)Te\(_6\) also displays a large \(Z\) at 100 K (17). In comparison, \(Z\) in
Na₅CoO₂ peaks at low temperatures whereas the curve for CsBi₄Te₅ (curve labeled CBT) falls steeply. The alloy Bi₃₋₁₋₂Sb₂ has long been known to display an even larger Z at low T (at 80 K, Z = 7 × 10⁻³ K⁻¹ for y ~ 0.12). However, it is electron-like. To realize its advantages in a Peltier device operating below 100 K, we need to pair Bi-Sb with a hole-type material with comparable Z, but the 35-year search has turned up no viable candidates. We calculate that an optimized device with NaₓCoO₂ (x = x_p) paired with Biₓ₋₁₋₂Sb₂ has a device figure-of-merit Z_D = 2.5 × 10⁻³ K⁻¹ at 80 K [Z_D = (S_n - S_p)(√ρ_nσ_n + √ρ_pσ_p)x⁻² where subscripts n and p index the 2 materials]. This value is higher than any reported to date. Further enhancement of Z in NaₓCoO₂ seems possible if we degrade κ.

Methods
Sodium metal (0.5 g) and tetrahydrofuran (THF) (30 mL) in a pyrex tube were warmed at 100 °C in an oil bath and stirred. Benzenophene (2 g) was added and the solution heated until it turned blue from the formation of the benzenophene ketyl radical anion. As-grown crystals of Na₀.₇₅CoO₂ were placed along a pipette-like tube and immersed in the blue solution of the sodium radical anions. The pyrex tube was quickly capped and heated for 4 days at 100 °C. Finally, the crystals were extracted and washed with THF and ethanol to eliminate trace sodium.

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Supplementary information posted online.

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Supplementary Information

Breakdown of scaling in Sample 10*
We provide more details on the measurements and analysis of the thermopower $S$ and resistivity $\rho$ in the phase-separated region $H_2+H_3$, especially in the extreme case $x \to 1^-$ represented by Sample 10*.

![Graph](image)

FIG. 1: Comparison of the scaled curves of $p\alpha(T)$ in Sample 10* with those in the batch Samples 4–9* (the scale factor $\rho = 200$ in Sample 10*). Above 100 K, the scaled curve matches those in 4–9*. Below 100 K, the additional contribution which we identify with $\alpha_1$ in the $x = 1$ phase becomes prominent. The peak value of $\alpha_1$ is 0.85 A/mK. This additional term causes the thermopower $S(T)$ in 10* to be distinct in profile from Samples 4–9* (see Fig. 2a of the text).

As noted in the text, the simplest interpretation of the scaling behavior in the curves of the Peltier conductivity $\alpha$ vs. $T$ is to assume that the hole carriers strongly segregate into parallel layers throughout each crystal. The layers must remain robustly connected electrically even at 4 K (otherwise we would not have the metallic profile in $\rho$ with the large residual resistivity ratios RRR~20). Additivity of the currents implies that the observed $\alpha$ and $\sigma$ are given by

$$\alpha(T) = f\alpha_p(T) + (1-f)\alpha_1(T),$$
$$\sigma(T) = f\sigma_p(T) + (1-f)\sigma_1(T),$$

where subscripts $p$ and 1 refer to quantities evaluated at $x = \sigma_p$ and 1, respectively.

The similarity of the $\rho$-$T$ profiles in Fig. 1 of the text implies that all of $J$ is carried by the conducting layers. Setting $\sigma_1 = 0$, we have for the observed thermopower

$$S(T) = S_p(T) + \left(1-f\right)\frac{\alpha_1(T)}{\sigma_p(T)},$$

with $S_p = \alpha_p/\sigma_p$.

In Samples 5–9*, in which the curves of $\alpha$ vs. $T$ may be scaled to that in Sample 4, the term $(1-f)\alpha_1$ must be negligible compared with $f\alpha_p$ in Eq. 3 (Sample 6 is excluded). Further, if the second term in Eq. 5 is negligible (i.e. $f > 0.05$), all the profiles of $S(T)$ should be identical to $S_p$ (Sample 4). We find that, apart from a 20% spread in magnitude, the curves of $S(T)$ are indeed closely similar in Samples 4–9*.

![Graph](image)

FIG. 2: Curves of the in-plane thermal conductivity $\kappa$ vs. $T$ in Samples 3–8 of Na$_8$CoO$_2$ (Panel a) and in Sample 10* (Panel b). The magnitude of $\kappa = 8$–10 W/mK above 50 K in Samples 3–7 is characteristic of doped layered perovskites. In Sample 10* ($x \approx 1$), $\kappa$ attains much larger values, possibly reflecting the pristine nature of the Na ordering. It is of the same order as crystals in the charge-ordered insulating state ($x = 0.5$).

This spread reflects difficulties in establishing the absolute values of $S$ and $\rho$ accurately. The size of the contact pads (50-100 µm) relative to that of the crystals (400–700 µm on a side) leads to uncertainties of ±10% in estimating the voltage lead separation. This is exacerbated by the large electrical anisotropy $\rho_c/\rho$ where $\rho_c$ is the $c$-axis resistivity, which causes a small admixture of $\rho_c$ into the measured “in-plane” resistance despite deliberate care at optimal contact pad placement. We suspect that the latter factor is the main factor that spoils exact scaling of the $\rho$-$T$ profiles. Altogether, we estimate a combined uncertainty of ±15% in the absolute values of

$\alpha_p$, $\sigma_p$, and $\sigma_1$. Further, if we identify $\alpha_1$ in $x = 1$ as the only contribution, the scale factor $f$ is given by

$$f = \frac{\alpha_1}{\alpha_p + \alpha_1}.$$
$\rho$. Within this uncertainty, we see that, in Samples 4–9*, the profiles of $S$ vs. $T$ remain strikingly similar despite the 50-fold increase in $\rho$ in these samples.

The prominent exception is Sample 10*. As shown in Fig. 1, the scaled curve $p\alpha(T)$ matches those in the other samples above 100 K. The value of the scale factor $p \sim 200$ inferred from this plot is also consistent with the resistivity data ($\rho(300) \sim 240$ m$\Omega$cm nominally equals $\rho(300)$ in Sample 4 multiplied by $p$). Below 100 K, however, a further contribution, which we identify with $\alpha_1(T)$ in Eq. 3, becomes dominant. We note that the actual peak value of $\alpha_1$ is $\sim 0.85$ A/mK, which is unresolvable in Fig. 3a of the text. While this is a very small value, it can make the second term in Eq. 3 comparable to the first if $f$ becomes very small. This is the case in Sample 10* near 50 K, for which $f\alpha_\rho \sim 0.68$ A/mK. Hence, in this extreme limit, we estimate that 1 in 200 of the layers carries the applied current to produce a “metallic” resistivity profile resembling that in Sample 4 (apart from the scale factor). In principle, the observed thermopower and $\alpha$ should also match that of 4. However, in Sample 10*, the term in $\alpha_1$ dominates that of the conducting layers below 100 K and ruins the scaling behavior.

**Thermal conductivity**

For completeness, we show the in-plane thermal conductivity measured in some of the samples in Fig. S2. These curves were used in computing the figure of merit $Z = S^2/\rho\kappa$, with $\kappa$ the in-plane thermal conductivity. Throughout the region $H_2$, $\kappa$ has the modest value 10 W/mK, quite typical of layered perovskites (Fig. S2a). However, in the limit $x = 1$, $\kappa$ becomes very large (Fig. S2b), attaining values in the charge-ordered state at $x = 0.5$.

**Dimensionless Figure of Merit $ZT$**

Some authors prefer to use the dimensionless figure-of-merit $ZT$ in place of $Z$. For comparison, we have re-plotted the curves of $Z$ vs. $T$ in Fig. 2b of the text as $ZT$ vs $T$ in Fig. S3. An interesting feature of these curves is that $ZT$ attains a prominent maximum at temperatures between 60 and 100 K in the layered cobaltate. By comparison, in high-performance thermoelectric materials based on doped Bi$_2$Te$_3$ the maximum in $ZT$ occurs in the interval 200–300 K (see for e.g. Chung et al. 2). The rapid fall of $ZT$ in the Bi$_2$Te$_3$ family reflects the semi-metallic nature of the bands. In the cobaltates, however, the peaking of $ZT$ at much lower $T$ is a consequence of the very narrow bands and the magnetic correlations that are present because of strong interaction between carriers.

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