

# Anomalous high-temperature Hall effect on the triangular lattice in $\text{Na}_x\text{CoO}_2$

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(Dated: May 8, 2003)

The Hall coefficient  $R_H$  of  $\text{Na}_x\text{CoO}_2$  ( $x = 0.68$ ) behaves anomalously at high temperatures ( $T$ ). From 200 to 500 K,  $R_H$  increases linearly with  $T$  to 8 times the expected Drude value, with no sign of saturation. Together with the thermopower  $Q$ , the behavior of  $R_H$  provides firm evidence for strong correlation. We discuss the effect of hopping on a triangular lattice and compare  $R_H$  with a recent prediction by Kumar and Shastri.

PACS numbers: 72.15.Gd, 71.10.Hf, 71.27.+a, 74.72.-h

The layered cobaltates are known to exhibit fairly high conductivities for perovskites. The discovery by Terasaki, Sasago, and Uchinokura [1] of enhanced thermopower in the layered Na-doped cobaltate  $\text{Na}_x\text{CoO}_2$  provided the first hint that these materials may harbor unusual electronic properties stemming from strong Coulomb interaction. Recently, interest in the cobaltates has escalated with the report of Takada *et al.* [2] that superconductivity occurs below  $\sim 5$  K in the oxyhydrate  $\text{Na}_x\text{CoO}_2 \cdot y\text{H}_2\text{O}$ . In addition, Wang *et al.* [3] reported that the thermopower  $Q$  in  $\text{Na}_x\text{CoO}_2$  ( $x = 0.68$ ) is completely suppressed by a 10-Tesla longitudinal magnetic field. The field suppression of  $Q$ , constituting direct evidence for a large spin-entropy term in the Seebeck coefficient, implies that a strong-correlation picture is necessary to describe the electronic transport properties. Superconductivity in  $\text{Na}_x\text{CoO}_2 \cdot y\text{H}_2\text{O}$  has been confirmed by several groups [5].

Motivated by the observed field-suppression of  $Q$ , we have measured in detail the Hall effect in  $\text{Na}_x\text{CoO}_2$  ( $x \simeq 0.68$ ), and found that the dependence of the Hall coefficient  $R_H$  on temperature  $T$  is anomalous. Above 200 K, the Hall coefficient  $R_H$  displays a steep,  $T$ -linear increase with no signs of saturation up to our highest  $T$  (500 K). The linear increase continues through a previously unreported weak transition at  $T_D = 430$  K. In addition to the anomalous high-temperature behavior, the Hall angle and resistivity are also highly unusual at low- $T$ .

Several groups have proposed phase diagrams for the layered cobaltates based on the resonating valence bond (RVB) theory applied to the triangular lattice [8–10]. Independent of our Hall measurements, Kumar and Shastri [9] recently predicted that, on the triangular lattice, the high-frequency Hall coefficient  $R_H(\omega)$  should be linear in  $T$ . We compare our experiment with this interesting prediction.

$\text{Na}_x\text{CoO}_2$  is comprised of layers of edge-sharing tilted octahedra. Each octahedron is made up of a Co ion surrounded by six O atoms at the vertices. Within each  $\text{CoO}_2$  layer, the Co ions occupy the sites of a triangular lattice. Doping is accomplished by Na ions which partially occupy the sites of a triangular lattice between the  $\text{CoO}_2$  layers. With the Na content fixed at  $x$ , the ratio of  $\text{Co}^{3+}$  to  $\text{Co}^{4+}$  is  $x : (1 - x)$ . As common in cobaltates,

the splitting between the  $e_g$  and  $t_{2g}$  states in each octahedron is so large that the Co ions are always in their low-spin states. A further trigonal distortion splits the highest lying  $t_{2g}$  state (called  $A_g$ ) from the remaining 2  $E_g$  states. In the  $\text{Co}^{4+}$  ion, the  $A_g$  state is occupied by one electron, while the  $E_g$  states are completely full. According to band-structure calculation [4], the Fermi level (for  $x = 0.5$ ) falls near the top of the band derived from the  $t_{2g}$  states. At  $x = 0$  (all Co ions of formal valence  $\text{Co}^{4+}$ ), the band formed from the  $A_g$  state is half-filled. Within the strong-interaction picture favored by the  $Q$ -suppression experiment [3], this half-filled band is a Mott insulator. Increasing the Na content  $x$  is equivalent to doping away from the half-filled Mott limit by adding electrons.

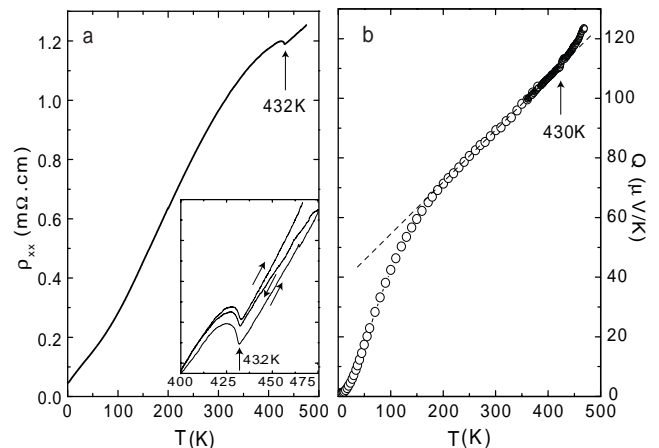


FIG. 1: (a) The in-plane resistivity  $\rho$  of  $\text{Na}_x\text{CoO}_2$  ( $x = 0.68$ ).  $\rho$  is linear in  $T$  from 2 to 80 K, but has a steeper slope above 100 K. The inset shows slight hysteresis in  $\rho$  in the vicinity of the transition at  $T_D = 430$  K. (b) The in-plane thermopower  $Q$  of  $\text{Na}_x\text{CoO}_2$ . The anomaly at  $T_D$  is just resolved in  $Q$ .

In our crystals, the Na content is determined [3] by inductive coupled plasma analysis to be  $x = 0.68$ , which implies that the ratio of  $\text{Co}^{3+} : \text{Co}^{4+}$  is 2 : 1. This is confirmed by a plot of the inverse in-plane susceptibility  $\chi^{-1}$  which displays a Curie-Weiss behavior with a slope consistent with this ratio of  $\text{Co}^{4+}$  ions with  $S = \frac{1}{2}$  (the Weiss temperature is  $\theta_W \sim 55$  K) [3].

As shown in Fig. 1, the in-plane resistivity varies linearly from 2 to 100 K with a slope  $d\rho/dT = 2.45 \mu\Omega\text{cm/K}$  about 5 times larger than in optimally-doped  $\text{YBa}_2\text{Cu}_3\text{O}_7$ . At high  $T$ ,  $\rho$  reveals a weakly hysteretic transition at  $T_D = 430$  K. Because the transition does not impact qualitatively the overall behavior of  $\rho$ ,  $Q$  and  $R_H$ , we associate it with an entropically driven order-disorder transition of the Na ions. The ‘metallic’ profile of  $\rho$  suggestive of a large Fermi Surface (FS), juxtaposed with a large Curie-Weiss susceptibility [3, 6] indicative of fluctuating local moments with antiferromagnetic (AF) coupling, presents an interesting dichotomy if we assume that the same electrons are responsible for transport and magnetization. In fact, the metallic profile of  $\rho$  masks a set of anomalous transport properties which we describe next.

As noted [1], the thermopower  $Q$  is about 10 times larger than predicted by the Fermi-liquid expression  $Q = (\pi^2/3)(k_B/e)(T/T_F)$  with a Fermi temperature  $T_F \sim 10^4$  K. A clue to this enhancement derives from the sensitivity of  $Q$  to a longitudinal magnetic field  $\mathbf{H}$ . Wang *et al.* [3] found that, below 20 K,  $Q$  is increasingly suppressed by  $\mathbf{H}$ , until at 2 K, it is driven to zero by a field of 10 T. The suppression provides direct evidence that spin entropy contributes a dominant fraction of the enhanced  $Q$ . The curve of  $Q$  vs.  $H$  fits closely to a simple model of non-interacting spins with  $s = \frac{1}{2}$  and a Lande  $g$ -factor of  $2.2 \pm 0.1$  (Ref. [3]). The plot in Fig. ?? shows that  $Q$  increases with nominally constant slope  $dQ/dT$  from 200 K to about 450 K, above which the slope increases slightly. The transition at  $T_D$  is barely resolved as a weak peak.

In view of the unusual  $Q$ , it is natural to investigate other transport properties. The Hall coefficient was previously reported [1] to be negative and only weakly  $T$  dependent in the restricted range of  $T$  between 4 and 130 K. When we extended the measurements above 200 K, we found the suprisingly strong  $T$  dependence shown in Fig. 2. Near 200 K,  $R_H$  changes sign and begins a steep increase that shows no sign of saturation up to our highest  $T \sim 500$  K, apart from a weak anomaly at the transition at  $T_D$ . The slope of  $R_H$  between 200 and 500 K is nearly independent of  $T$  away from the anomaly at  $T_D$ . The ratio 2 : 1 of the formal valence charge implies that the carrier density equals  $8.65 \times 10^{21} \text{ cm}^{-3}$ , and a Drude value for the Hall coefficient of  $|R_H^0| = 0.71 \times 10^{-9} \text{ m}^3/\text{C}$ . Here, we see that  $R_H$  at 500 K is  $\sim 8$  times larger than  $R_H^0$ .

Because this Hall profile is so starkly different from the standard  $R_H$  profile in conventional metals, we have adopted several precautions and checks. We used two methods that complement each others strengths. Method 1 is the standard practice of sweeping  $H$  and measuring the Hall voltage  $V_H$  at fixed  $T$ . At each  $T$ ,  $H$  is slowly ramped from -14 T to +14 T and then back to -14 T to yield 2 measurements of  $R_H$ . Method 2 is the technique of Sample *et al.* [12] in which  $H$  is fixed while  $T$  is varied very slowly. Each measurement of  $R_H$  is made by elec-

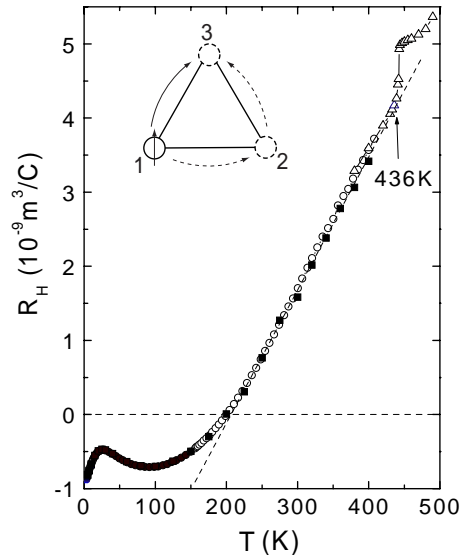


FIG. 2: The  $T$  dependence of the Hall coefficient  $R_H$  in  $\text{Na}_x\text{CoO}_2$  showing anomalous  $T$ -linear increase between 200 and 500 K. The open circles are measurements using Method 2 on Sample 1. Solid squares (open triangles) are data taken with Method 1 (2) on Sample 2. The step anomaly at 450 K reflects the effect of the disorder transition at  $T_D$ . The inset shows the hopping conductivity on 3 sites. Interference between the direct process  $a_{31}^{(1)}$  (solid arrow) and the second-order process  $a_{321}^{(2)}$  (broken arrows) leads to a Hall current.

tronically toggling between the voltage and current leads to extract the antisymmetric component of the resistivity tensor. Method 1 allows checks for non-linearities in  $V_H$  vs.  $H$ , but is error-prone if  $T$  drifts significantly during the field ramp. Method 2 provides a high-density trace of  $R_H$  vs.  $T$  and is robust against contact noise, but is unreliable if  $R_H$  varies with  $H$ . With method 2,  $R_H$  is seen to have an anomaly at the transition  $T_D$ , but resumes its  $T$ -linear trend several degrees above  $T_D$ . Method 1 reveals that  $R_H$  is strictly independent of  $H$  up to 14 T above 20 K. Below 20 K,  $V_H$  reveals a slight curvature vs.  $H$ . As shown in Fig. 2, the 2 methods agree well over the whole range of  $T$ .

In conventional metals, the empirical rule that  $R_H$  must saturate to a constant above a ‘Hall scattering’ temperature  $\Theta_H$  is nearly universally obeyed in non-ferromagnetic metals. Here  $\Theta_H$  is the temperature above which the average momentum  $\mathbf{q}$  of the available scattering excitation exceeds the largest Fermi Surface (FS) caliper. For phonon scattering,  $\Theta_H \simeq s\Theta_D$ , where  $s = 0.2-0.3$  and  $\Theta_D$  is the Debye temperature. [In  $\text{Na}_{0.5}\text{CoO}_2$ ,  $\Theta_D = 380$  K (Ref. [7]), so we would have  $\Theta_H \sim 100$  K if phonon scattering were predominant.] The basis for this rule is clearest in the two-dimensional (2D) FS, where the Hall conductivity  $\sigma_H$  is proportional to the area  $\mathcal{A}_\ell$  swept out by the mean-free-path  $\vec{\ell}(\mathbf{k})$  as the wavevector  $\mathbf{k}$  goes around the FS [14]. For  $T > \Theta_H$ , an electron can always encounter an excitation with large

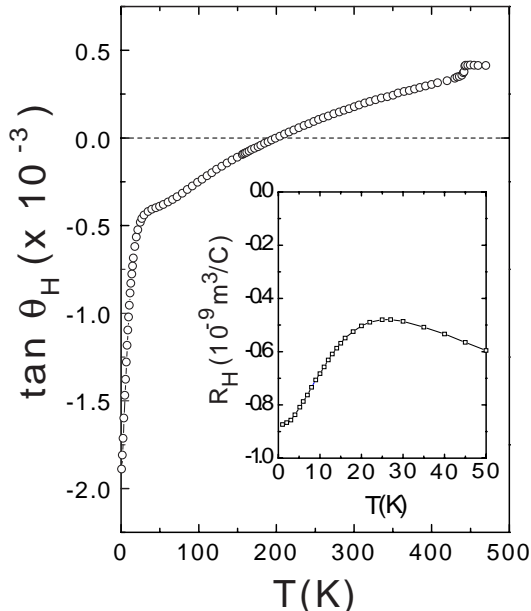


FIG. 3: The  $T$  dependence of the Hall angle  $\tan \theta_H$  (measured at 1 T) in  $\text{Na}_x\text{CoO}_2$ . The profile suggests a crossover to a different scattering regime near 25 K. At low  $T$ ,  $|R_H|$  begins to increase rapidly before saturating below 3 K (inset).

enough  $|\mathbf{q}|$  to scatter it to an arbitrary point on the FS. The  $\mathbf{k}$  dependence of  $\ell(\mathbf{k})$  then becomes independent of  $T$  apart from an overall scale factor. Hence the *geometric shape* of  $\mathcal{A}_\ell$  is  $T$ -independent, and its magnitude is rigorously proportional to  $\ell_{max}^2$ , where  $2\ell_{max}$  is the maximum caliper of the swept area. As the conductivity  $\sigma \sim \ell_{max}$ , this immediately implies that  $R_H$  is independent of  $T$ . In the published literature of the Hall effect in metals that are non-ferromagnets [13], this empirical rule is rigorously obeyed (even in systems with both hole and electron FS pockets and in 3d metals with FS ‘monsters’). The only known exception is the cuprate family. The strong violation of this empirical rule provided an early, conspicuous clue [15] that the charge transport in the cuprates is anomalous. In Fig. 2, the violation is just as striking as in the cuprates, but has the opposite trend.

A different perspective of the anomalous Hall effect is provided by the Hall angle  $\tan \theta_H = \sigma_H/\sigma$ , which is displayed in Fig. 3. In conventional metals,  $\tan \theta_H$  is proportional to  $\ell_{max}$ , and must therefore decrease as  $T$  increases. Here, we see just the opposite trend.  $\tan \theta_H$  *increases* with  $T$  right through the zero-crossing at 200 K as well as the disorder transition at  $T_D$ .

The sharp change in slope near 25 K in  $\tan \theta$  vs.  $T$  implies that the Hall response crosses over to a distinct regime at low  $T$ . As shown in the inset to Fig. 3, the magnitude of  $R_H$  increases steeply below 25 K and saturates to a constant only below 3 K. However,  $\rho$  is rigorously  $T$ -linear from 80 K down to  $\sim 2$  K as noted above (see Fig. 4). These profiles of  $\rho$  and  $R_H$  are reminiscent of the corresponding curves in the cuprates (except

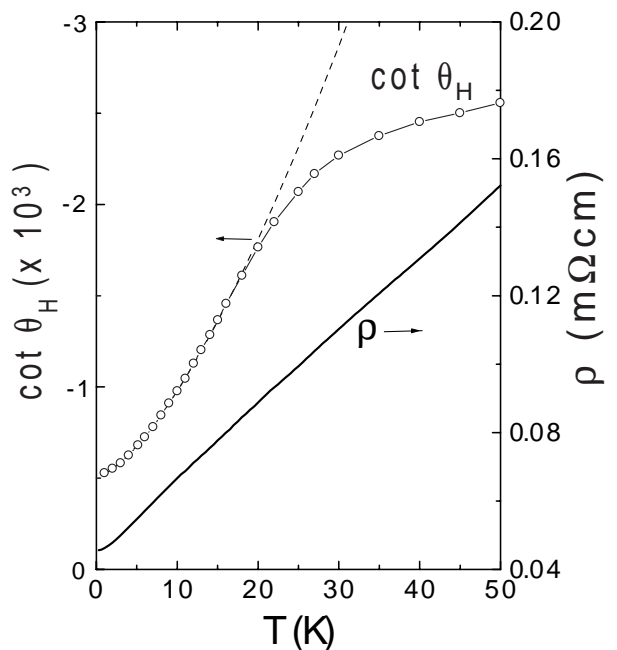


FIG. 4: The  $T$  dependence of  $\rho$  and  $\cot \theta_H$  (measured at 1 T) below 50 K. The fit to  $-\cot \theta_H \sim T^n$  (dashed line) shows that  $\rho_{xy}$  is strongly  $T$  dependent because the Hall angle exponent  $n = 1.5$  is larger than the power-law exponent  $n' = 1$  of the transport lifetime.

there the curves extend to 500 K or higher and  $R_H$  is positive). Following the analysis of Chien *et al.* [15] in the cuprates, we find that  $\cot \theta_H$  is well-fitted by the expression  $a + bT^n$  with  $n = 1.5$  (dashed line in Fig. 4). This implies that the strong  $T$  dependence of  $|R_H|$  below 25 K results from distinct power-law exponents for the Hall-angle lifetime ( $n = 1.5$ ) and the transport lifetime obtained from  $\rho$  ( $n' = 1$ ). Interestingly, the temperature scale over which this holds is about 10-20 times smaller than in the cuprates. This analysis suggests that, below 25 K, the carriers in  $\text{Na}_x\text{CoO}_2$  enter into a strong-correlation regime that involves the same ‘strange-metal’ physics as observed in the cuprates. The reduction of the Hall-angle exponent from 2 to 1.5 also matches well the observed reduction from optimally doped to overdoped cuprates.

We return to the high-temperature behavior of  $R_H$ . The Hall effect problem in cuprates has motivated many theoretical investigations of  $R_H$  in the  $t$ - $J$  model. Recently, Kumar and Shastry (KS) applied to  $\text{Na}_x\text{CoO}_2$  a series expansion technique [11] to calculate the high-frequency limit of the Hall coefficient  $R_H^*$  (the small parameter is  $\beta t$  where  $t$  is the hopping amplitude and  $\beta = 1/k_B T$ ). For a triangular lattice, KS obtain [9, 11]

$$R_H^* = -\frac{a^2 d k_B T}{8|e|} \frac{(1 + \delta)}{t \delta(1 - \delta)}, \quad (1)$$

where  $a$  is the Co-Co bond length,  $d$  the interlayer spacing, and  $\delta$  the doping away from half-filling.

In Fig. 2,  $R_H$  is  $T$ -linear between 200 and 500 K. If we fit this linear portion to Eq. 1, we find that  $t = 25$  K, consistent with  $\beta t < 1$  and a negative sign for  $t$ . However, it is not obvious *a priori* that the prediction for  $R_H^*$  can be compared meaningfully with the dc data in Fig. 2 (moreover, the theory does not predict the weaker dependence on  $T$  below 100 K).

The singular behavior of  $R_H$  is intimately related to charge transport on the triangular lattice. It is helpful to recall electrons hopping on a lattice (Fig. 2, inset). The Hall current arises from the Peierls phase factor  $e^{i\alpha}$  acquired around the minimal closed loop, where  $\alpha = e\phi/\hbar$  is proportional to the flux  $\phi$  piercing the loop. For the 3-site problem (site indices 1,2,3), Holstein [16, 17] computed the transition rate for hopping from site 1 to 3 in a field, and found that the direct, first-order hopping amplitude  $a_{31}^{(1)}$  interferes with the second-order amplitude  $a_{321}^{(2)}$  (describing the process  $1 \rightarrow 2 \rightarrow 3$ ), to yield a giant enhancement of the Hall mobility (Fig. 2, inset) [16], so that  $\sigma_H \sim t_{13}t_{32}t_{21} \sim t^3 e^{i\alpha}$  (with  $t_{ij}$  the complex hopping amplitude between sites  $i, j$  in a field). However, this non-interacting, hopping model obviously does not describe the physics here.

In the  $t$ - $J$  model calculation of KS, transport around a loop on the triangular lattice gives likewise  $\sigma_H \sim (\beta t)^3 \sin \alpha$  [9]. Since  $\sigma \sim (\beta t)^2$ , we have  $R_H \sim$

$(\beta t)^{-1}$ , which implies a  $T$ -linear increase. In the strong-correlation problem, the singular behavior in Eq. 1 is a consequence of transport on the triangular lattice. It is clearly important to verify theoretically whether the domain of validity of Eq. 1 extends to the dc regime in the  $t$ - $J$  model.

The accumulated evidence increasingly support the strong-interaction picture in the layered cobaltate. Initially, observations of an enhanced  $Q$  [1] and a Curie-Weiss susceptibility [6] in the presence of a ‘metallic’  $\rho$  provided early hints of strong correlation. Later, direct evidence for dominant spin entropy contribution to the thermopower came from the effect of  $H$  on  $Q$  [3]. The steep increase in  $R_H$  at high temperatures, as well as the cuprate-like behavior of  $R_H$  and  $\rho$  below 25 K, reported here provide further evidence for strange-metal behavior. Both the field suppression of  $Q$  and the Hall profile in Fig. 2 provide striking examples of how strong interaction can change *qualitatively* electronic transport behavior from conventional behavior even at temperatures up to 500 K. Hopefully, a systematic search may uncover more examples of  $T$ -linear  $R_H$  in layered perovskites with triangular lattices.

We thank B. S. Shastry for enlightening discussions, and acknowledge support from a MRSEC grant (DMR 0213706) from the National Science Foundation.

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