Charge-ordering, commensurability and metallicity in the phase diagram of layered \( \text{Na}_x\text{CoO}_2 \).

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The phase diagram of non-hydrated \( \text{Na}_x\text{CoO}_2 \) has been determined by changing the Na content \( x \) using a series of chemical reactions. As \( x \) increases from 0.3, the ground state goes from a paramagnetic metal to a charge-ordered insulator (at \( x = \frac{1}{2} \)) to a ‘Curie-Weiss metal’ (around 0.70), and finally to a weak-moment magnetically ordered state \( (x > 0.75) \). The unusual properties of the state at \( x = \frac{1}{2} \) (including particle-hole symmetry at low \( T \) and enhanced thermal conductivity) are described. The strong coupling between the Na ions and the holes is emphasized.

Research on oxide conductors has uncovered many interesting electronic states characterized by strong interaction, which include unconventional superconductivity, and charge- or spin-ordered states. Recently, attention has focussed on the layered cobaltate \( \text{Na}_x\text{CoO}_2 \). At the doping \( x \sim \frac{1}{2} \), \( \text{Na}_x\text{CoO}_2 \) exhibits an unusually large thermopower. Although the resistivity is metallic, the magnetic susceptibility displays a surprising Curie-Weiss profile, with a magnitude consistent with antiferromagnetically coupled spin-\( \frac{1}{2} \) local moments equal in number to the hole carriers. The thermopower at 2.5 K is observed to be suppressed by an in-plane magnetic field. This implies that the enhanced thermopower is largely due to spin entropy carried by strongly correlated holes (Co\(^{4+}\) sites) hopping on the triangular lattice. When intercalated with water, \( \text{Na}_x\text{CoO}_2\cdot y \text{H}_2\text{O} \) becomes superconducting at or below 4 K for \( \frac{1}{2} < x < \frac{3}{4} \). These experiments raise many questions. Is the Curie-Weiss state at \( x = \frac{1}{2} \) continuous with the \( x = \frac{3}{4} \) state surrounding superconductivity? Are commensurability and charge-ordering effects important? To address these questions, we have completed a study of the phase diagram of non-hydrated \( \text{Na}_x\text{CoO}_2 \). As \( x \) increases from 0.3 to 0.75, we observe a series of electronic states, the most interesting of which is an insulating state at \( x = \frac{1}{2} \) that involves charge ordering of the holes together with the Na ions. We identify details specific to the triangular lattice, especially in the metallic state from which the superconducting composition evolves, and comment on recent theories.

Starting with powder or single-crystal samples with \( x \sim 0.75 \), we vary \( x \) by specific chemical deintercalation of Na (Fig. 1 caption). Powders of \( \text{Na}_x\text{CoO}_2 \) were made by solid-state reaction of stoichiometric amounts of Na\(_2\)CO\(_3\) and Co\(_3\)O\(_4\) in oxygen at 800 C. Sodium de-intercalation was then carried out by treatment of samples in solutions obtained by dissolving I\(_2\) (0.2 M, 0.04 M) or Br\(_2\) (1.0 M) in acetonitrile. After magnetic stirring for five days at ambient temperature, they were washed with copious amounts of acetonitrile and multiple samples were tested by the ICP-AES method to determine Na content. Unit-cell parameters were determined by powder X-ray diffraction (XRD) with internal Si standards. For the transport studies, we first grew a boule (with \( x = 0.75 \)) in an optical furnace by the floating-zone technique. Crystals cleaved from the boule (1.5 mm \( \times \) 2 mm \( \times \) 0.2 mm) were immersed in solutions of I\(_2\), Br\(_2\) in acetonitrile or NaClO\(_3\) in water for up to 2 weeks to deintercalate sodium. Because of the strong sensitivity of the electronic states to \( \Delta x \), it was essential to fine-tune the deintercalation times and conditions until high uniformity of the Na distribution was achieved (as measured by the line-width of the XRD). Moreover, by combining powder XRD and inductively-coupled plasma analysis (ICP) experiments, we measured accurately the variation of the \( c \)-axis lattice parameter vs. \( x \) (Fig. 1B). Figure 1A shows the systematic variation of the magnetic susceptibility \( \chi \) with \( x \). Previous work shows that for \( x \approx \frac{1}{2} \), \( \chi \) vs. \( T \) follows the Curie-Weiss law \( \chi = C/(T + \theta) \) with \( \theta \approx 70 \) K. Above \( x = \frac{1}{2} \), we find that, at \( x = 0.75 \), \( \chi \) is slightly rounded below 20 K, consistent with the appearance of a weak magnetization \( M \approx 0.03 \mu_B \) per Co with \( \mu_B \) the Bohr magneton. A spin-density-wave (SDW) state at 0.75 has been suggested. When we decrease \( x \) below \( \frac{1}{2} \), the Curie-Weiss divergence in \( \chi \) is progressively reduced with decreasing \( x \) until it vanishes at \( \frac{1}{2} \). Close inspection of \( \chi \) at \( \frac{1}{2} \) reveals the existence of 2 sharp cusps at \( T_{c1} = 88 \) K and \( T_{c2} = 53 \) K (arrows). These 2 transitions signal the onset of an insulating state which we discuss shortly. In this charge-ordered state, \( \chi \) remains independent of the magnetic field \( H \), which is inconsistent with magnetic ordering. With further decrease of \( x \) below \( \frac{1}{2} \), the dependence of \( \chi \) vs. \( x \), the in-plane resistivity \( \rho \) shows a dramatic change in behavior across \( x = \frac{1}{2} \) (Fig. 1B). At all \( x \) values away from \( x = \frac{1}{2} \), \( \rho \) is ‘metallic’ in its \( T \) dependence. For e.g., in the well-studied Curie-Weiss state (\( x = 0.68, 0.71 \)), \( \rho \) has a characteristic \( T \)-linear profile below 100 K. At higher
In contrast to these metallic states, insulating behaviour reflects the onset of weak magnetic order discussed above. Near 20 K in agreement with previous work [11], this doping ($x = 0.75$), $\rho$ shows a distinct change-in-slope near 20 K in agreement with previous work [11]. This reflects the onset of weak magnetic order discussed above. In contrast to these metallic states, insulating behaviour abruptly appears at $x = 0.75$. Initially, $\rho$ in this sample increases gradually as $T$ falls towards $T_{c1}$ and $T_{c2}$, where it exhibits weak anomalies (note change in scale). Below $T_{c2}$, however, $\rho$ rises rapidly to reach $\sim 20$ m$\Omega$cm at 4 K. This insulating state is confined to a narrow interval in $x$. At our lowest doping $x = 0.31$, we recover a high-conductivity metallic state. Below 30 K, $\rho$ follows a $T^2$ behavior and falls to a value (9 $\mu$Ocm) that is $\sim$5 times lower than at $x = 0.71$.

The results from $\chi$ and $\rho$ imply the phase diagram displayed in Fig. 2. The dominant feature in the $T$-$x$ plane is the narrow insulating state at $x = \frac{1}{2}$ which separates two distinct metallic states. Below $\frac{1}{2}$, we have a ‘paramagnetic metal’ with high conductivity whereas, above $\frac{1}{2}$, we have a ‘Curie-Weiss’ metallic state in which a $T$-linear resistivity $\rho$ coexists with a $\chi$ that is Curie-Weiss like $\frac{1}{2}$.

What is the nature of the insulating state at $x = \frac{1}{2}$? An important feature specific to this state is revealed by electron-diffraction studies (Fig. 2B). Even at 300 K, the Na ions at $x = \frac{1}{2}$ order as a superstructure with lattice vectors $a\sqrt{3} \hat{x}$ and $2a\hat{y}$ in the basal plane with $a$ the hexagonal lattice parameter. By contrast, at other doping levels, the superstructure Bragg spots are either much weaker or absent.

The long-range nature of the Na superstructure is brought out clearly by the thermal conductivity $\kappa$ measured parallel to the layers (as in layered oxides, $\kappa$ here is dominated by the phonons). Because phonons are strongly scattered by disorder in the Na sublattice, we expect the phonon mean-free-path $\ell_{ph}$ to be much longer at $\frac{1}{2}$ than at neighboring $x$ values. This is strikingly confirmed by the curves of $\kappa$ vs. $T$ (Fig. 3). In the metallic samples ($x = 0.31$ and 0.71), $\kappa$ is only weakly $T$ dependent and relatively small at all $T$. However, in the crystal with $x = \frac{1}{2}$, it rises steeply below $T_{c2}$ to 300 W/mK, an exceptionally high value that is comparable to that observed in high-purity quartz and diamond. Hence both the diffraction and $\kappa$ results provide strong evidence that, in sharp contrast with the metallic states, the Na ions at
Recent transport [5, 12], magnetic [4], and angle-resolved photoemission (ARPES) [13] experiments point to the conclusion that strong correlation is essential for understanding the electronic properties of Na$_x$CoO$_2$. On the triangular lattice in the CoO$_2$ layer, a fraction (1 − $x$) of the sites are occupied by itinerant spin $\frac{1}{2}$ holes (Co$^{3+}$) hopping in a diamagnetic background of Co$^{3+}$ ions [2]. The hopping amplitude $t$ for $x \sim \frac{1}{2}$ measured by ARPES [13] is quite small ($\langle |t| \rangle \sim 7$ meV). The Fermi Surface encircles the $\Gamma$ point, consistent with a negative sign for $t$.

Recently, several groups have applied the $tJ$ Hamiltonian to Na$_x$CoO$_2$ [14, 15, 16, 17]. The derived phase diagram is strongly informed by the classical lattice-gas model which predicts that, on the triangular lattice, the electrons (holes) crystallize into a $\sqrt{3} \times \sqrt{3}$ structure at $x = \frac{1}{2}$ (Fig. 1B). However, at $\frac{1}{2}$, commensurability effects are weakest and charge ordering is not favored. We also note that the density of states calculated in 2D tight-binding approximation [12, 15, 16] reveals no sharp anomaly at $x = \frac{1}{2}$ if $t < 0$ (a van-Hove singularity does occur at $x = \frac{1}{2}$ if $t > 0$). Hence the observed insulating state is quite unexpected.

The phase diagram in Fig. 2 reveals a characteristic feature of Na$_x$CoO$_2$, namely, the strong influence of the Na ions on the electronic properties. The occurrence of the insulating state seems to require a strong interaction between the ions and holes even though they occupy separate layers. For either charge species alone on the triangular lattice at $x = \frac{1}{2}$, the liquid state seems to be more stable at finite temperature. However, if both populations are present, density fluctuations in one will strongly influence the other. The incipient localization of the holes is evident at 300 K as indicated by the weakly rising $\rho$ (Fig. 1B). In turn, as the amplitude of the hole-density modulation grows, it becomes more favorable energetically for the Na ions to order. The strong coupling leads to a steep increase in both modulation amplitudes until a transition occurs in which the carriers condense into an insulating charge-ordered state. First-principles density functional calculations for $x = \frac{1}{2}$ [18] show a very sharp peak in the density of states at the Fermi energy. This may account for the enhanced sensitivity to Na ordering at this particular doping.

It is interesting to compare the paramagnetic metal with the Curie-Weiss metal. As noted, at low $T$, $\sigma$ is $\sim$5 times higher in the former. In the sample with $x = \frac{1}{2}$ order with very long range correlation even at $T \sim 300$ K.

Further insight into the insulating state is provided by the Hall coefficient $R_H$ (Figs. 3A and C). At $\frac{1}{2}$, we find that, above 200 K, $R_H$ is hole-like with a $T$-independent value equivalent to a Hall density $1/eR_H = 1.8 \times 10^{21}$ cm$^{-3}$. (In metallic samples, however, $R_H$ is $T$ dependent; see below). Near $T_{c1}$, $R_H$ rises to a weak maximum and then plunges to large negative values. Below $T_{c2}$, it increases dramatically in magnitude to a peak value 250 times greater than its magnitude above 200 K. The giant increase in $|R_H|$ implies that the itinerant carrier density $n$ decreases by $\sim$2 orders of magnitude. The profile of the in-plane thermopower $S$ is qualitatively similar. $S$ changes sign near $T_{c1}$, and attains a large negative peak below $T_{c2}$. However, the relative increase in magnitude ($\sim$20) is smaller.

The behavior of $R_H$ at low $T$ reveals an unusual feature of the insulating state. $|R_H|$ falls steeply towards zero as $T \to 0$. This contrasts with the usual behavior in semiconductors where it diverges as $1/n$ (as $n \to 0$). In general, we have $R_H = \sigma_H/H\sigma^2$, with $\sigma_H$ the Hall conductivity and $\sigma = 1/\rho$ the conductivity. The decrease of $R_H$ to zero as $T \to 0$ implies that $\sigma_H$ must vanish faster than the rate at which $\rho^2$ is increasing. The vanishing of the Hall current at low $T$ implies that the charge excitations exhibit strict particle-hole symmetry. They are neither hole-like nor electron-like in their response to the applied field.
0.31, the nearly $T$-independent value of $R_H$ at low $T$ gives a Hall density $= 2.8 \times 10^{22} \text{cm}^{-3}$, which is in agreement with the 2D hole density calculated from $n_{2D} = (2/\sqrt{3}a^2)(1-x)$, where $a = 2.82 \text{Å}$ is the lattice parameter of the triangular lattice. The large hole density and high conductivity at low $T$ implies that screening of charge fluctuations is quite effective at 0.31. Accordingly, its transport properties are more conventional than those of the Curie-Weiss metal. In the latter, the thermopower is greatly enhanced by a large spin-entropy component \cite{4}. The susceptibility has a Curie-Weiss profile with a magnitude consistent with a spin-$\frac{1}{2}$ local-moment population equal to the hole concentration $(1-x)$. These properties are anomalous from the viewpoint of a conventional metal. Finally, as shown in Fig. 3C, this anomalous behavior appears to be intrinsic to the triangular lattice in the regime $k_BT$ $\geq |t|$. The hole-like sign of $R_H$ at high $T$ is consistent with $t < 0$ consistent with ARPES \cite{13, 15, 17}. The $T$-linear dependence of $R_H$ is present at $x = 0.31$ but much weaker. As discussed above, the transport properties in these 2 metallic states are again very different from those in the charge-ordered phase at $x = \frac{1}{2}$ that separates them.

Finally, we remark that the superconducting state produced by intercalation with H$_2$O evolves from the paramagnetic metal which is separated from the Curie-Weiss state by the charge-ordered insulator. It is unlikely that antiferromagnetic correlations, so strongly visible at $x = \frac{2}{3}$, play a role in the superconducting state. Moreover, in the paramagnetic metal, we have not observed any evidence for $\sqrt{3} \times \sqrt{3}$ charge ordering, nor any evidence for a ferromagnetic instability. The large carrier density ($\sim 3 \times 10^{22} \text{cm}^{-3}$ at $x = 0.31$) is 10 times larger than in the cuprates (doped at 0.3). However, the larger effective mass $m^*$ here may reduce the superfluid density $n_s/m^*$ to a value comparable to that observed in the overdoped limit in cuprates.

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