

Charge Ordering, Commensurability, and Metallicity in the Phase Diagram of the Layered Na_xCoO_2

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The phase diagram of nonhydrated Na_xCoO_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 $x = \frac{1}{2}$), then 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 $\frac{1}{2}$ (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.

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Research on oxide conductors has uncovered many interesting electronic states characterized by strong interaction, which include unconventional superconductivity, and charge- or spin-ordered states [1,2]. Recently, attention has focused on the layered cobaltate Na_xCoO_2 . At the doping $x \sim \frac{2}{3}$, Na_xCoO_2 exhibits an unusually large thermopower [3]. Although the resistivity is metallic, the magnetic susceptibility displays a surprising Curie-Weiss profile [4], with a magnitude consistent with antiferromagnetically coupled spin- $\frac{1}{2}$ local moments equal in number to the hole carriers [5]. The thermopower at 2.5 K is observed to be suppressed by an in-plane magnetic field [5]. 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 [6] for $\frac{1}{4} < x < \frac{1}{3}$ [7–9]. These experiments raise many questions. Is the Curie-Weiss state at $\frac{2}{3}$ continuous with the $\frac{1}{3}$ state surrounding superconductivity? Are commensurability and charge-ordering effects important? To address these questions, we have completed a study of the phase diagram of nonhydrated Na_xCoO_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 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 $\text{Na}_{0.77}\text{CoO}_2$ were made by a solid-state reaction of stoichiometric amounts of Na_2CO_3 and Co_3O_4 in oxygen at 800 °C. Sodium deintercalation 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 (M is “molar”). After magnetic stirring for 5 days at ambient temperature, they were washed with copious amounts of acetonitrile and multiple samples were tested by the inductively coupled plasma-atomic emission spectrometry (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 two weeks to deintercalate sodium. Because of the strong sensitivity of the electronic states to Δx , it was essential to fine-tune the deintercalation times and conditions until high uniformity of the Na distribution was achieved (as measured by the linewidth 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. 1(c)].

Figure 1(a) shows the systematic variation of the magnetic susceptibility χ with x . Previous work [4,5] shows that for $x \sim \frac{2}{3}$, χ vs T follows the Curie-Weiss law $\chi = C/(T + \theta)$, with $\theta \sim 70$ K. Above $\frac{2}{3}$, we find that, at $x = 0.75$, χ is slightly rounded below 20 K, consistent with the appearance of a weak magnetization M ($\sim 0.03 \mu_B$ per Co, with μ_B the Bohr magneton). A spin-density-wave (SDW) state at 0.75 has been suggested [10,11]. When we decrease x below $\frac{2}{3}$, the Curie-Weiss divergence in χ is progressively reduced with decreasing x until it vanishes at $\frac{1}{2}$. Close inspection of χ at $\frac{1}{2}$ reveals the existence of two sharp cusps at $T_{c1} = 88$ K and $T_{c2} = 53$ K (arrows). These two transitions signal the onset of an insulating state, which we discuss shortly. In this

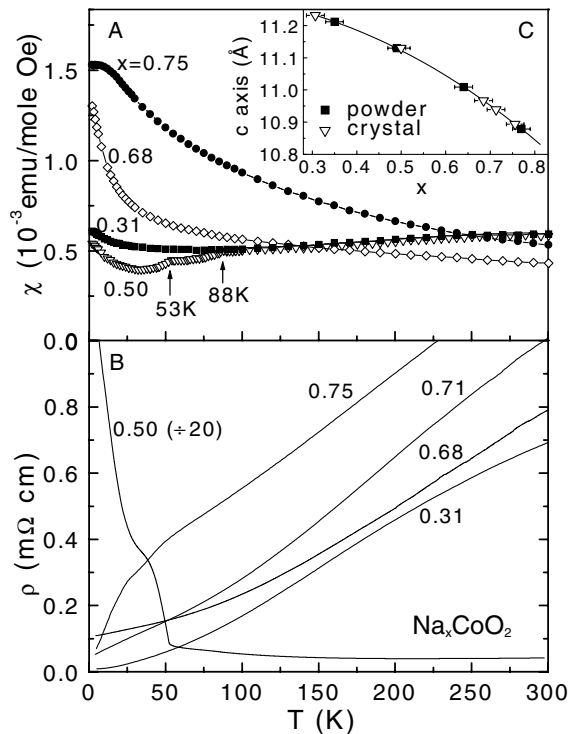


FIG. 1. The susceptibility χ (a) and in-plane resistivity ρ (b) of single crystals of Na_xCoO_2 with x determined by ICP (c). In panel (a), χ is measured in an in-plane field $H = 5$ T ($\mathbf{H} \perp \hat{\mathbf{c}}$). In the crystal with $x = 0.75$, χ fits the Curie-Weiss form $\chi = C/(T + \theta)$, with $\theta \sim 150$ K and $C = 0.224$ emu K/Oe mole. For $x = 0.5$, sharp transitions are observed at T_{c1} and T_{c2} (arrows). Panel (b) shows the T dependence of ρ at selected x . Insulating behavior is observed at $x = 0.5$ (data displayed at lower scale), in contrast to metallic behavior in the rest. At low T , ρ is T linear for $x = 0.71$ but varies as T^2 for $x = 0.3$. In panel (c), the c -axis lattice parameter measured by XRD is plotted against the Na content x fixed by ICP in powder samples.

charge-ordered state, χ remains independent of the magnetic field H , which is inconsistent with magnetic ordering. With a further decrease of x below $\frac{1}{2}$ to $x = 0.31$, the profile of χ becomes relatively featureless, although its magnitude remains large compared with the Pauli susceptibility in conventional metals.

In contrast with the smooth evolution of χ vs x , the in-plane resistivity ρ shows a dramatic change in behavior across $x = \frac{1}{2}$ [Fig. 1(b)]. At all x values away from $x = \frac{1}{2}$, ρ is “metallic” in its T dependence. For example, the well-studied Curie-Weiss state ($x = 0.68, 0.71$), ρ has a characteristic T -linear profile below 100 K [5]. At higher doping ($x = 0.75$), ρ shows a distinct change in slope near 20 K, in agreement with previous work [11]. This reflects the onset of the weak magnetic order discussed above. In contrast to these metallic states, insulating behavior abruptly appears at $x = \frac{1}{2}$. Initially, ρ 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, ρ rises rapidly to reach ~ 20 m Ω 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, ρ follows a T^2 behavior and falls to a value ($9 \mu\Omega$ cm) that is ~ 5 times lower than at $x = 0.71$.

The results from χ and ρ 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 [5] coexists with a χ that is Curie-Weiss-like [4,5].

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. 2(b)]. Even at 300 K, the Na ions at $x = \frac{1}{2}$ order as a superstructure with lattice

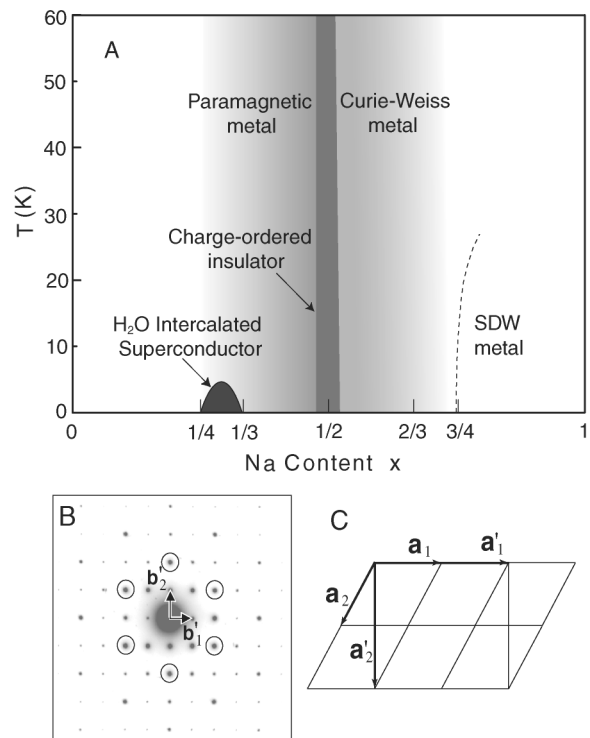


FIG. 2. The phase diagram of nonhydrated Na_xCoO_2 (a), room temperature electron diffraction pattern of a crystal with $x = \frac{1}{2}$ (b), and the Na superstructure lattice (c). In panel (a), the charge-ordered insulating state at $\frac{1}{2}$ is sandwiched between the paramagnetic metal at 0.3 and the Curie-Weiss metallic state at 0.65–0.75. The superconducting state is obtained on intercalation with H_2O [6,7]. In panel (b), the diffraction pattern is taken along [001] with 200 kV electrons in a Phillips CM200 electron microscope (sample nominally at 300 K). Bragg spots of the hexagonal lattice are encircled. The spots located at $n_1\mathbf{b}'_1 + n_2\mathbf{b}'_2$ correspond to the supercell with lattice vectors \mathbf{a}'_1 and \mathbf{a}'_2 , drawn in panel (c) (the superlattice spots are caused primarily by the ordering of Na ions).

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 κ measured parallel to the layers (as in layered oxides, κ here is dominated by the phonons). Because phonons are strongly scattered by disorder in the Na sublattice, we expect the phonon mean free path ℓ_{ph} to be much longer at $\frac{1}{2}$ than at neighboring x values. This is strikingly confirmed by the curves of κ vs T (Fig. 3). In the metallic samples ($x = 0.31$ and 0.71), κ 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 κ results provide strong evidence that, in sharp con-

trast with the metallic states, the Na ions at $x = \frac{1}{2}$ 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. 3(a) and 3(b)]. At $\frac{1}{2}$ we find that, above 200 K, R_H is holelike with a T -independent value equivalent to a Hall density $1/eR_H = 1.8 \times 10^{21} \text{ cm}^{-3}$. (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 ~ 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 (~ 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 $T \rightarrow 0$. This contrasts with the usual behavior in semiconductors where it diverges as $1/n$ (as $n \rightarrow 0$). In general, we have $R_H = \sigma_H/H\sigma^2$, with σ_H the Hall conductivity and $\sigma = 1/\rho$ the conductivity. The decrease of R_H to zero as $T \rightarrow 0$ implies that σ_H must vanish faster than the rate at which ρ^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 holelike nor electronlike in their response to the applied field.

Previous transport [5,12], magnetic [4], and angle-resolved photoemission spectroscopy (ARPES) [13] experiments point to the conclusion that strong correlation is essential for understanding the electronic properties of Na_xCoO_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^{4+}) hopping in a diamagnetic background of Co^{3+} ions [5]. The hopping amplitude t for $x \sim \frac{2}{3}$ measured by ARPES [13] is quite small ($|t| \sim 7$ meV). The Fermi surface encircles the Γ point, consistent with a negative sign for t .

Recently, several groups have applied the t - J Hamiltonian to Na_xCoO_2 [14–17]. 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 $x = \frac{1}{3}$ ($\frac{2}{3}$) [17]. 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 [14–16] 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_xCoO_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

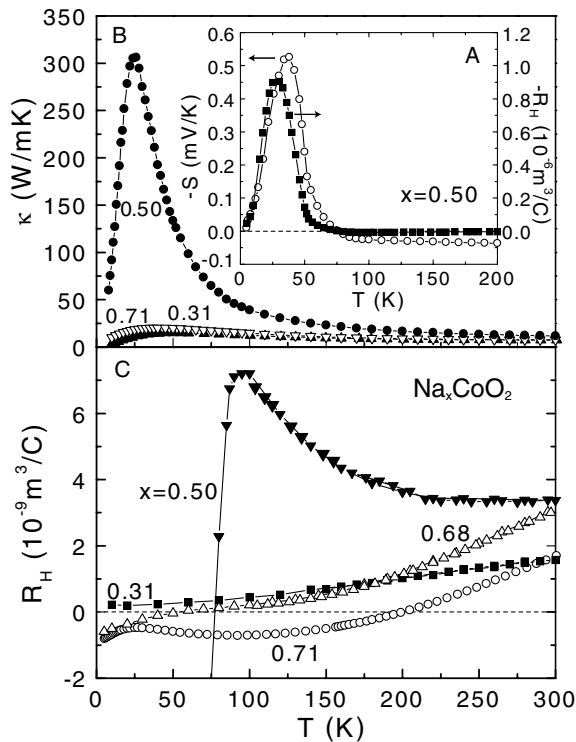


FIG. 3. The thermopower S and the Hall coefficient R_H in Na_xCoO_2 for $x = \frac{1}{2}$ (a), and plots of the in-plane thermal conductivity κ (b), and R_H (c) for several values of x . In panel (a), both $|S|$ and $|R_H|$ begin to increase steeply just below T_{c2} (88 K) and attain maxima at 40 and 30 K, respectively (note $-S$ and $-R_H$ are plotted). Below the peak values, they fall towards zero as $T \rightarrow 0$, consistent with a particle-hole symmetric state. In panel (b), κ at $x = \frac{1}{2}$ rises to a very large peak value comparable to that of quartz, whereas it remains small at all other x . Panel (c) shows that the curve of R_H vs T at $x = 0.50$ is qualitatively different from all other x values. In the metallic samples, R_H increases with T , consistent with strongly interacting carriers hopping on a triangular lattice.

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 ρ [Fig. 1(b)]. 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 , σ is ~ 5 times higher in the former. In the sample with $x = 0.31$, 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 $a = 2.82 \text{ \AA}$ 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 [5]. 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. 3(c), R_H is initially negative at low T but becomes positive near 200 K (for $x = 0.71$) and displays an unusual T -linear increase over a broad range of T [12]. Holstein [19] has shown that coherent interference leads to a T -linear dependence of R_H for electrons hopping on a triangular lattice. A similar T -linear behavior has been derived for correlated holes by Kumar and Shastry [15] for the high-frequency $R_H(\omega)$. This anomalous behavior appears to be intrinsic to the triangular lattice in the regime $k_B T \geq |t|$. The holelike sign of R_H at high T is consistent with $t < 0$ consistent with ARPES [13,15,17]. The T -linear dependence of R_H is present at $x = 0.31$ but is much weaker. As discussed above, the transport properties in these two metallic states are again very different from those in the charge-ordered phase at $x = \frac{1}{2}$ that separates them. Although we reason that this phase is charge ordered, we note that the superlattice spots in Fig. 2(b) refer to Na ion ordering occurring above 300 K and direct evidence for charge ordering of the holes has not yet been obtained. Further work is needed to confirm this inference.

Finally, we remark that the superconducting state produced by intercalation with H_2O 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 $x \sim \frac{2}{3}$, 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 ten 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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