Strong Correlations Produce the Curie-Weiss Phase of Na_xCoO_2

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Within the t-J model we study several experimentally accessible properties of the 2D-triangular lattice system Na_xCoO_2, using a numerically exact canonical ensemble study of 12 to 18 site triangular toroidal clusters as well as the icosahedron. Focusing on the doping regime of $x \sim 0.7$, we study the temperature dependent specific heat, magnetic susceptibility, and the dynamic Hall coefficient $R_H(T, \omega)$ as well as the magnetic field dependent thermopower. We find a crossover between two phases near $x \sim 0.75$ in susceptibility and field suppression of the thermopower arising from strong correlations. An interesting connection is found between the temperature dependence of the diamagnetic susceptibility and the Hall coefficient. We predict a large thermopower enhancement, arising from *transport corrections* to the Heikes-Mott formula, in a model situation where the sign of hopping is reversed from that applicable to Na_xCoO_2.

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The physics of the two-dimensional triangular lattice system sodium cobaltate Na_xCoO_2 (NCO) is fascinating [1], combining strong electron correlations and thermoelectric physics. A Curie-Weiss metallic phase for dopings $x \sim 0.7$ has been reported [2] where the observed physical variables display an unusual mix of behaviors that are hybrid between those of good metals and of insulating systems challenging theory severely. The thermopower of NCO is nearly 10 times higher than expected from typical metals, generating excitement in the engineering and material science communities, particularly applied to thermoelectric devices. Here we show that strong electron correlations, along with the geometrically frustrated lattice of NCO, hold the key to explaining this mysterious state of matter. We examine several experimentally accessible properties of NCO within the t-J model [3–5]. We find that strong electron correlations capture the essential physics and our results compare well with experiment.

In NCO the low spin Cobalt ion valence fluctuates between a Co^{4+} (spin 1/2) and a Co^{3+} (spin 0) configuration; the number of Co^{3+} states is precisely x. The Co ions form a triangular lattice, and photoemission [6,7] is consistent with a single, holelike, band with hopping $t < 0$ and $n = 1 + x$ electrons satisfying the Luttinger volume count.

The t-J model describes strongly correlated electron systems by forbidding double occupancy of lattice sites. We apply this model to NCO after an electron-hole transformation, requiring $t \rightarrow -t$ and hole doping $|1 - n|$. A nonzero J couples nearest neighbor electrons via their spin degree of freedom. For such strongly correlated systems perturbation theory is doomed to failure from the outset and we make progress through numerical exact diagonalization on systems containing 12, 14, and 18 sites on toroidal clusters [periodic boundary conditions (BC)] and on ladder clusters (open BC in one direction) [8]. Thermodynamics is considered within the canonical ensemble.

The Hilbert spaces of these finite systems are very big (up to ~80 000 states) and grow exponentially with the number of sites. Therefore, all available symmetries are used to reduce the dimension of the matrices that arise to large but manageable proportions. However, Peierls phase factors [9] are needed to describe an applied magnetic field, which breaks or reduces the translational invariance, thereby limiting us somewhat. By using a judicious choice of the BC and of phases on bonds [10], we achieve a fairly small nonzero flux per plaquette of π/N_f, where N_f is the total number of triangular faces on the lattice [8]. The ladder systems, however, enable an infinitesimal flux to be chosen.

For NCO, photoemission supports a value for the hopping of $t = -100$ K and we adopt it in this work. This value is suggested by the ARPES data [6] on the loss of coherence of the quasiparticles as well as the dispersion in the composition range $x \sim 0.7$. The T dependence of the chemical potential $\mu(T) - \mu(0)$ is another route to estimating t [11].

Figure 1(a) shows the electronic specific heat $C_v(T)$, and is compared with that for noninteracting electrons with the same hopping. We find that the effect of correlations is a shift in the peak to a smaller temperature and suppression of its overall weight. This is expected since the Gutzwiller projection in the t-J model reduces the number of available states and hence the entropy. Because of a finite system size induced gap in the spectrum, we expect an exponential behavior of $C_v(T)$ for $T \leq 20$ K, the typical gap value. Taking this into account, we are able to extract the linear electronic contribution γT. The value of γ is enhanced by ~1.5 over the noninteracting value; this enhancement depends only slightly on J (neglecting the exponential increase at $T < 20$ K due to the finite-system-induced gap) and varies with system size by 0.2. $J = 40$ K (i.e., $0.4|t|$), which is fixed by the experimental system through a comparison of the Curie-Weiss temperature with computations [2,8].

In Fig. 1(b)–1(f) we present the spin susceptibility $\chi(T)$ for several dopings around $x \sim 0.7$. In the band limit $x \rightarrow 1$, as in the upper two panels (as well as results not shown), we find the expected weakly T dependent but J insensitive

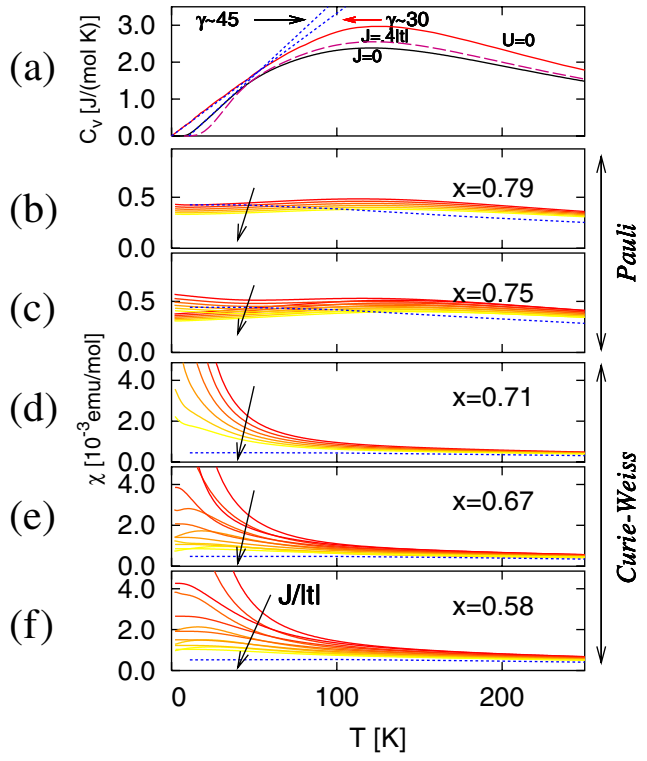

FIG. 1 (color online). Specific heat and susceptibility. (a) Specific heat $C_v(T)$ for $x = 0.72$, computed on the 18-site cluster, comparison of $J = 0$ (bottom) with $J/|t| = 0.4$ (middle) and bare (Hubbard $U = 0$) specific heat (top), dotted straight lines show linear fits and γ values for $J = 0$ and $U = 0$ in units of $\mathrm{mJ/(mol\,K^2)}$. (b)–(f) Susceptibility $\chi(T)$ for dopings around $x \sim 0.7$. The dotted curves indicate the bare susceptibility, and arrows indicate the evolution of $J/|t|$ from 0 to 0.5 in steps of 0.1 (red to yellow). Note the change of scale in different panels. These results combine two different clusters, a 12-site torus ($x = 0.58,\ 0.67,\ 0.75$) and a 14-site torus ($x = 0.71,\ 0.79$). The difference in $x = 0.71$ and $x = 0.75$ shows that $\chi(T)$ transitions from a Curie-Weiss to Pauli paramagnetic behavior in this range.

Pauli paramagnetic behavior. When x is lowered below $x = 0.75$ (bottom three panels), $\chi(T)$ shows strong Curie-Weiss-like T and J dependence, and is significantly renormalized from the noninteracting value at low T. This indicates a crossover to the strong-correlation induced local moment behavior for $x < 0.75$ which closely parallels experimental findings [2]. In this Curie-Weiss phase, the behavior at high T is described by the Curie-Weiss form $\chi(T) = \frac{1}{3}\frac{1}{v}\frac{\mu_B^2 p_{\mathrm{eff}}^2}{k_B(T-\theta)}$ with a negative Weiss temperature θ and effective magnetic moment p_{eff}; $v = V/N$ is the unit cell volume. When continuing the analysis to $x \to 0$, antiferromagnetic (AFM) correlations increase and we find that $\theta(x, J) = -cJ_{\mathrm{eff}}(x)$ where $J_{\mathrm{eff}}(x) = J(1 + c''x|t|) + c'x|t|$, with $c = 4.0$, $c' = 0.01425$, and $c'' = -0.9175$. The c' term originates in the kinetic antiferromagnetism of the frustrated lattice [14], and signifies that even in the absence of J, there is a tendency for AFM order, i.e., in a direction opposite to the usual Nagaoka mechanism for the square lattice [15].

Experimentally, the Hall coefficient of NCO is remarkable in many respects. Most striking is the unbounded linear increase with temperature of the Hall coefficient R_H. To understand this we perform the brute force exact summations of Kubo's formulas for various conductivities [9] by introducing a level width, i.e., a broadening $\omega \to \omega + i\eta$ with η equal to the mean energy level spacing. In addition, we evaluate the high frequency limit [3] of R_H (called R_H^*) for all T. Recall that the high T estimates of R_H^* led to a prediction [3,9] of the linear T dependence of the Hall constant for NCO, which was successfully verified [16]. We are thus able to provide a purely theoretical benchmarking of this idea as well, subject of course to the limitations of the finite-size clusters.

Focusing on the region of doping around $x \sim 0.7$, Fig. 2(a) shows the Hall coefficient as a function of temperature and frequency. We find that the Hall coefficient is

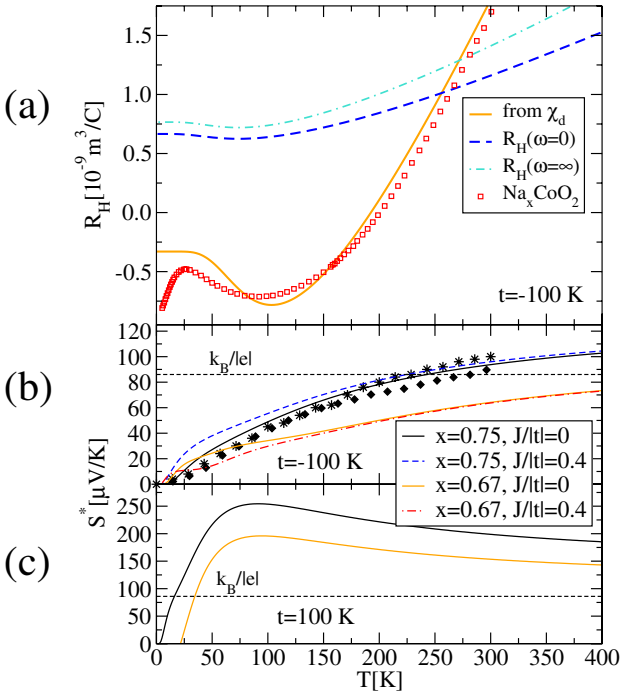

FIG. 2 (color online). Hall coefficient and thermopower. (a) Comparison of several results for the Hall coefficient $R_H(T)$ at $x = 0.75$ with experiment in Ref. [16] at $x = 0.71$ (red squares): R_H^* (blue dot-dashed line), $R_H(\omega = 0)$ (blue dashed line), R_H (orange solid line) derived from χ_d (at $x = 0.83$, ladder); the dc limit required a broadening of the frequency $\omega \to \omega + i\eta$ with $\eta \approx 3|t|$ to eliminate finite-size artifacts. All results are for 12-site clusters and $J/|t| = 0$. (b) Infinite frequency thermopower S^* versus T for a 12-site torus at $x = 0.75$ and $x = 0.67$. The solid black and dashed blue lines correspond to $J/|t| = 0$, and 0.4 at $x = 0.75$, respectively, while the solid orange and dashed-dotted red lines correspond to $J/|t| = 0$, and 0.4 at $x = 0.67$, respectively. $S^*(T)$ for $t = -100$ K relevant for NCO. The diamonds and stars represent measured thermopower for NCO at $x = 0.68$ from Refs. [2,13]. (c) Our prediction for $S^*(T)$ for the case when the sign of the hopping is reversed ($t = 100$ K).

relatively insensitive to frequency, in keeping with the original expectations [3,9,17]. All curves show a minimum near $T = 100$ K, and an unbounded linear increase for $T > 200$ K. The slope of R_H^* as found in the clusters is in agreement with results from high-temperature expansions [3]. The experimental curve, unlike theory, has a change of sign and also a pronounced minimum at $T \sim 100$ K. We cannot reproduce the change of sign. While we could fit the high T slope more accurately, it requires a smaller value of hopping $t \sim 35$ K, as already noted [3]. Such a choice would make most other variable fits less sensible. Hence we conclude that while the data [16] are largely as expected from theory, in detail it is still not possible to reconcile the change in sign as well as the magnitude of the slope with theory. Therefore, the Hall coefficient still offers a considerable challenge to both theorists and experimentalists.

In an alternate effort to understand further the data [16] at lower $T \sim 100$ K, we note that the curvature of the (Landau) diamagnetic susceptibility χ_d (obtained by inserting Peierls phases) and the Hall constant are curiously related in our computation via

$$T\partial^2\chi_d/\partial T^2 = f(x)\partial^2 R_H/\partial T^2, \tag{1}$$

where $f(x)$ is a function depending on doping x. We integrate Eq. (1) to arrive at the Hall constant from our χ_d, yielding a good overall fit of data. The problem with the slope and the negative intercept at low T are forgiven in this approach since one fits the two constants, but it does capture the ubiquitous minimum at $T \sim 100$ K, with a slight J dependence [8]. While the Landau diamagnetism is very small compared to the paramagnetic susceptibility for narrow band systems, it might yet be accessible to experiments. This is so since it is anisotropic in space (being planar), in contrast to the isotropic Pauli susceptibility, and hence torque magnetometry [18] could help disentangle these terms.

The thermopower of NCO is striking in its large magnitude [13] ~ 100 μV/K and also in its surprising sensitivity to an applied magnetic field [2]. A formulation for the thermopower has been recently given [17] in the high frequency limit in the same spirit as the Hall constant. We note that the thermopower can be written as a sum of a transport and the Heikes-Mott term as $S(\omega, T) = S_{\mathrm{Tr}}(\omega, T) + S_{\mathrm{HM}}(T)$, where the Heikes-Mott term is $S_{\mathrm{HM}}(T) = \frac{\mu(0)-\mu(T)}{q_e T}$, and the transport term is

$$S^*_{\mathrm{Tr}}(T) = \lim_{\omega\to\infty} S_{\mathrm{Tr}}(\omega, T) = \frac{q_e[\Delta(T) - \Delta(0)]}{T\langle\tau^{xx}\rangle}. \tag{2}$$

Here $q_e = -|e|$ is the electronic charge and $\hat{\tau}_{xx}$ is the diagonal part of the stress tensor [9,17]. The term S_{HM} is entropic in origin [19]. Detailed expressions for Δ as an expectation of a many-body operator in the t-J model are given in Eq. (83) of Ref. [17], and in a longer work [8].

The main approximation in Ref. [17] is to use the high ω limit of $S(\omega, T)$ (called S^*), and is expected to be numerically quite reasonable, in parallel to the behavior of the Hall constant reported in this work. At low T the two contributions to S vanish separately as we have written them, and in general we find that for $t < 0$ (the case of NCO) the entropic part is by far the dominant term. For the opposite case ($t > 0$) the transport term comes into play in a dominant way, and leads to very interesting behavior as we shall show.

We first discuss the thermopower in the absence of magnetic field. Figure 2(b) shows the T and J dependence of S^* for x relevant to the Curie-Weiss phase. The Heikes-Mott term dominates over the transport term and the frequency dependence of the thermopower (evaluated via Kubo formulas) is found to be quite weak in this range of doping for $t < 0$ relevant to NCO [8], and thus the high frequency approximation is as good as exact. We find our results compare well with the experimental data [2,13]. We now sharpen the prediction [from Eq. (88) of Ref. [17]] that reversing the sign of hopping leads to a maximum in S^* as a function of T. Figure 2(c) indeed shows such a behavior and provides an estimate of the expected enhancement in S^*, a factor of 2 to 3 over the frustrated case of NCO and also of the expected temperature scale $T_{\mathrm{max}} \sim |t|$. It would be interesting to check this experimentally. A part of the enhancement for $t > 0$ arises from the prominent peak in the single particle density of states coming close to the Fermi level. Our numerics show that interactions further amplify this effect considerably (a factor of $\sim$2).

Next we consider the effects of a magnetic field of strength B (perpendicular to the plane) on the thermopower. The field induced change of the transport term arises from the Peierls factors, and is found to be a very small fraction ($\sim$0.001) of the change in the Heikes-Mott term. The field dependence of the chemical potential is significant and responsible for the overall change. In Fig. 3(a) we show the normalized $S_{\mathrm{HM}}(B, T)$ for several dopings as function of B/T. This scaling with B/T is very similar to the one found in Ref. [2], both qualitatively and quantitatively. In Fig. 3(b)–3(d) we find a crossover for $x \sim 0.75$ from a weakly B-dependent $S(B, T)$ at $x \geq 0.75$ to the Curie-Weiss phase where S is greatly suppressed by B. This crossover is similar to the one seen in the T dependence of the spin susceptibility. These results confirm the interpretation [2] in terms of spin entropy as the leading contribution to the field suppression and also provide a guide to what one can expect at high magnetic fields that are not accessible experimentally.

We next make a few comments about the overall behavior of the thermopower and Hall constant as a function of filling in strong coupling theories. As noted earlier [9,20], while band theory predicts a single zero crossing of the Hall constant as n increases from $0 \to 2$, a strongly correlated electron system has three crossings. In precisely the same sense, the thermopower also has three zero crossings for a correlated band system. We demonstrate this for the triangular lattice. In Fig. 4(a) and 4(b) we show the filling dependence of both the Hall constant and the thermopower.

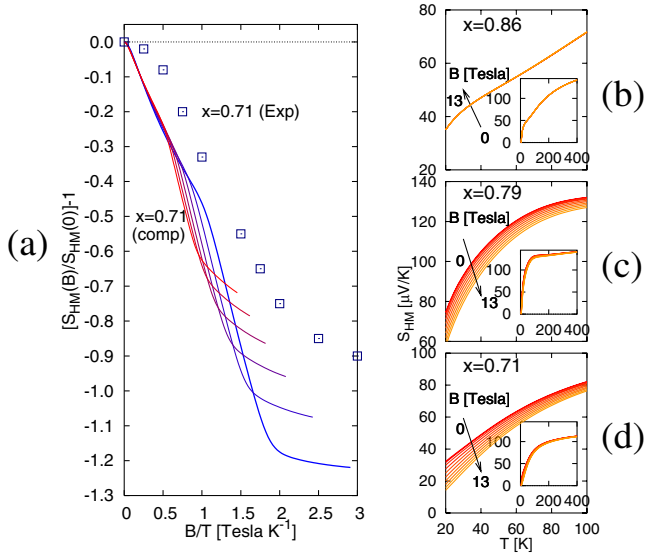

FIG. 3 (color online). Magnetic field dependence of the thermopower. (a) $S_{\mathrm{HM}}(B)$ normalized to $S_{\mathrm{HM}}(0)$ shows the relative suppression of S_{HM} with B for temperatures $T = (100, 120, 140, 160, 180, 200)$ K (blue to red); horizontal axis is rescaled by $1/T$ as done in Ref. [2]. (b)–(d) $S_{\mathrm{HM}}(T)$ for several doping values around $x = 0.71$ and several values of B from 0 T to 13 T (red to orange). Note that for $x > 0.75$ the field dependence becomes very weak. The insets display the full temperature behavior of S_{HM} out to $T = 400$ K. All data for $J = 0$. Finite J reduces the field suppression.

The divergence of the Hall constant at half filling is forced by the carrier freeze out accompanying the Mott-Hubbard gap, and is less pronounced in the triangular lattice than in the square lattice [9]. For the thermopower we expect similar results for the square lattice.

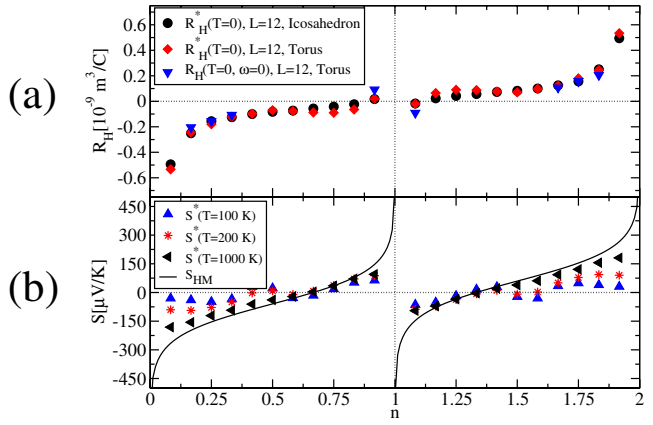

FIG. 4 (color online). Hall coefficient and thermopower as a function of filling n. (a) Filling dependence of $R_H^*(T = 0)$ for a 12-site torus (black circles) and icosahedron (red diamonds) as well as $R_H(T = 0, \omega = 0)$ for the 12-site torus (blue triangles) all for $J/|t| = 0$. (b) Filling dependence of $S^*(T)$ for $T = 100$ K, 200 K, and 1000 K (blue triangle, red star, black triangle) for $J/|t| = 0$ on a 12-site torus. The solid black line is S_{HM} at infinite T. The dotted lines in both panels are guides to the eye indicating zero R_H and S and half filling ($n = 1$).

The hopping parameter t ($\sim$100 K), used here to reconcile a considerable body of experimental data with theory, is much smaller than that in high T_c systems $t \sim 3000$ K. This value is also smaller, by a factor of 10, than the one found in local density approximation studies [21,22], and should motivate further studies of the difficult problem of projecting a multiband system onto a single band model systematically. In conclusion, our work shows that strong correlations account for the observed dramatic behavior of the Curie-Weiss metallic phase in considerable quantitative detail.

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