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Non-Fermi liquid behavior in the layered Na_xCoO_2

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The specific heat in the temperature region of 100 mK–360 K and in magnetic fields of 0 and 9 T, as well as the susceptibility from 2 to 360 K and in a magnetic field of 1 T have been measured in the layered Na_xCoO_2 (x = 0.65, 0.70, and 0.75) oxides. Analysis of the data revealed non-Fermi liquid behavior. The character of the observed anomalies seems to be connected to the mesoscopic phase separation, underlining the impact of disorder on the low-lying excitations in cobaltates.

PACS: **71.27.+a** Strongly correlated electron systems; heavy fermions;
73.43.Nq Quantum phase transitions;
74.20.Mn Nonconventional mechanisms.

Keywords: cobaltates, specific heat, non-Fermi liquid behavior, phase separation, magnetic susceptibility.

Introduction

The layered Na_xCoO_2 and its hydrated counterpart represent a d-electron system, in which the interplay of reduced dimensionality, magnetic frustration and electron correlations drives the system towards new quantum phases. Besides the multitude of open fundamental problems it also offers promising technological applications: superconductivity [1] and the unique combination of high thermo-power with low electrical resistivity [2].

Reminiscent of high-T_C superconductors and manganite materials, the Na_xCoO_2 system is extremely sensitive to doping and preparation protocols. In fact, the diverse properties are a consequence of the complexity arising from the disorder inherent in this system. The Na_xCoO_2 is considered a two-dimensional (2D) Mott insulator doped with electrons via sodium, which serves as a charge reservoir between the CoO_2 layers. The Co atoms are arranged on a triangular lattice, and this configuration generates the geometrical frustration of the antiferromagnetic interactions in the system. Consequently, the issue of the magnetic ground states with respect to quantum effects and spin frustration becomes appealing. As the extra electron from sodium converts the originally magnetic Co^{4+} ($3d^5$) ions with spin $S = 1/2$ into nonmagnetic Co^{3+} ($3d^6$) ones, stronger magnetic features might be naively expected in the low doping regime. However, the opposite is true. Strong frustration interferes with the magnetic ordering, and the magnetic phases were observed only for doping levels of $x \geq 0.7$ [3,4]. The low-doped systems show conventional metallic character with Pauli-like paramagnetism and only light electron mass renormalization [5] (the linear specific heat coefficient $\gamma \sim 12$–16 mJ/(mol·K^2)); however, when hydrated it becomes superconducting [1]. On the other hand, the higher-doped systems exhibit curious Curie–Weiss like metallic behavior and substantial electron mass enhancement [6] ($\gamma \sim 25$–30 mJ/mol·K^2) typical for strongly correlated electron systems. Even though there are several hints of unconventional metallic behavior with non-Fermi liquid features such as anomalous resistivity and spin-lattice relaxation behavior [7,8], the mass-enhanced Fermi liquid ground state is considered [9]. In this article the fundamental issue of the nature of the magnetic fluctuations and their influence on the electronic behavior at low temperature in the sodium doped cobalt oxides is addressed.

Experimental

The Na_xCoO_2 polycrystalline samples with nominal Na content of x = 0.65, 0.70, and 0.75 (hereafter denoted as Na65, Na70, and Na75, respectively), the doping regime where a magnetic order is about to form, were prepared by the rapid heat-up method [10]. X-ray powder diffraction confirmed the samples to be a single phase of hexagonal γ-Na_xCoO_2 with lattice parameter a around 2.827 Å for all samples, while c = 10.939, 10.907, and 10.892 Å for x = 0.65, 0.70, and 0.75, respectively. Specific heat measurements from 2.5 to 360 K have been performed in magnetic fields of zero and 9 T using the conventional Quantum Design PPMS-9 device. This instrument was also used for the susceptibility measurements performed at 1 T and over the same range of temperature. The specific heat from 100 mK to 3 K was measured by the dual slope method, using a ^{3}He–^{4}He refrigerator, TLE-200 Oxford Instruments.

Results and discussion

The susceptibility results are consistent with the finding of other authors [3,4] and the temperature behavior was similar for all three samples. Generally speaking the response is characterized by an increase on cooling (resembling local moment behavior), a steep increase below 10 K (reminiscent of heavy fermions and Kondo systems), and a small kink around 26–28 K (possibly the manifestation of short-range magnetic ordering).

The specific heat data can be seen on Fig. 1. Focusing on the low temperature region, we found a pronounced upturn of the C/T data below 10 K (note the correspondence with the susceptibility behavior), sensitive to the magnetic field. This usually indicates emerging low-level excitations. The fact that they can be progressively suppressed by the magnetic field points to magnetic character of these excitations. For closer inspection of this feature we investigated the specific heat at lower temperatures. As it might have been expected, the low-temperature behavior of the specific heat for all the samples showed divergence from the Fermi liquid predictions (Fig. 2,*a*). In this temperature region the electronic contribution $C = \gamma T$ is dominant and the Sommerfeld coefficcient γ for Fermi liquids should be independent of T when approaching $T = 0$.

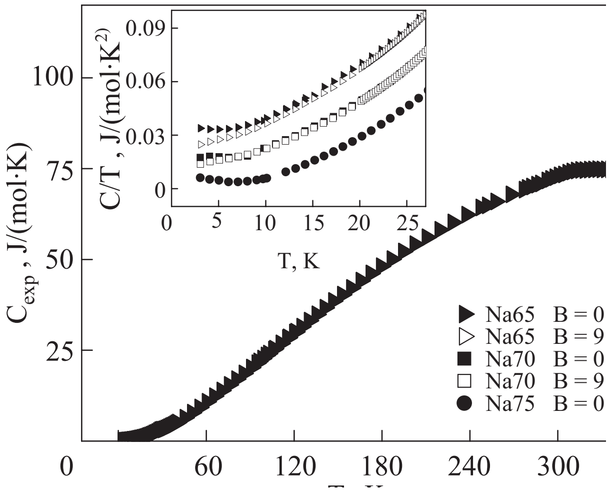

Fig. 1. Specific heat experimental data for the Na65 sample. Inset: The C/T data for all three samples, measured in magnetic field of 0 T (full symbols) and 9 T (hollow symbols). The Na70 and Na75 data are shifted for clarity down by 0.015 and 0.03 J/mol·K^2, respectively.

For more detailed analysis of the observed anomalies we considered two NFL scenarios: (i) the spin fluctuation theory for a 2D antiferromagnet [11] predicts a logarithmic divergence of C/T and $\chi \sim -\ln T$; and (ii) the Griffiths phase scenario [12] predicts the $T^{-1+\lambda}$ law for C/T and χ with the same parameter λ. The comparison of the analyses of C and χ (Figs. 2 and 3) suggests that for the Na65 and Na70 samples the prediction for Griffiths phase scenario provides better description of the experimental data. However, for the Na75 sample it should be noted, that the data can be described by both dependences quite reasonably.

It should be stressed that the values of λ obtained from the analysis of specific heat and susceptibility below 10 K agree especially for the Na65 and Na70 samples extremely well. We found a substantial coincidence between the upper temperature limit for the validity of power law behavior of the susceptibility and between the results of several resonance studies implying some change in electronic states around this temperature. More specifically, Mössbauer studies on Fe enriched samples have implied slow spin relaxation phenomena just below 10 K [13]; further, anomalous low-temperature behavior of the spin-lattice relaxation time T_1 has been observed by ^{23}Na nuclear magnetic resonance measurements in $Na_{0.7}CoO_2$ [8]. Interestingly, $1/T_1$ was found to follow a T^n relation below 10 K with $n = 0.73$. These notions are consistent with the existence of Griffiths phases, characterized by typically slow dynamics. The parameter λ is a non-universal exponent, tunable by the disorder strength. It indicates how «close» the system is to the normal Fermi liquid state, characterized by $\lambda = 1$. Phenomenology shows that its typical values lie in the range 0.7–1 for heavy fermion compounds, whereas doped semiconductors have a more singular response with λ in the range 0.3–0.4 [14]. With respect to the obtained values the cobaltates rank to the former group. It might be speculated that in the higher doped «magnetic» side of the phase diagram spin fluctuations, while at lower doping disorder effects play the dominant role in electronic behavior.

Let us discuss briefly the possible microscopic background of the observed behavior in this system. Griffiths phases are common in the proximity to magnetic phase transitions of percolating character [15]. Nevertheless, they can occur in the absence of any form of magnetic ordering as well, as in the disordered Kondo-lattice case (electronic Griffiths phases) [16]. To produce an anoma-

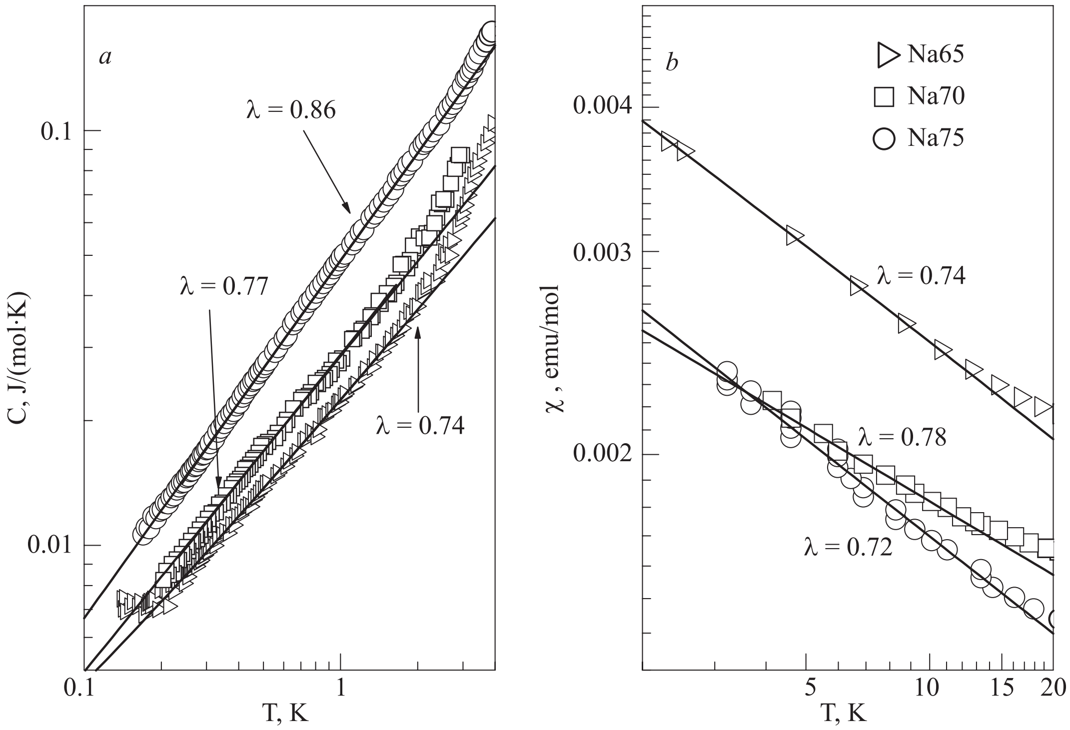

Fig. 2. Log-log plots of specific heat C (*a*) and magnetic susceptibility χ (*b*) vs temperature. Solid lines represent the fits to power law dependences C/T and $\chi \sim T^{-1+\lambda}$.

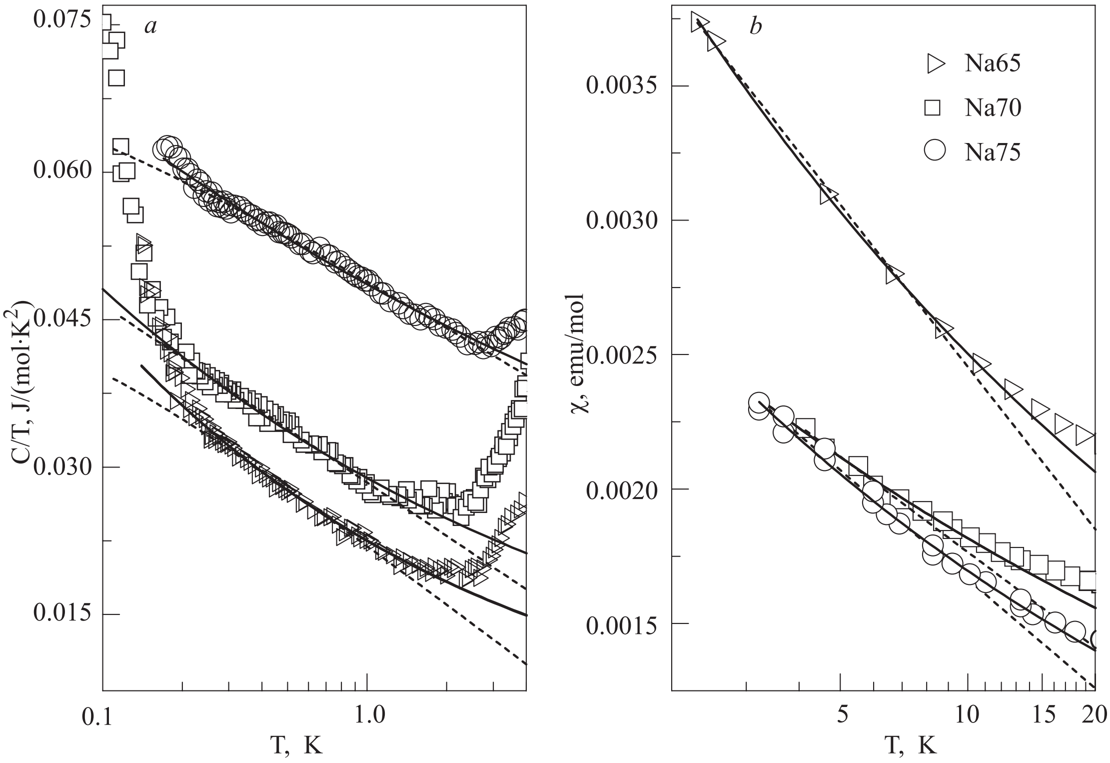

Fig. 3. Semilog plots of specific heat over temperature C/T (*a*) and magnetic susceptibility χ (*b*) vs temperature. Dotted lines represent the best fits to the logarithmic dependences C/T and $\chi \sim \ln T$. For comparison the power law fits are also shown, represented by solid lines.

lous power-law divergence, only an assembly of fluctuators, whose energy scales are distributed in a power-law fashion, are needed, and these fluctuators can be magnetic clusters as well as Kondo spins. The Na_xCoO_2 system of concentrations under study is at the verge of magnetic ordering: only short-range magnetic order (finite magnetic clusters or in the correlated direction even infinite magnetic layers) is present below ~ 80 K [17]. However, we should keep in mind that the precursors of the magnetic clusters with wide size-distribution, i.e. the mesoscopic regions consisting of Co^{4+} ions, are formed at much higher temperatures, around 250 K, this process is governed by charge ordering [18,19]. According to the Griffiths scenario these clusters are able to tunnel at low enough temperatures between the two different configurations with reversed sign of staggered magnetization. The scenario of quantum tunnelling seems to be consistent also with the temperature evolution of the magnetic entropy (Fig. 4), obtained from the specific heat data after subtraction of both the lattice and electronic contributions [17]. One can observe a weaker temperature dependence of this entropy below 10–12 K (Fig. 4 inset). The entropy decrease becomes slower because of additional degrees of freedom, which slow down the entropy removal upon cooling. Simple entropy considerations [14] allow to estimate roughly the average cluster size N in this region. The entropy of a cluster being a two-level system is $k_B \ln 2$, the total entropy $S = nk_B \ln 2$, if n is the number of clusters. In the case of a mole of spins, S is a molar entropy and:

$$S/N_A = nk_B \ln 2/N_A = k_B \ln 2/N$$

Thus $N \sim R\ln 2/S$, leading to $N \sim 1600$ in our system. Taking into account two-dimensionality, this number represents approximately 40×40 spins in the clusters, that is really a mesoscopic scale. Realizing that the cluster size is probably not significantly affected by temperature after completion of charge ordering, this can be the upper estimate of the cluster size in addition to the lower estimate of 6 lattice steps as proposed in [19].

Conclusion

To summarize, our specific heat and magnetic susceptibility analysis at low temperatures on polycrystalline Na_xCoO_2 oxides with $x = 0.65$, 0.7, and 0.75 gives evidence of anomalous metallic behavior of non-Fermi liquid character. Closer inspection reveals low-lying electronic quantum states resembling Griffiths phases. The underlaying microscopic mechanism is likely of magnetic character, related to the mesoscopic phase separation, i.e. the coexistence of partially ordered magnetic regions with Fermi liquid electrons.

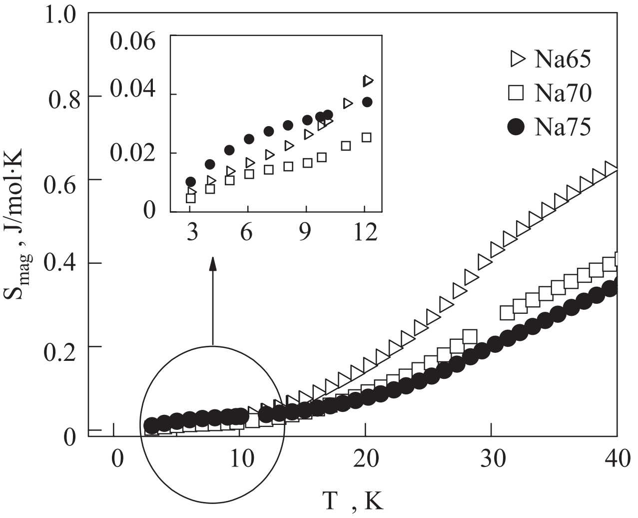

Fig. 4. Temperature evolution of the magnetic entropy at low temperatures.

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