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# Heat capacity studies of magnetic phase transition in sodium-rich $Na_xCoO_2$ ($0.73 \leq x \leq 0.87$)

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Specific heat measurements in the temperature region from 2 to 50 K in magnetic field up to 10 T, oriented parallel and perpendicularly to the $CoO_2$ layers were carried out on a series of high-quality single-crystals of $Na_xCoO_2$ ($x$ = 0.73, 0.76, 0.77, 0.78 and 0.87). Surprisingly, sharp lambda type anomaly was observed only for the concentration $x$ = 0.76 at temperature (21.80 ± 0.02) K, for all the remaining doping levels round anomaly in experimental data was visible at temperature ~ 20 K, indicating a smeared magnetic phase transition. While the magnetic field oriented perpendicularly to the $CoO_2$ layers shifts the temperature of this anomaly to lower values, parallel magnetic field has no influence on it, what indirectly supports the idea of *A*-type antiferromagnetic ordering in studied systems.

PACS: 75.30.Kz Magnetic phase boundaries (including magnetic transitions, metamagnetism, etc.);
**71.27.+a** Strongly correlated electron systems; heavy fermions;
75.40.Cx Static properties (order parameter, static susceptibility, heat capacities, critical exponents, etc.).

Keywords: cobaltates, specific heat, magnetic phase transition, *A*-type antiferromagnetism.

## Introduction

Transition metal oxide $Na_xCoO_2$ is a subject of intense study for its unusually high thermoelectric power [1], for the discovery of superconductivity in hydrated $Na_{0.3}CoO_2$ [2] and for very rich phase diagram with various electronic and magnetic ground states as a function of $x$. It is a paramagnetic metal at $x \sim 0.3$, a charge-ordered insulator at $x = 0.5$ and then a «Curie–Weiss metal» at $x \sim 0.7$ [3] with unconvential electronic behavior [4–6]. For $x$ in the range 0.75–0.9 a magnetic transition with $T_N$ between 19 and 27 K was observed [7–10].

Recent neutron scattering studies of $Na_{0.75}CoO_2$, $Na_{0.82}CoO_2$, and $Na_{0.85}CoO_2$ have established that the magnetic order and dynamics are consistent with an *A*-type antiferromagnetic structure, in which a ferromagnetic interaction was revealed within the $CoO_2$ layers and the layers themselves interact antiferromagnetically [11–13]. Moreover, the latest studies of correlation effects via cellular clusters by means of the rotationally invariant slave boson method provide a theoretical support for intralayer ferromagnetic order in highly doped $Na_xCoO_2$ [14].

Specific heat studies confirm the antiferromagnetic phase transition at 22 K [8,15,16], and recently a further ferromagnetic phase transition was observed at 8 K in $Na_{0.85}CoO_2$ [17]. This transition the authors clearly connect to the rearrangement of sodium ions at around 200 K, which leads to a phase separation.

Despite a lot of experimental and theoretical work concerning the study of $Na_xCoO_2$, many questions about the magnetic state of cobaltates are still unresolved, besides the *A*-type antiferromagnetic ordering [15] also a spin-density-wave scenario is considered [16,20], or the coexistence of this two types of magnetically ordered state is assumed [8].

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In the present paper we investigate the specific heat of sodium-rich $Na_xCoO_2$ and the influence of the orientation of magnetic field on the phase transition. We observed a round anomaly corresponding to the phase transition for all samples except the $x = 0.76$ concentration having a lambda type anomaly, in this respect the influence of the cluster character on the phase transition is discussed. The observed effect of magnetic field oriented parallel and perpendicularly to the $CoO_2$ planes on the phase transition is in agreement with the *A*-type antiferromagnetic ordering.

## Experimental

High quality single-crystal samples of $Na_xCoO_2$ with $x = 0.73$, 0.76, 0.77, 0.78 and 0.87 were grown in an optical floating zone furnace with four 300 W halogen lamps installed as infrared radiation sources. Starting feed and seed materials were prepared from $Na_2Co_3$ and $Co_3O_4$ of 99.9% purity with the nominal composition of $Na_xCoO_2$. To ensure homogeneous and pure phase all the process procedures were carefully controlled and examined using x-ray diffraction. The composition of the as-grown crystals were determined by energy dispersive x-ray analysis (EDX), the sodium composition distribution was homogeneous with error less up to 2 at.%. The growth details are described in Refs. 18, 19.

Specific heat of samples in magnetic field up to 10 T oriented parallel and perpendicularly to the *ab* ($CoO_2$) plane has been measured in the temperature range from 2 to 50 K using the conventional Quantum Design PPMS-14 equipment. Because the recent experimental works [17] pointed to possible changes of sample properties by cooling procedure, we used the same cooling rates for all samples to ensure the identical conditions for specific heat measurements.

## Results and discussion

The specific heat data for single-crystals in magnetic field of 0, 9 and 10 T for both orientation of field, i.e., perpendicularly and parallel to the *ab* plane, are shown in Figs. 1,*a* and *b*. As we can see, relatively sharp lambda type anomaly is visible at (21.80 ± 0.02) K for concentration $x = 0.76$, while for other concentrations smeared anomalies in specific heat can be observed around 20 K. The differences are better visible on Fig. 2, after subtraction of the lattice contribution to specific heat, fitted numerically. The lambda type anomaly indicates magnetic ordering, consistent with previous experimental results, showing similar phase transition in specific heat at about 22 K [8,16,20]. The origin of the broad anomaly at ~ 20 K might be attributed to the cluster character of the system, ordering in the clusters can smear the transition. This is in agreement with the previous evidence of the intrinsically

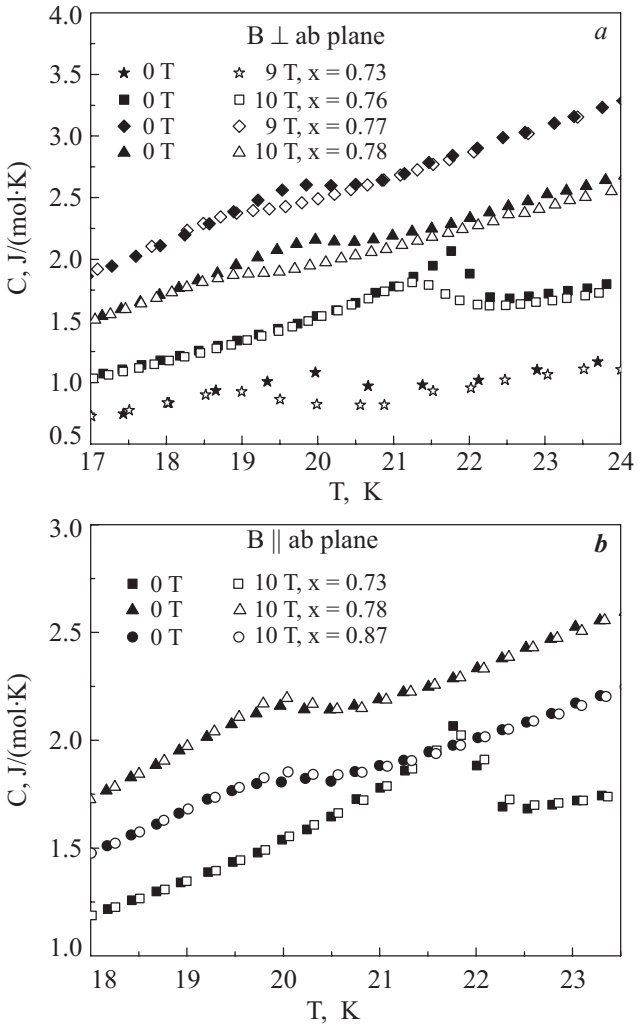


*Fig. 1.* Specific heat of $Na_xCoO_2$ for various concentrations *x*. Magnetic field oriented perpendicularly to the *ab* plane (*a*). Specific heat of $Na_xCoO_2$ for selected concentrations. Magnetic field oriented parallel to the *ab* plane (*b*).

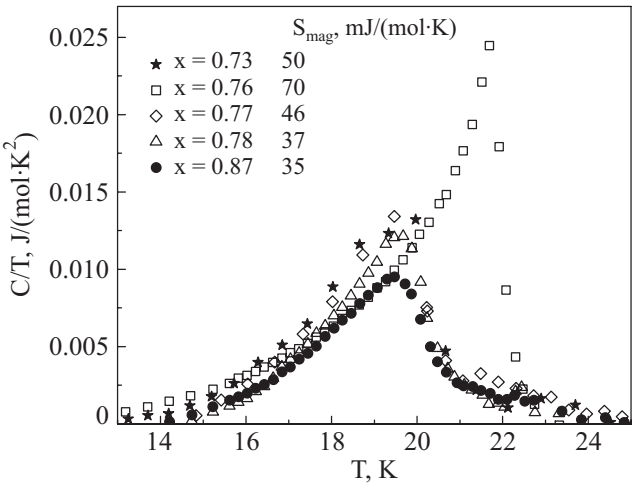


*Fig. 2.* Comparison of the phase transition anomaly and the involved entropy for different Na doping.

inhomogeneous magnetic state related to the Na doping [21]. Even though there are strong indications (EPR and NMR measurements [22], neutron scattering results [23,24] and STM investigations [25]) that this inhomogeneity is of mesoscopic scale, the observed coexistence of two magnetic phases, ordering at different temperatures [17], represents an example when the system is macroscopically phase separated. Thus, the intense debate about the character of inhomogeneities in cobaltates has still not come to the end.

The cluster structure originates from several competing effects in the system, the impact of which changes upon doping. Geometric frustration of antiferromagnetic interactions on triangular lattice is gradually lifted by Na addition, consequently, there must exist a critical doping at which frustration ceases and the system orders. Recent Monte Carlo study tracks the smearing influence of geometric frustration on specific heat [26]. On the other hand, Na doping leads to magnetic dilution of the system, which can smear the transition again. In terms of the above reasoning, the concentration $x = 0.76$ might represent a critical doping, at which the percolating cluster structure can develop a long range magnetic order; eventually at which the long range Na superstructure formation, which is observed on 3/4 doped $Na_{0.75}CoO_2$ samples by high energy x-ray diffraction [27] can promote the long range magnetic ordering as well. According to Fig. 2, the entropy involved in the magnetic phase transition for all samples is very small, it has maximum obviously at doping $x = 0.76$, but even in this case it reaches only ~ 0.07 J/(mol·K). If magnetic phase transition corresponded to the long range magnetic ordering of localized $Co^{+4}$ spins, we would expect the entropy associated with the transition to be of order $0.24R \ln 2 \sim 1.38$ J /(mol·K). This value is 20 times larger than entropy found experimentally and supports the idea about unconventional magnetic ordering, such as spin density wave [16,28].

The magnetic field applied perpendicular to the *ab* plane shifts the magnetic phase transition towards lower temperatures (Fig. 1,*a*). On the other hand, magnetic field oriented parallel to the *ab* planes has no influence on specific heat, as it can be seen from Fig. 1,*b*. The fact that the specific heat anomaly about 20 K is sensitive only to the magnetic field oriented perpendicularly to the $CoO_2$ layers is in accordance with the picture, in which the magnetic moments within the $CoO_2$ layers point out of layers and are likely ferromagnetically coupled, while the interlayer interactions are antiferromagnetic.

Detailed study of the influence of perpendicular magnetic field between 0 and 9 T on the specific heat of single-crystal $Na_{0.77}CoO_2$ is illustrated in Fig. 3. In magnetic fields from 0 to 3 T no significant influence on specific heat is visible, the dependences are almost identical. As the magnetic field is increased from 3 to 9 T, the phase transition critical temperature $T_N$, estimated as a peak temperature of the anomaly, gradually shifts to lower values. Similar tendency was observed in specific heat study under magnetic field up to 14 T applied perpendicularly to the *ab* plane, with metamagnetic phase transition at 8 T [29]. Inset of Fig. 3 shows the phase diagram of the sample $Na_{0.77}CoO_2$. By extrapolation to zero temperature we guessed very roughly the saturation magnetic field as ~ 133 T ~ 7.7 meV, which gives idea about the strength of interlayer interactions. These values are quite reasonable, not far from that estimated by neutron scattering [15].

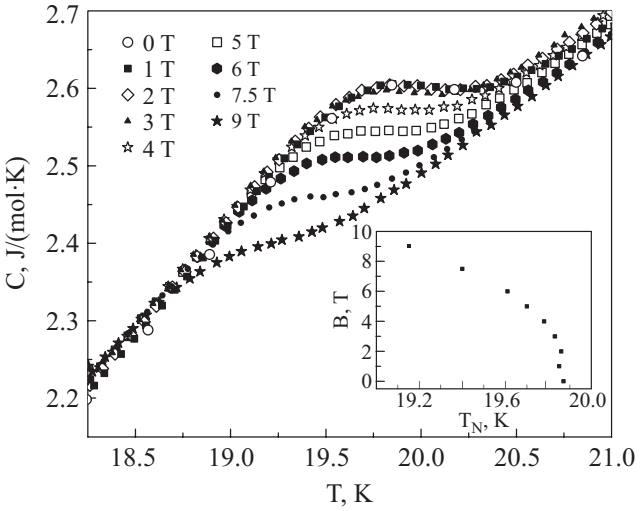


*Fig. 3.* Influence of perpendicular magnetic field up to 9 T on specific heat of $Na_{0.77}CoO_2$. Inset: Phase diagram for single crystal $Na_{0.77}CoO_2$ .

## Conclusion

We have measured the specific heat of sodium-rich single crystals of $Na_xCoO_2$, with attention to the influence of Na doping on the magnetic phase transition. Surprisingly, sharp lambda type anomaly was observed only for the concentration $x = 0.76$ at temperature (21.80 ± 0.02) K, for all the remaining doping levels both below and above $x = 0.76$ round anomaly in experimental data was visible at temperature ~ 20 K, indicating a smeared magnetic phase transition, likely as a consequence of competing magnetic frustration and dilution effects. The influence of the cluster character on the phase transition was discussed. The influence of magnetic field, applied parallel and perpendicularly to *ab* plane, indirectly supports the *A*-type ferromagnetism.

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