Proceedings of the 15th Czech and Slovak Conference on Magnetism, Košice, Slovakia, June 17–21 2013

Thermodynamic and Magnetotransport Properties of High Quality $Na_{0.77}CoO_2$ Single Crystals

A. Baran[a,*], A. Zorkovská[b], M. Kajňaková[c], C.T. Lin[d] and A. Feher[c]

[a]Department of Physics, Faculty of Electrical Engineering and Informatics, Technical University of Košice, Park Komenského 2, 042 00 Košice, Slovakia

[b]Institute of Geotechnics, Slovak Academy of Sciences, Watsonova 45, 040 01 Košice, Slovakia

[c]Institute of Physics, Faculty of Science, P. J. Šafárik University, Park Angelinum 9, 041 54 Košice, Slovakia

[d]Max-Planck-Institute for Solid State Research, Heisenbergstrasse 1, D- 70569 Stuttgart, Germany

Heat capacity and electrical resistivity of high-quality $Na_{0.77}CoO_2$ single crystals was systematically studied as a function of temperature and magnetic field. Anomalies at 20 K have been observed both in the heat capacity and the electrical resistivity. The broad bump in the heat capacity indicates a smeared magnetic phase transition. Magnetic fields up to 9 T, oriented perpendicularly to the *ab* plane, reduce the temperature of this anomaly in accordance with the assumption of A-type antiferromagnetic ordering. The low temperature upturn observed in resistivity below 20 K for slow cooling is also suppressed by the magnetic field. This anomaly is probably the consequence of the interplay of several different mechanisms, including the Kondo effect, electron-electron interactions, and electron-phonon scattering.

DOI: 10.12693/APhysPolA.126.360

PACS: 75.20.Hr, 75.40.Cx, 75.47.–m

1. Introduction

The layered sodium cobaltate Na_xCoO_2 has attracted considerable experimental and theoretical attention due to its rich phase diagram with many unusual states, for instance a superconductor state at $x = 0.3$ after intercalation by water, charge ordered insulator at $x = 0.5$, unconventional magnet [1] and nonFermi liquid metal at higher doping [2]. This is a result of various competing phenomena, such as strong electron correlations, magnetic correlations, and geometrical frustration, which are strongly sensitive to Na concentration. Na doping introduces charge carriers into Na_xCoO_2 and changes the spin-half Co^{4+} into spinless Co^{3+} in the CoO_2 layers. Thus, it enhances the conductivity and relaxes the magnetic frustration. Recently, the influence of the cooling rate on the structure and magnetic properties has been observed, which is related to the mobility of sodium ions and to the formation of specific sodium superstructures [3].

We study the heat capacity and electrical resistivity of $Na_{0.77}CoO_2$. A non-typical phase transition, sensitive to the magnetic field, was observed in heat capacity around 20 K. At the same temperature and only for a slow cooling rate, the low temperature upturn was visible in electrical resistivity, which is slightly suppressed by strong magnetic field.

2. Experimental

Single crystals of $Na_{0.77}CoO_2$ were grown in an optical floating zone furnace. 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. The composition of the as-grown crystals was determined by energy dispersive X-ray analysis.

For measurement of both the in-plane resistivity by four-probe method and the heat capacity from 300 K down to 2 K, the PPMS-9 Quantum Design device was used. The applied magnetic field up to 9 T was oriented perpendicularly to the sample plane, which corresponds to the *ab* plane. The resistivity was measured at two different cooling rates, standard cooling at 10 K/min and slow cooling at ~ 0.2 K/min.

3. Results and discussion

The heat capacity of $Na_{0.77}CoO_2$ in the temperature range of 2 – 30 K is shown in Fig. 1. The broad bump around 20 K observed in heat capacity, indicates a smeared magnetic phase transition. Magnetic fields up to 9 T, oriented perpendicularly to *ab* plane, shift the transition temperature to lower values, while parallel magnetic fields have no influence on it [4]. This fact is in accordance with the assumption of A-type antiferromagnetic ordering, suggested for Na_xCoO_2 at $x > 0.75$ in ref. [5]. Fitting the linear part of the C/T vs. T^2 dependence allows to estimate the electronic heat capacity coefficient, $\gamma = 11$ mJ/mol/K^2, which hints at the strong electron correlations in the system.

The resistivity at slow cooling shows typical metallic behavior down to 20 K, but below this temperature, a strong resistivity upturn was observed (Fig. 2). Interestingly, it occurs at the same temperature as the anomaly in the heat capacity, and it underlines the magnetic origin of this anomaly. Magnetic fields up to 5 T only slightly suppress the upturn, while 9 T induces more visible effect. For fast cooling, no upturn was observed.

The low temperature resistivity upturn may arise from various mechanisms, e.g. Kondo scattering, e-e interac-

*corresponding author; e-mail: anton.baran@tuke.sk

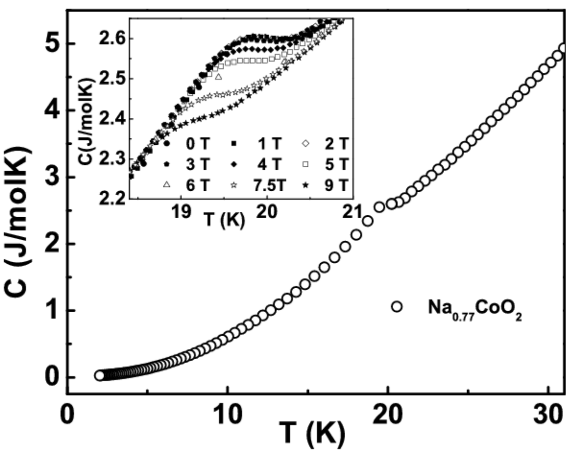

Fig. 1. Heat capacity of $Na_{0.77}CoO_2$. Inset: Influence of the magnetic field, perpendicular to the *ab* planes, on the transition.

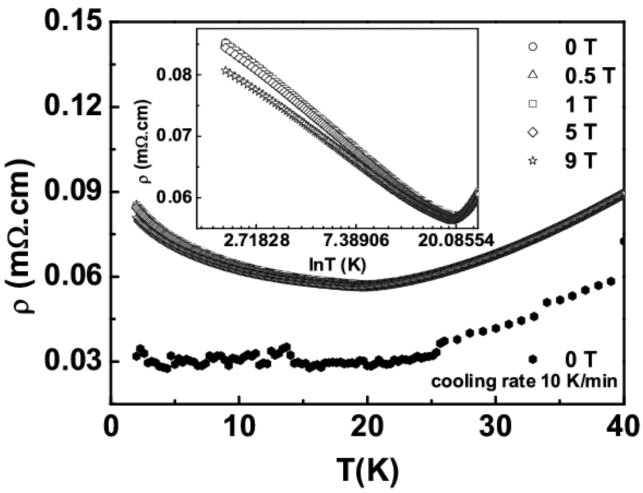

Fig. 2. Resistivity of $Na_{0.77}CoO_2$ measured in magnetic fields perpendicular to the *ab* planes.

tions enhanced by disorder, or weak localization effects due to the finite dimension of the system. For the Kondo effect, the resistivity follows a $-\ln T$ dependence, and magnetic fields reduce the upturn. In disordered systems, the resistivity upturn can be a result of e-e interactions. The resistivity is proportional to $-T^{1/2}$ and magnetic fields enhance the effect.

The resistivity around and below 20 K has been analyzed, taking into consideration the above mentioned mechanisms, in addition to the inelastic electron-phonon process following the T^5 dependence far below the Debye temperature. The experimental data of $\rho(T)$ are well described by the formula $\rho = \rho_0 - \rho_K \ln T - \rho_{e-e}T^{1/2} + \rho_P T^5$, in which the term for the Kondo effect is the dominant one. The field dependence of ρ_K and ρ_{e-e} is in accordance with theoretical assumptions (inset of Fig. 3).

The origin of the Kondo effect observed below the magnetic phase transition could be explained by the existence of magnetic clusters in the Co layers, which are coupled to Na vacancy clusters between Co layers [6]. The Na superstructure is stabilized only while slow cooling and the magnetic clusters above or below them act as scattering centres. On the other hand, for fast cooling, the Na ions are in a non-equilibrium state, the resistivity is dispersed at low temperature, and no upturn was observed.

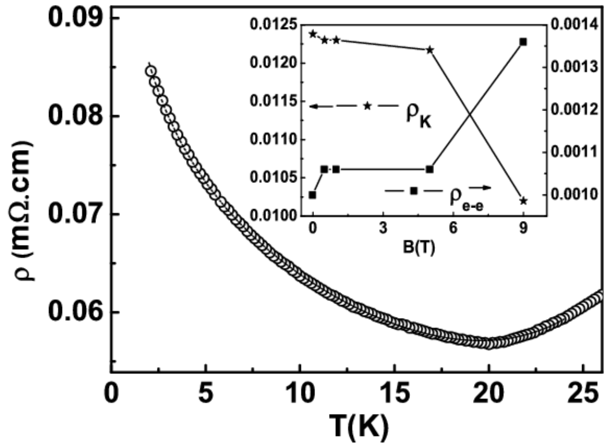

Fig. 3. Fitting of $\rho(T)$ by equation $\rho = \rho_0 - \rho_K \ln T - \rho_{e-e}T^{1/2} + \rho_P T^5$. Inset: Field dependence of the dominant coefficients.

4. Conclusions

In summary, heat capacity and electrical resistivity of the $Na_{0.77}CoO_2$ has been studied from 300 K down to 2 K. A smeared magnetic phase transition was observed at 20 K, which corresponds to A-type antiferromagnetic ordering. A resistivity upturn below the phase transition, observed at slow cooling, is sensitive to magnetic field and is well described by a Kondo-type behavior.

Acknowledgments

This work was supported by the projects VEGA 1/0145/13 and ITMS26220120047

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