Vol. **113** (2008) *ACTA PHYSICA POLONICA A* No. 1

Proceedings of the CSMAG'07 Conference, Košice, July 9–12, 2007

Low Temperature Anomalies in the Specific Heat and Magnetic Susceptibility of $Na_{0.7}CoO_2$ Samples

A. Baran, A. Zorkovská, A. Feher

Centre of Low Temperature Physics of the Faculty of Science UPJŠ
and Institute of Experimental Physics, SAS, 041 54 Košice, Slovakia

J. Šebek, E. Šantavá, J. Hejtmánek, M. Veverka

Institute of Physics AS CR, 18221 Prague, Czech Republic

I. Bradarić

The "Vinča" Institute of Nuclear Sciences, 11001 Belgrade, Serbia

and M. Ružička

Faculty of Chemical and Food Technology, STU, 812 43, Bratislava, Slovakia

We present a comparative study of $Na_{0.7}CoO_2$ samples obtained from three different sources and prepared by different methods. The specific heat and magnetic susceptibility measurements in the temperature range 2–300 K show substantial influence on the observed anomalies, which underlines that the system is extremely sensitive to preparation protocols.

PACS numbers: 75.40.Cx, 72.80.Ga

1. Introduction

The layered cobaltates Na_xCoO_2 have attracted much attention because of their unusual transport and magnetic properties [1] and because of the recent discovery of superconductivity in the hydrated $Na_{0.35}CoO_2 \cdot 1.3H_2O$ [2]. The properties of Na_xCoO_2 are strongly dependent on the Na ions concentration and change from paramagnetic metal, through charge ordered insulator and Curie–Weiss metal to magnetically ordered metal ($0.7 < x < 0.9$) with increasing concentration [3].

Samples with concentration $x = 0.7$ on the boundary of magnetically ordered and nonmagnetic phases in the phase diagram [3] have been investigated.

2. Samples

Three $Na_{0.7}CoO_2$ samples were obtained by different preparation methods.

Sample (1): the sample was prepared in the "Vinča" Institute of Nuclear Sciences, Belgrade, by the conventional synthesis method involving the "rapid heat-up" technique. A stoichiometric mixture of 99.99% purity Co_3O_4 and Na_2CoO_3 was thoroughly ground, and placed in a furnace and preheated at 750°C for 12 h. The obtained samples were reground and annealed for 15 h at 850°C in air.

Sample (2): the outgoing materials were $Co(NO_3)_2 \cdot 6H_2O$ and $NaNO_3$ prepared by reaction of Na_2CO_3 in diluted HNO_3. The calcination was carried out at 800°C in air for 98 h and the final reaction was carried out by annealing at 950°C in oxygen atmosphere for 12 h and with cooling rate 0.5 K/min. The sample was prepared in the Institute of Physics, AS CR, Prague.

Sample (3): CH_3COONa was converted to Na_2O at 200°C and homogenized with Co_2O_3 of 99.99% purity. After homogenization the sample was sintered at 620°C for 16 h, then it was ground and repeatedly homogenized and melted at 870°C. The sample was prepared at the Faculty of Chemical and Food Technology, Bratislava.

All samples were polycrystalline and single phased.

3. Experimental results and discussion

Specific heat in magnetic field 0 T and magnetic susceptibility in field 0.1 T have been measured in the temperature range 2–300 K using the conventional Quantum Design PPMS-9 equipment.

The obtained data of specific heat are shown in Fig. 1 in C/T vs. T^2 coordinates in order to emphasize the features. The dependences for sample (1) and (2) are very similar. Two anomalies are visible, small jump around 28 K and an upturn below 10 K. These anomalies seem to be interrelated. The first feature goes weak and the second one becomes more pronounced for the sample (2) compared to the sample (1). Both anomalies become suppressed for sample (3).

The anomaly at 28 K might have several origins: it might be attributed to the presence of impurities and their possible magnetic ordering (most possibly Co_3O_4 which exhibits antiferromagnetic transition at temperature $T_N = 33$ K). Although X-ray analysis does not show any Co_3O_4, it might reside in sample (1) under detection limit, because of the preparation root going out from Co_3O_4. The anomaly at 28 K may originate also from intrinsic inhomogeneity, the mesoscopic phase separation into magnetic clusters and metallic non-magnetic matrix in the sample [4], namely to the magnetic short-range ordering in the clusters.

The second anomaly, the upturn below 10 K, indicates possible non-Fermi liquid behavior, which can be well described by the Griffiths phase scenario [5]. This is also based on inhomogeneity, the coexistence of nonmagnetic matrix and magnetic clusters, which are able to tunnel at low enough temperatures. The

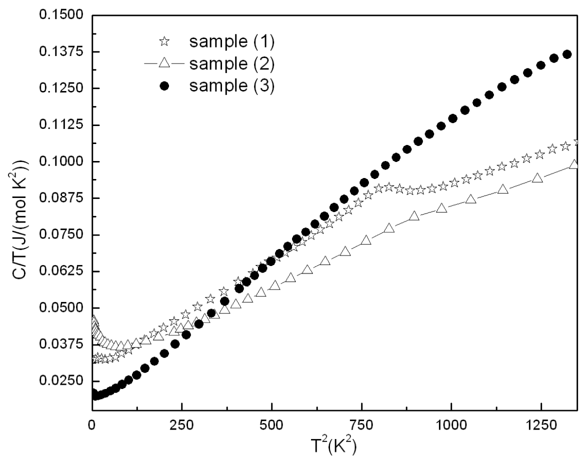

Fig. 1. C/T vs. T^2 dependence of $Na_{0.7}CoO_2$.

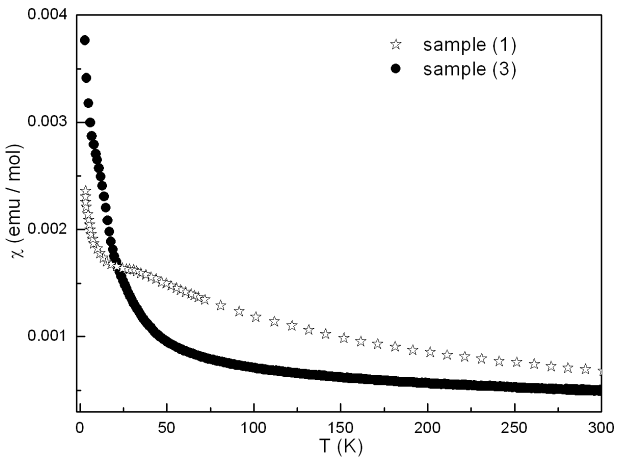

Fig. 2. Magnetic susceptibility of samples (1) and (3) in temperature region from 2 K to 300 K in magnetic field 100 mT.

cluster sizes and their distribution influence the intensity of the upturn. It can be concluded that due to the different preparation process the sample (2) has a finer structure with smaller cluster sizes, while in sample (1) residual Co_3O_4 phases may occur. The complete absence of the anomaly at 28 K for sample (3) suggests that this sample is the most homogeneous among all.

The magnetic susceptibility χ of sample (1) shows a small bump at $T = 30$ K (Fig. 2), in good agreement with the specific heat measurements, indicating short--range ordering. The susceptibility follows the Curie–Weiss law in the temperature range 50–300 K with the Pauli susceptibility of 9×10^{-5} emu mol^{-1} and a negative Weiss temperature $\theta = -131$ K, in good correspondence with [6]. Magnetization curves do not show hysteresis. The susceptibility of sample (3) is substantially different. It also follows the Curie–Weiss law in the temperature range 50–300 K, but with very different Pauli susceptibility 35×10^{-5} emu mol^{-1} and Weiss temperature $\theta = -36$ K, indicating a certain tendency towards more itinerant ferromagnetic character. Instead of the anomaly at 30 K there is a broad bump at 10 K. Preliminary magnetization measurements suggest that this temperature has to do with some kind of ferromagnetic transition, as the magnetization curves taken below this temperature, at 2 K, show hysteresis. Closer investigation of this transition is under progress.

4. Conclusion

The differences in the specific heat and susceptibility among samples (1), (2), and (3) have revealed that the properties are very sensitive to the preparation process and to the presence of inhomogeneities in the samples even if their amount is under the structural analysis resolution limit. Samples (1) and (2) are similar, with differences in the cluster size and Co_3O_4 impurity level. On the other hand, sample (3) appears substantially different both in specific heat and magnetic behavior. It appears the most homogeneous one, presenting some kind of ferromagnetic transition, the nature of which is under current investigation.

Acknowledgments

This work was supported by the Grant Agency VEGA, project No. 1/3027/06, by the Science and Technology Assistance Agency under contracts No. 20-005204, the Czech and Slovak bilateral project No. SK-CZ-09206 and Research Project AVZO10100520. I. Bradarić was supported by the Serbian Ministry of Science, Technology and Development, grant No. 141014/2006.

References

[1] T. Motohashi, R. Ueda, E. Naujalis, T. Tojo, I. Terasaki, T. Atake, M. Karppinen, H. Yamauchi, *Phys. Rev. B* **67**, 064406 (2003).

[2] K. Takada, E. Takayama-Muromachi, F. Izumi, R.A. Dilanian, T. Sasaki, *Nature (London)* **422**, 53 (2003).

[3] M.L. Foo, Y. Wang, S. Watauch, H.W. Zandbergen, T. He, R.J. Cava, N.P. Ong, *Phys. Rev. Lett.* **92**, 247001 (2004).

[4] P. Caretta, M. Mariani, C.B. Azzoni, M.C. Mozzati, I. Bradarić, I. Savić, A. Feher, J. Šebek, *Phys. Rev. B* **70**, 024409 (2004).

[5] A.H. Castro-Neto, G. Castilla, B.A. Jones, *Phys. Rev. Lett.* **81**, 3531 (1998); A. Zorkovská, J. Šebek , E. Šantavá, I. Bradarić, A. Feher, *Low Temp. Phys* **33**, 944 (2007).

[6] T. Takeuchi, M. Matoba, T. Aharen, M. Itoh, *Physica B* **312-313**, 719 (2002).