Physica C 469 (2009) 162–167

Contents lists available at ScienceDirect

Physica C

journal homepage: www.elsevier.com/locate/physc

Spin-singlet superconductivity and antiferromagnetic correlations for the field-aligned powder of the triangular lattice $Na_xCoO_2 \cdot yH_2O$

Masashige Onoda *, Kenjiro Takao, Tomohiro Ikeda

Institute of Physics, University of Tsukuba, Tennodai, Tsukuba 305-8571, Japan

ARTICLE INFO

Article history:
Received 18 November 2008
Received in revised form 18 December 2008
Accepted 11 January 2009
Available online 21 January 2009

PACS:
74.70.Dd
76.60.Cq
76.60.Gv
76.60.Lz

Keywords:
Co oxide
Triangular lattice
NMR
NQR

ABSTRACT

Nuclear magnetic resonance and relaxation measurements of the ^{59}Co nuclei for the well-defined field-aligned powder of the triangular lattice superconductor $Na_xCoO_2 \cdot yH_2O$ with a nearly *optimal* composition for the transition temperature T_c have been performed. Detailed analyses indicate that the Knight shifts for the directions parallel and perpendicular to the CoO_2 plane and the spin-lattice relaxation rates, taken by making an inevitable deterioration of specimen minimal, are significantly smaller than most of the data reported to date, and that this compound is classified into one of the unconventional spin-singlet superconductors as suggested by recent works for single crystals with a lower T_c. A small enhancement of two-dimensional antiferromagnetic spin correlations at some nonzero wave vector may emerge near T_c.

1. Introduction

Since the proposal of a resonating-valence-bond theory for a triangular lattice system with Heisenberg interaction, a great deal of attention has been paid to geometrically frustrated spin systems [1,2]. The discovery of superconductivity in $Na_xCoO_2 \cdot yH_2O$ with the transition temperature $T_c \approx 5$ K, where $x \simeq 0.3$ and $y \simeq 1.3$ [3], as well as the possible application to thermoelectric devices in the parent compound Na_xCoO_2 [4] has accelerated investigations of this system.

Na_xCoO_2 has a crystal structure basically described in terms of CoO_6 octahedra which are joined by sharing edges to form a two-dimensional triangular lattice of Co ions [5]. Many of works in the triangular lattice Co oxides are performed for the γ phase that has a two-layer structure with a trigonal prismatic environment for Na. As x increases from $\approx$0.3 to $\approx$0.8 in this phase, the ground state goes from a normal metal to a Curie–Weiss metal through a poor metallic state at $x \approx 0.5$ accompanied with a partial valence order of Co [6,5]. The end-member composition CoO_2 has two kinds of phases; one has a CdI_2-type structure [7] and another phase corresponds to a three-layer structure that has light stacking faults [8]. Both phases, where the Co ions may be in a low-spin $3d^5$ configuration due to the strong crystal field, basically exhibit metallic properties [8,9]. The superconductivity emerges around $Na_{0.3}CoO_2$ when water molecules are intercalated in between the Co layers. Recently, structural model of this compound has been examined with an interpenetration of two layered subsystem structures, the CoO_2 part and the Na part [10]. The highest T_c for $Na_xCoO_2 \cdot yH_2O$ with $y = 1.3$ is $T_c = 4.8$ K, although there exists a significant difference for the x versus T_c diagrams reported to date [11,12].

In $Na_xCoO_2 \cdot yH_2O$, there has been a debate as to whether the pairing occurs in a spin-singlet or triplet channel. This would be clarified with nuclear magnetic resonance (NMR) measurements for ^{59}Co. However, previous Knight shift data for the ^{59}Co nuclei have resulted in controversial conclusions [13–16]; for a field-aligned powder with $T_c \simeq 4.6$ K prepared using a fluorinert, the Knight shift K^c parallel to the hexagonal c-axis or perpendicular to the CoO_2 plane does not decrease within experimental accuracy of 0.08% at temperatures below T_c, while K^{ab} parallel to the ab-plane decreases with decreasing temperature [13,14]. On the contrary, for the aligned crystals [15] and single crystals [16] with a lower T_c, both K^c and K^{ab} decrease below T_c. Here, T_c for the c-axis is rather low as compared with the optimal value, because it would be due to possibly small values of the upper critical field H_{c2} in this direction [17,18]. A singlet–triplet debate also exists in theoretical aspects; some theories propose singlet pairing mechanisms and others triplet pairing [19].

* Corresponding author. Tel.: +81 29 853 4450; fax: +81 29 853 6618.
E-mail address: onoda@sakura.cc.tsukuba.ac.jp (M. Onoda).

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doi:10.1016/j.physc.2009.01.006

According to the previous papers [12–16], the spin-echo spectra for the ^{59}Co nuclei have significantly large linewidth, which would make a precise determination of the Knight shift difficult without a careful simulation of spectra. For the measurements of detailed properties, the single-crystal specimens are highly desired. However, the present soft-chemical synthesis rarely provides a good quality of crystals. Although the NMR measurements for single-crystal specimens have been done, the superconducting volume fraction for the specimens used is not touched.

In order to clarify a kind of pairing channel, precise measurements for the Knight shifts for the direction normal to the CoO_2 layers are required. In addition, in order to obtain precise sets of NMR and nuclear quadrupole resonance (NQR) data, comprehensive measurements and analyses are very necessary making an inevitable deterioration of the specimen minimal, since it will veil intrinsic microscopic properties. For these purposes, a good-quality of the specimen and the careful alignment of powder are necessary. In this work, the magnetic susceptibility and magnetic resonance data for the field-aligned powder of $Na_xCoO_2 \cdot yH_2O$ with a paraffin are described. The details regarding the sample preparation and the measurements are written in Section 2. The superconducting diamagnetisms are described in Section 3.1, and the various NMR and NQR data for the field-aligned powder with a nearly *optimal* composition for T_c are provided in Section 3.2. Discussions and conclusions are presented in Sections 4 and 5, respectively.

2. Experiments

2.1. Sample preparations

Polycrystalline specimens of the nominal compound $Na_{0.7}$ CoO_2 were synthesized as follows: appropriate mixtures of Na_2CO_3 and Co_3O_4 dried at 573 K for 12 h were pressed into pellets at a pressure of 2.5×10^7 N m^{-2}, which were put in an electric furnace kept at 1073 K in air and annealed for 18 h, and then quenched to room temperature [20]. Through intermediate grindings, this process was done twice. Next, following a previous method [21], the pellets were put in the furnace kept 1173 K in O_2 atmosphere and annealed for 18 h, and at 1023 K for 6 h, and then cooled to 623 K for 12 h. Polycrystalline specimens of $Na_xCoO_2 \cdot yH_2O$ were prepared by the soft chemistry method: 10^{-3} kg of $Na_{0.7}CoO_2$ in a flask, heated in vacuum in order to remove moisture, was mixed with 170 ml of 0.0976 mol l^{-1} of Br_2 dissolved in acetonitrile in Ar through 4 days of stirring. Filtered product was washed with dehydrated acetonitrile. After evaporation of acetonitrile, it was mixed with 300 ml of ultrapure water by stirring for 3 days. Excess water was removed from the filtered surface-wet product in a saturated vapour.

2.2. Field-alignments of powders

123.1 mg of $Na_xCoO_2 \cdot yH_2O$ was mixed with 132.1 mg of a paraffin solution through several minutes of stirring, and then the specimen dispersed in a paraffin was prepared as a randomly oriented powder. Putting it into a pure quartz tube, and rotating the heated tube about the axis perpendicular to the magnetic field [22], the specimen aligned to the *c*-axis was obtained, since $\chi^{ab} > \chi^c$, χ^{ab} and χ^c being the magnetic susceptibilities for the *ab*-plane and the *c*-axis, respectively.

2.3. Measurement methods for magnetization, NMR and NQR

The magnetic susceptibilities for the randomly oriented powder and the field-aligned powder to the *c*-axis were measured with a SQUID susceptometer at temperatures between 2 and 15 K. The NMR and NQR measurements of the ^{59}Co nuclei for the two kinds of field-aligned specimens of $Na_xCoO_2 \cdot yH_2O$, hereafter referred to as NCOH# 1 and NCOH# 2, were performed with a standard coherent pulsed technique in the temperature region between 1.9 and 40 K. The oscillating field of NQR for the field-aligned powders was applied perpendicular to the *c*-axis. The spectra were taken by recording the spin-echo intensities with the magnetic field or frequency varied stepwise, and also measured by the Fourier transform (FT) technique for the small linewidth. In addition, the FT NMR measurements of the ^{23}Na nuclei for NCOH#2 were done between 3 and 10 K. The randomly oriented powder and the field-aligned powder of NCOH#1 were preserved in a freezer except for the measurements, while the field-aligned powder of NCOH#2 was kept at temperatures below 40 K *until all of the measurements were completed*. As will be described below, in order to keep away a deterioration of the specimen and to accumulate precise NMR and NQR data, it is necessary to keep the specimen at sufficiently low temperatures.

3. Results

3.1. Superconducting diamagnetism

Fig. 1a–c show the temperature dependences of the magnetic susceptibilities of NCOH#1; χ^p for the randomly oriented powder, and χ^c and χ^{ab} for the field-aligned powder with the zero-field cooled (ZFC) and field cooled (FC) conditions under the external field H = 1 mT. The significant Meissner diamagnetism is observed with $H \| c$. These data may indicate the present specimen to be one of good quality specimens, considering that it is dispersed in a paraffin. T_c's defined as the temperature at which the susceptibility begins to decrease are $T_c \simeq 4.7$ and 4.5 K for the randomly oriented powder and the field-aligned powder, respectively.

The magnetic susceptibilities of NCOH#1 were taken several times on the NMR and NQR measurements. As the time passed, T_c decreased and the absolute values of ZFC Meissner diamagnetism at 2 K also decreased as follows: for the passing time of 14 days, $T_c \simeq 4.4$ K and $\chi^{ab} = -0.20 \times 10^{-3}$ emu g^{-1}; and for 33 days, $T_c \simeq 4.1$ K and $\chi^{ab} = -0.14 \times 10^{-3}$ emu g^{-1}.

3.2. Quadrupole interaction parameters, Knight shifts and spin-lattice relaxation times

3.2.1. $Na_xCoO_2 \cdot yH_2O$#1

The NQR spectra of the ^{59}Co nuclei that come from the transition of $\Delta m = \pm\frac{5}{2} \leftrightarrow \pm\frac{7}{2}$ for the powder and the field-aligned powder of NCOH#1 are shown in Fig. 2a. The center of spectra ν_c corresponds to $\nu_c \simeq 3\nu_Q(1 - \eta^2/10)$ [23], where ν_Q is the quadrupole frequency expressed as

$$\nu_Q = 3e^2qQ/[2I(2I-1)h] \quad (1)$$

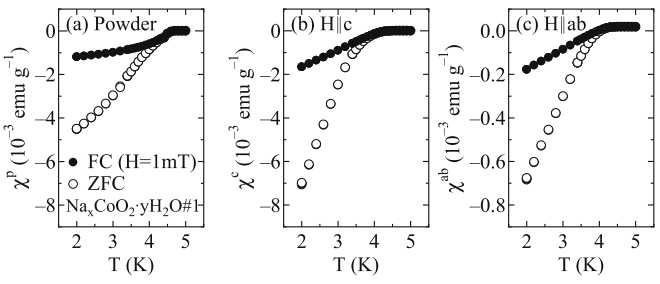

Fig. 1. The temperature dependences of the magnetic susceptibilities of $Na_xCoO_2 \cdot yH_2O$#1 under ZFC and FC conditions for (a) the randomly oriented powder; (b) the *c*-axis; and (c) the *ab*-plane of the field-aligned powder.