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Static magnetic order in $Na_{0.75}CoO_2$ detected by muon spin rotation and relaxation

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The nature of the magnetic transition of the Na-rich thermoelectric $Na_{0.75}CoO_2$ at 22 K was studied by positive muon-spin-rotation and relaxation (μ^+SR) spectroscopy, using a polycrystalline sample in the temperature range between 300 and 2.5 K. Zero-field μSR measurements indicated the existence of a static internal magnetic field at temperatures below 22 K ($=T_m$). The observed muon-spin precession signal below T_m consisted of three components with different precession frequencies, corresponding to three inequivalent μ^+ sites in the $Na_{0.75}CoO_2$ lattice. The total volume fraction of the three components was estimated as $\sim$21% at 2.5 K; thus, this magnetic transition was not induced by impurities but is an intrinsic change in the magnetism of the sample, although the sample was magnetically inhomogeneous otherwise. On the other hand, a similar experiment on a $Na_{0.65}CoO_2$ sample exhibited no magnetic transition down to 2.5 K; which indicates that the average valence of the Co ions is responsible for inducing the magnetic transition at 22 K.

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I. INTRODUCTION

The layered cobaltite, Na_xCoO_2 with $x\sim0.5$,[1–3] is known to exhibit metallic conductivity σ and an extraordinarily large Seebeck coefficient S (above $+100$ μV/K at 300 K) simultaneously, probably due to a strong correlation between the $3d$ electrons of the Co ions.[4] The crystal structure of Na_xCoO_2 with $0.5 \leqslant x \leqslant 0.75$ was reported to be a bronze-type hexagonal system of space group $P6_3/mmc$ ($a=0.2833$ nm and $c=1.082$ nm for $x=0.71$).[5] In this structure, the single CoO_2 sheets and the single disordered Na planes form alternating stacks along the hexagonal c axis.

The CoO_2 sheets, in which a two-dimensional-triangular lattice of Co ions is formed by a network of edge-sharing CoO_6 octahedra, are believed to be the conduction planes. This is because the CoO_2 sheet is a common structural component for all known thermoelectric layered cobaltites, i.e., Na_xCoO_2, $Ca_3Co_4O_9$,[6–8] and $Bi_2Sr_2Co_2O_y$.[9–11] Moreover, if the interaction between $3d$ electrons plays a significant role on their transport properties, such interaction should also affect the magnetism of these cobaltites.

Recently, Motohashi *et al.* studied the bulk susceptibility of polycrystalline $Na_{0.75}CoO_2$ and reported the existence of a magnetic transition at 22 K ($=T_m$) accompanying the increase in the slope of the resistivity-vs-T curve and the appearance of the large positive magnetoresistance effect. No transitions were found in $Na_{0.65}CoO_2$ down to 2 K.[12] Interestingly, both σ and S of $Na_{0.75}CoO_2$ were significantly larger than those of $Na_{0.65}CoO_2$.[13] In other words, the thermoelectric properties of Na_xCoO_2 seem to be enhanced by the magnetic interaction between $3d$ electrons which induces the magnetic transition.

The measurements on heat capacity C_p and spontaneous magnetization suggested that only a very small fraction (less than 1%) of the $Na_{0.75}CoO_2$ sample changed to the magnetic phase even at 2 K,[12] although the sample was confirmed to be single phase by powder x-ray diffraction analysis at ambient temperature, leaving open the possibility that the magnetic transition is due to an undetected impurity phase. However, such small impurity phase is unlikely to induce the observed change in the transport properties below T_m. Therefore, to investigate the magnetism of Na_xCoO_2 in greater detail, we have measured both weak ($\sim$100 Oe) transverse-field positive muon-spin rotation and relaxation (wTF-μ^+SR) and zero-field (ZF-) μ^+SR spectra in both $Na_{0.75}CoO_2$ and $Na_{0.65}CoO_2$ at temperatures below 300 K. The former method is sensitive to local magnetic order *via* the shift of the μ^+ spin precession frequency and the enhanced μ^+ spin relaxation, while ZF-μ^+SR is sensitive to weak local magnetic (dis)order in samples exhibiting quasistatic paramagnetic moments.

II. EXPERIMENTAL

Samples of $Na_{0.75}CoO_2$ and $Na_{0.65}CoO_2$ were synthesized by a modified solid state reaction technique, i.e., a ‘‘rapid heat-up’’ technique, which was developed by Motohashi *et al.*[13] to control the Na content precisely, using reagent-grade Na_2CO_3 and Co_3O_4 powders as starting materials. The mixed powder was placed into the furnace, which was pre-

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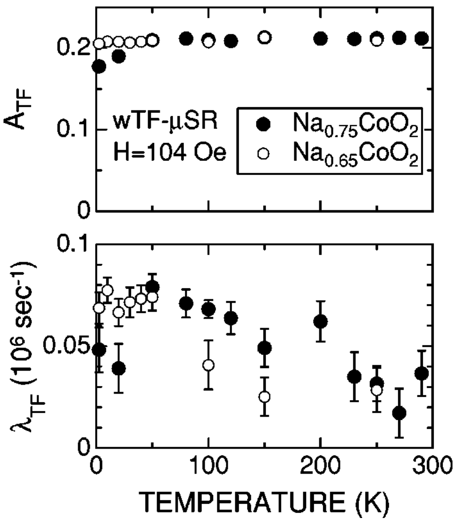

FIG. 1. The temperature dependences of (a) A_{TF} and (b) λ_{TF} for $Na_{0.75}CoO_2$ and $Na_{0.65}CoO_2$. The data were obtained from fits of the wTF-μ^+SR time spectra using Eq. (1).

heated at 750 °C, and fired for 12 h. The fired powder was thoroughly ground and pressed into a plate of 10 mm length, 15 mm width, and 3 mm thickness, and then the plate was sintered at 900 °C for 12 h.

Powder x-ray diffraction studies indicated that the samples were single phase of a hexagonal structure of space group $P6_3/mmc$, i.e., γ-Na_xCoO_2 phase. The lattice parameters of the $Na_{0.75}CoO_2$ sample were calculated as $a=0.2828$ nm and $c=1.0884$ nm, and for $Na_{0.65}CoO_2$, $a=0.2826$ nm and $c=1.0926$ nm. The preparation and characterization of the samples were reported in detail elsewhere.[12,13] The μ^+SR experiments were performed on the M20 surface muon beam line at TRIUMF. The experimental setup and techniques were described elsewhere.[14]

III. RESULTS

The wTF-μ^+SR spectra for both samples were fitted in the time domain with an exponentially damped (relaxing) precessing signal:

$$A_0P(t)=A_{TF}e^{-\lambda_{TF}t}\cos(\omega_\mu t+\phi), \qquad (1)$$

where A_0 is the initial asymmetry, $P(t)$ is the muon-spin polarization function, ω_μ is the muon Larmor frequency, ϕ is the initial phase of the precession, and A_{TF} and λ_{TF} are the asymmetry and exponential relaxation rate.

Figures 1(a) and 1(b) show the temperature dependences of A_{TF} and λ_{TF} for $Na_{0.75}CoO_2$ and $Na_{0.65}CoO_2$. Below 300 K, A_{TF} for $Na_{0.75}CoO_2$ is almost constant (~ 0.21) down to 50 K, then A_{TF} decreases further at lower T, and $A_{TF}=0.018$ at 2.5 K, while A_{TF} for $Na_{0.65}CoO_2$ is nearly independent of T down to 2.5 K. On the other hand, λ_{TF} for both samples increases slightly with decreasing T due to the effect of the nuclear magnetic moments in the paramagnetic state. A marked decrease in λ_{TF} is observed below 50 K only for $Na_{0.75}CoO_2$. These results clearly indicate that $Na_{0.75}CoO_2$ undergoes a magnetic transition below 50 K. Since A_{TF} is roughly proportional to the volume of paramagnetic phases in the sample, the volume fraction V_F of the magnetic phase at the lowest temperature measured is estimated to be $\sim 14\%$.

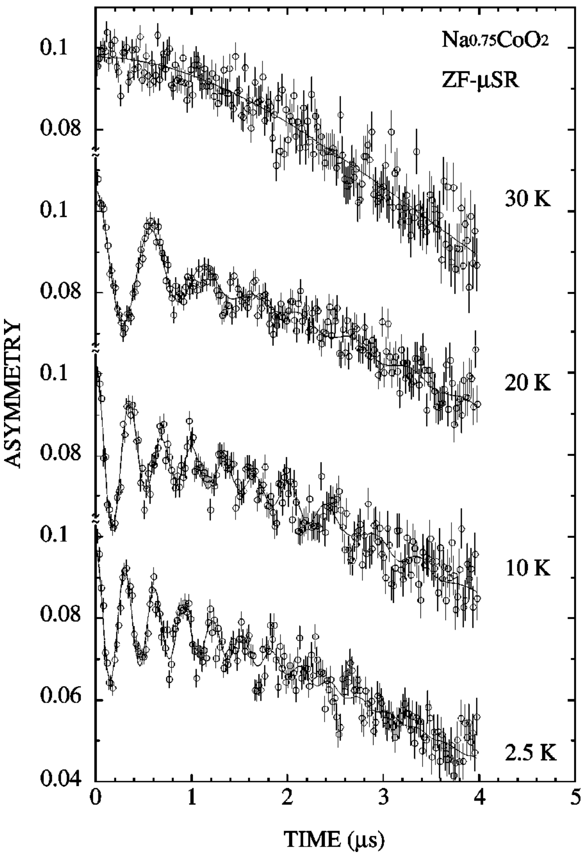

FIG. 2. The ZF-μ^+SR time spectra of $Na_{0.75}CoO_2$ obtained at 30, 20, 10, and 2.5 K; the solid lines represent the results of fitting using Eq. (2).

In order to investigate the magnetism in $Na_{0.75}CoO_2$ below 22 K in greater detail, ZF-μ^+SR measurements were carried out at 30, 25, 22, 15, 10, and 2.5 K. The resulting time spectra, displayed in Fig. 2, show a clear oscillation due to quasistatic, microscopic, internal fields at temperatures below T_m.

Figure 3 shows the Fourier transform of the ZF-μ^+SR time spectrum at 2.5 K. There are one main peak at 3.3 MHz

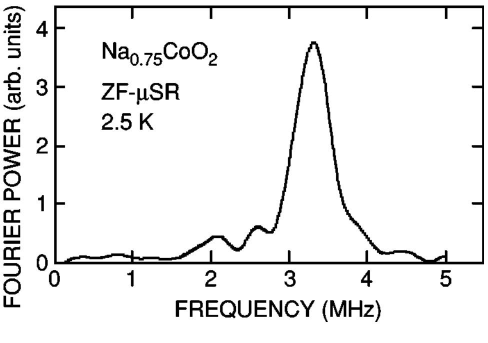

FIG. 3. Fourier transform of the ZF-μ^+SR time spectrum from Fig. 2 at 2.5 K.

and two minor peaks at 2.6 and 2.1 MHz; and the main peak corresponds to the oscillation in Fig. 2.

Indeed, the ZF-μ^+SR time spectra were best fitted with a combination of three exponential relaxation functions (for the signals due to a clear static magnetic field) and a Gaussian Kubo-Toyabe function (for the signal from muon sites experiencing disordered magnetic fields):

$$\begin{aligned} A_0P(t)=&A_1e^{-\lambda_1 t}\cos(\omega_{\mu,1}t+\phi)+A_{\mathrm{KT}}G_{zz}^{\mathrm{KT}}(t,\Delta)\\ &+A_2e^{-\lambda_2 t}\cos(\omega_{\mu,2}t+\phi)\\ &+A_3e^{-\lambda_3 t}\cos(\omega_{\mu,3}t+\phi), \end{aligned} \tag{2}$$

where A_0 is the empirical maximum experimental muon decay asymmetry, A_i and λ_i ($i=1$, 2 and 3) are the asymmetries and exponential relaxation rates associated with the three oscillating signals, A_{KT} is the asymmetry of the Gaussian Kubo-Toyabe signal, and Δ is the static width of the local frequencies at the disordered sites, and

$$\omega_{\mu,i}\equiv 2\pi\nu_{\mu,i}=\gamma_\mu H_{\mathrm{int},i} \tag{3}$$

(where γ_μ is muon gyromagnetic ratio) is the muon precession frequency in the characteristic local magnetic field $H_{\mathrm{int},i}$ due to the static magnetic field.

The static Gaussian Kubo-Toyabe function is

$$G_{zz}^{\mathrm{KT}}(t,\Delta)=\frac{1}{3}+\frac{2}{3}(1-\Delta^2t^2)e^{-\Delta^2t^2/2}. \tag{4}$$

Figures 4(a–e) show the temperature dependences of (a) A_i and A_{KT}, (b) the volume fraction of the three exponential relaxation signals (V_{F}), (c) λ_i, (d) $\nu_{\mu,i}$, and (e) ϕ in $Na_{0.75}CoO_2$. The volume fraction V_{F} was calculated as;

$$V_{\mathrm{F}}=\frac{\sum_{i=1}^{n}A_i}{\sum_{i=1}^{n}A_i+A_{\mathrm{KT}}}. \tag{5}$$

Below 22 K, A_i and A_{KT} have finite values and both A_1 (main component) and A_{KT} are almost constant at temperatures below T_{m}. The magnitude of A_1 is larger than those of A_2 and A_3 by one order of magnitude, as expected from the Fourier-transform spectrum (see Fig. 3). However, the ratio between A_{KT} and A_1 is $\sim$4.5 at 2.5 K; this indicates that $\sim$ 80% muons in the sample experience a disordered magnetic field. Since the magnetic properties of Na_xCoO_2 are highly sensitive to *x*, a slight reduction in *x* makes the sample nonmagnetic in the whole range of temperature.[12] Indeed, the wTF-μ^+SR experiment on the Na-poor sample, $Na_{0.65}CoO_2$, exhibited no magnetic ordering down to 2.5 K (see Fig. 1). Thus, the $Na_{0.75}CoO_2$ sample, although structurally single phase, is found to be partially nonmagnetic, i.e., magnetically inhomogeneous, probably because of a low local Na concentration.

The V_{F}-vs-T curve is also fairly flat ($\sim$20%) below T_{m}, similarly to the A_1-vs-T curve. This indicates that $\sim$20% of the sample exhibits the transition to the ordered phase at 22 K, and the volume of the ordered phase does not change down to 2.5 K. Since $V_{\mathrm{F}}=21\%$ at 2.5 K, it is concluded that this transition is not induced by impurity phases but is an intrinsic behavior of the $Na_{0.75}CoO_2$ sample. Moreover, this suggests that the ordered phase is responsible for the change in the transport properties below T_{m}.

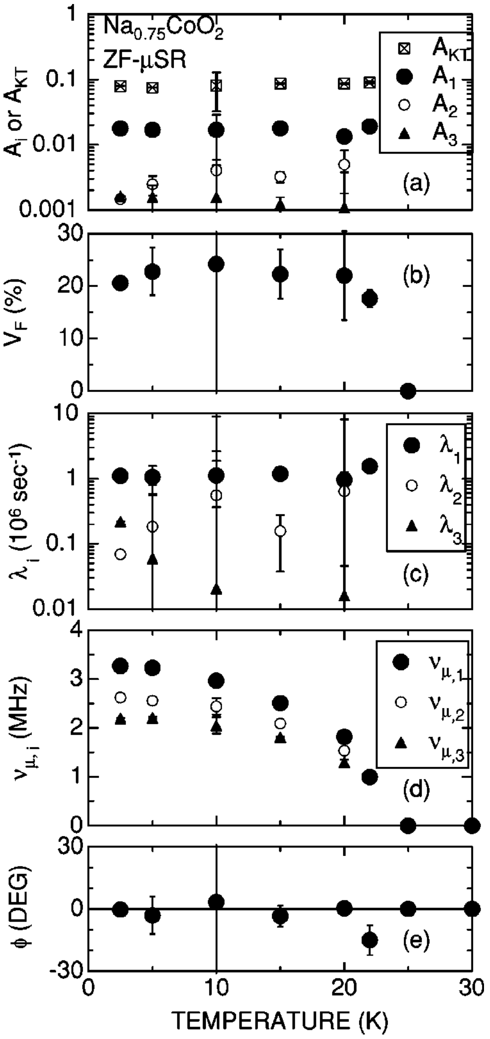

FIG. 4. Temperature dependences of (a) A_i and A_{KT}, (b) V_{F}, (c) λ_i, (d) $\nu_{\mu,i}$, and (e) ϕ for the $Na_{0.75}CoO_2$ sample. The data were obtained by fitting the ZF-μ^+SR time spectra to Eq. (2).

The internal magnetic fields of the three signals, i.e., $\nu_{\mu,i}$ with $i=1$, 2, and 3, exhibit a similar temperature dependence. That is, as T decreases, each $\nu_{\mu,i}$ increases, with a decreasing slope $d\nu_{\mu,i}d/dT$, and level off to a constant value below 5 K. Here, it is worth noting that the $\nu_{\mu,i}$-vs-T curve indicates the change in an order parameter of the transition. Thus, the moderate temperature dependence of $\nu_{\mu,i}$ just below T_{m} suggests that the transition is likely to be discontinuous, whereas $C_{\mathrm{p}}(T)$ supported a continuous transition.[12]

The values of ϕ range between 3.5 and -16 degrees [see Fig. 4(e)]. This fact, i.e., $\phi\sim 0$, indicates that the ordered phase is a either a usual ferromagnet, an antiferromagnet, a ferrimagnet, or a commensurate (C) spin-density wave (SDW) state but not an incommensurate (IC) SDW state, as found, for example, for $Ca_3Co_4O_9$[15] and the Zn and Si doped $CuGeO_3$ system.[16]

TABLE I. Structural parameters for $Na_{0.74}CoO_2$ with $a = 0.2840$ nm and $c = 1.0811$ nm (Ref. 17). g means the occupancy of the site.

Atom	Site	g	x	y	z
Na(1)	$2b$	0.23	0	0	1/4
Na(2)	$2d$	0.51	2/3	1/3	1/4
Co	$2a$	1.0	0	0	1/2
O	$4f$	1.0	1/3	2/3	0.0913

IV. DISCUSSION

The three exponential relaxation signals and their $\nu_{\mu,i}$-vs-T curves suggest that there are three inequivalent microscopically ordered μ^+ sites in the $Na_{0.75}CoO_2$ sample. The possible μ^+ sites are bound to the oxygen ions in the CoO_2 sheets (the O site) and the two vacant sites in the Na planes, namely, the Na(1) and Na(2) sites (see Table I).[17] The bond length d of Co-O, Co-Na(1), and Co-Na(2) are 0.1914, 0.2703, and 0.3161 nm, respectively. Since the dipolar field is proportional to d^{-3}, $H_{\rm int}^{\rm Na(1)}$, and $H_{\rm int}^{\rm Na(2)}$ should be rather small compared with $H_{\rm int}^{\rm O}$. This is inconsistent with the experimental result; that is, $(d_{\rm Co-Na(2)}/d_{\rm Co-O})^3 \sim 0.22$, while $\nu_{\mu,3}/\nu_{\mu,1} \sim 0.67$ at 2.5 K [see Fig. 4(d)]. Thus, positive μ^+ are unlikely to be located at the vacant Na sites but near the O site. The width of the Fast-Fourier transform and the relaxation of the oscillating signals suggest that the field at the O site is inhomogeneously broadened probably due to variations in the bond length $d_{\rm Co-O}$ caused by the excess Na in the Na planes.

The transition is obviously induced by the ordering of the Co spins in the CoO_2 sheets. If we assume that the muons experiencing the ordered field are bound to oxygen, then we can estimate the ordered Co moment as $\sim 0.18\mu_{\rm B}$ at 2.5 K, using $\nu_{\mu,1} = 3.3$ MHz and $d_{\rm Co-O} = 0.1914$ nm. Considering the number of the nearest-neighboring Co ions for the O site $(=3)$ and the small volume fraction of the magnetic phase $(\sim 21\%)$, this value is still 100 times larger than that estimated by the magnetization measurement $(1.2\times 10^{-4}\mu_{\rm B}$ at 2 K).[12] Such large discrepancy is difficult to explain based only on the present results.

The related compound, $Ca_3Co_4O_9$, i.e., $[Ca_2CoO_3]_{0.62}^{\rm RS}[CoO_2]$ where RS denotes a rocksalt-type subsystem, exhibits two magnetic transitions below 300 K;[15] one is a transition to an IC-SDW state at ~ 30 K and the other to a ferrimagnetic state at 19 K. The IC-SDW is considered to be induced by ordering of the Co moments in the $[CoO_2]$ subsystem, whereas the ferrimagnetic ordering is reported to be caused by the interlayer coupling between the Co moments in the $[CoO_2]$ and $[Ca_2CoO_3]$ subsystems.[18,19]

Therefore, there is a possibility that $Na_{0.75}CoO_2$ below $T_{\rm m}$ enters either a ferrimagnet or a commensurate SDW state, because such magnetic ordering would decrease the bulk magnetization drastically. In the former case, the Co moments are likely to align ferromagnetically in the CoO_2 sheets but antiferromagnetically along the c axis. In order to investigate the magnetism of Na_xCoO_2 in further detail, not only μ^+SR but also neutron diffraction and ^{59}Co-NMR measurements are necessary for single crystals with various x.

V. SUMMARY

We measured positive muon-spin-rotation and relaxation (μ^+SR) spectra in a polycrystalline $Na_{0.75}CoO_2$ sample below 300 K. At temperatures below 22 K $(=T_{\rm m})$, zero-field μ^+SR spectra exhibited clear oscillations due to static internal magnetic fields, although the volume fraction of the magnetically ordered phase was only $\sim 21\%$ at 2.5 K. Furthermore, the Co moment estimated by the present μ^+SR experiment was ~ 100 times larger than that estimated from the magnetization measurement. This suggested that the ordered phase is in either a ferrimagnet or a commensurate spin-density wave state. In addition, a large fraction of the muons, given by $A_{\rm KT}$ (KT background) was found to experience a broad distribution of fields, perhaps reflecting the disorder due to the excess Na.

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