Transactions of the Materials Research Society of Japan 29[6] 2737-2740 (2004)

Successive Magnetic Transitions in Thermoelectric Layered Cobaltite, $[Ca_2CoO_3]_{0.62}[CoO_2]$

J. Sugiyama, J. H. Brewer[1], E. J. Ansaldo[2], H. Itahara, K. Dohmae, Y. Seno, C. Xia and T. Tani
Toyota Central Research and Development Laboratories, Inc., Nagakute, Aichi 480-1192, Japan
Fax:81-561-63-6196, e-mail: e0589@mosk.tytlabs.co.jp
[1]TRIUMF and Canadian Institute for Advanced Research and Department of Physics and Astronomy, University of British Columbia, Canada, Vancouver, BC, Canada V6T 1Z1
[2]TRIUMF, 4004 Wesbrook Mall, Vancouver, BC, Canada V6T 2A3

A positive muon-spin-rotation and relaxation (μ^+SR) experiment on $[Ca_2CoO_3]_{0.62}[CoO_2]$, (*i.e.*, $Ca_3Co_4O_9$, a layered thermoelectric cobaltite) indicates the existence of two magnetic transitions at ~ 100 K and 400 – 600 K; the former is a transition from a paramagnetic to an incommensurate (**IC**) spin density wave (**SDW**) state. The anisotropic behavior of zero-field μ^+SR spectra at 5 K suggests that the **IC-SDW** propagates in the *a-b* plane, with oscillating moments directed along the *c*-axis. In addition, it is found that the long-range **IC-SDW** order completes below ~ 30 K, whereas the short-range order appears below 100 K. The latter transition is interpreted as a gradual change in the spin state of Co ions at temperatures between 400 and 600 K. These two magnetic transitions detected by μ^+SR are found to correlate closely with the transport properties of $[Ca_2CoO_3]_{0.62}[CoO_2]$.
Key words: thermoelectrics, layered cobaltites, magnetism, muon spin rotation

1. INTRODUCTION

A strong correlation between 3*d* electrons induces important physical properties in 3*d* metal oxides; *e.g.* high temperature superconductivity in cuprates, colossal magnetoresistance in manganites and probably good thermoelectric properties in layered cobaltites. Four cobaltites, $[Ca_2CoO_3]_{0.62}[CoO_2]$,[1-3] Na_xCoO_2,[4-6] $[Sr_2Bi_{2-y}Pb_yO_4]_x[CoO_2]$,[7,8] and $[Ca_2Co_{4/3}Cu_{2/3}O_4]_{0.62}[CoO_2]$,[9] are known to be good thermoelectrics because of their metallic conductivities and high thermoelectric powers, for reasons which are currently not fully understood. In order to find excellent thermoelectrics suitable for thermoelectric power generation for protecting the environment by saving energy resources and reducing the release of CO_2 into the atmosphere, it is crucial to understand the mechanism of the good thermoelectric properties in these layered cobaltites.

The layered cobaltites share a common structural component: the CoO_2 planes, in which a two-dimensional-triangular lattice of Co ions is formed by a network of edge-sharing CoO_6 octahedra. Charge carrier transport in these materials is thought to be restricted mainly to these CoO_2 planes, as in the case of the CuO_2 planes for the high-T_c cuprates. Since specific heat measurements on Na_xCoO_2 indicate a large thermal effective mass of carriers,[10] all these cobaltites are believed to be strongly correlated electron systems.

The crystal structure of $[Ca_2CoO_3]_{0.62}[CoO_2]$ consists of alternating layers of the triple rocksalt-type $[Ca_2CoO_3]$ subsystem and the single CdI_2-type $[CoO_2]$ subsystem stacked along the *c*-axis.[2,3,11] There is a misfit between these subsystems along the *b*-axis. Susceptibility (χ) measurements[2,12] indicate two magnetic transitions at 19 K and 380 K; the former is a ferrimagnetic transition (T_{FR}) and the latter is probably a spin-state transition (T_{SS}^{χ}). The temperature dependence of the resistivity ρ exhibits a broad minimum around 80 K [refs. 2,3,12] and a broad maximum between 400 and 600 K.[2] Although ρ appears to diverge with decreasing temperature below T_{FR}, it is worth noting that $\chi(T)$ shows no clear anomalies near 80 K or 600 K.

A recent positive muon spin rotation and relaxation (μ^+SR) experiment[12,13] indicated the existence of an incommensurate (**IC**) spin density wave (**SDW**) state below 100 K, which was not detected previously by other magnetic measurements.[2,3] Thus, the broad minimum around 80 K in the $\rho(T)$ curve suggests that the behavior of conduction electrons is strongly affected by the **IC-SDW** order in $[Ca_2CoO_3]_{0.62}[CoO_2]$. Nevertheless, we need more information to confirm the correlation between the transport properties and the **IC-SDW** in $[Ca_2CoO_3]_{0.62}[CoO_2]$; such as the structure of the **IC-SDW** and the subsystem in which the **IC-SDW** exists. Furthermore, T_{SS}^{χ} (~380 K) is too low to explain the whole change in the ρ (T) curve between 400 and 600 K, while the μ^+SR experiment showed a change in slope of the relaxation rate-*vs.*-T curve above 400 K.[13]

In order to further clarify the role of magnetism in thermoelectric layered cobaltites, we have measured both weak (~100 Oe) transverse-field positive muon spin rotation and relaxation (wTF-μ^+SR) and zero field (ZF-)μ^+SR time spectra in $[Ca_2CoO_3]_{0.62}[CoO_2]$ at temperatures below 700 K.

2. EXPERIMENT

Randomly oriented polycrystalline disks (~20 mm diameter and ~2 mm thick) of $[Ca_2CoO_3]_{0.62}[CoO_2]$ and $[Ca_{2-y}M_yCoO_3]_{0.62}[CoO_2]$ ($y \leq 0.33$, M=Sr, Y and Bi) were synthesized by a conventional solid state reaction technique.[12] A c-axis aligned polycrystalline $[Ca_2CoO_3]_{0.62}[CoO_2]$ plate (~$20 \times 20 \times 2$ mm^3) was synthesized by a reactive templated grain growth technique.[14] Single-crystal platelets of $[Ca_2CoO_3]_{0.62}[CoO_2]$ (~$5 \times 5 \times 0.1$ mm^3) were prepared by a $SrCl_2$ flux method.[15] The preparation and characterization of these samples were described in detail elsewhere.[12,14,15]

The μ^+SR experiments were performed on the **M20** or **M15** surface muon beam line at TRIUMF. The experimental setup is described elsewhere.[16]

3. RESULTS AND DISCUSSION

3-1. IC-SDW transition

In all the $[Ca_2CoO_3]_{0.62}[CoO_2]$ samples, the wTF-μ^+SR spectra in a magnetic field of H~100 Oe exhibit a clear reduction of the μ^+ precession amplitude below 100 K. The data were obtained by fitting the wTF-μ^+SR spectrum in the time domain with a combination of a slowly relaxing precessing signal and two non-oscillatory signals, one fast and the other slow relaxing: $A_{para}\exp(-\lambda_{para}t)\cos(\omega_\mu t+\phi) + A_{fast}\exp(-\lambda_{fast}t) + A_{slow}\exp(-\lambda_{slow}t)$, where ω_μ is the muon Larmor frequency, ϕ is the initial phase of the precession and A_n and λ_n (n=para, fast and slow) are the asymmetries and exponential relaxation rates of the three signals. The latter two signals (n=fast and slow) have finite amplitudes below T_{SDW}^{on}~100 K and probably suggest the existence of multiple muon sites in $[Ca_2CoO_3]_{0.62}[CoO_2]$.

Figures 1(a) and 1(b) show the temperature dependences of the paramagnetic asymmetry A_{para} (which is proportional to the volume fraction of a paramagnetic phase in the sample) and the corresponding relaxation rate λ_{para} in three $[Ca_2CoO_3]_{0.62}[CoO_2]$ samples: a randomly oriented polycrystalline sample,[12] a c-aligned polycrystalline sample, and single crystal platelets. The large decrease in A_{para} below 100 K (and the accompanying increase in λ_{para} indicate the existence of a magnetic transition with an onset temperature T_c^{on}~100 K and a transition width ΔT~70 K. The single crystal data suggest that the large ΔT is not caused by inhomogeneity of the sample but is an intrinsic property of this compound.

Figure 2 shows ZF-μ^+SR time spectra at 4.8 K in the c-aligned sample; the top spectrum was obtained with the initial μ^+ spin direction $S_\mu(0)$ perpendicular to the c-axis and the bottom one with $S_\mu(0)//\mathbf{c}$. A clear oscillation due to quasi-static internal fields is observed only when $S_\mu(0)\perp c$. The time interval from t=0 to the first zero crossing of that oscillation is roughly the same (1:1.2954) as the interval between the first and second zero crossings; this is a characteristic of a zeroth-order Bessel function of the first kind $J_0(\omega_\mu t)$ that describes the muon polarization evolution in an incommensurate spin density wave **IC-SDW** field distribution.[16,17]

Actually, the top oscillating spectrum was fitted using a combination of three signals: $A_{SDW}J_0(\omega_\mu t) + A_{KT}G_{ZZ}^{KT}(t, \Delta) + A_{tail}\exp(-\lambda_{tail}t)$, where A_{SDW}, A_{KT} and A_{tail} are the asymmetries associated with the three signals, $G_{ZZ}^{KT}(t, \Delta)$ is the static Gaussian Kubo-Toyabe function,

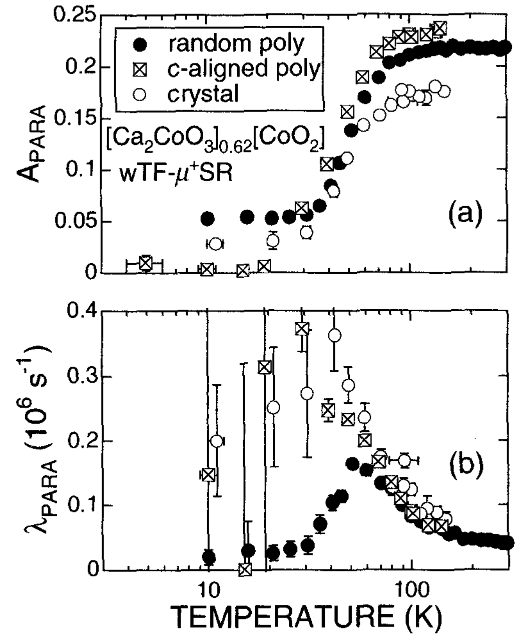

FIG. 1 (a) Paramagnetic μ^+ spin precession asymmetry A_{para} and (b) muon spin relaxation rate λ_{para} as a function of temperature for the three $[Ca_2CoO_3]_{0.62}[CoO_2]$ samples: a randomly oriented polycrystalline disk (●) [ref. 12], a c-axis aligned polycrystalline plate (□) and single crystal (**sc**) platelets (○). For the **sc** platelets, both the value of A_{para} above 100 K and the change in A_{para} below 100 K are smaller than those in the polycrystalline samples. This is because the muon momentum was decreased from 28 to 25 MeV/c for the **sc** measurements to stop muons in the thin platelets (~100 μm thickness), causing a small background signal from muons stopping elsewhere.

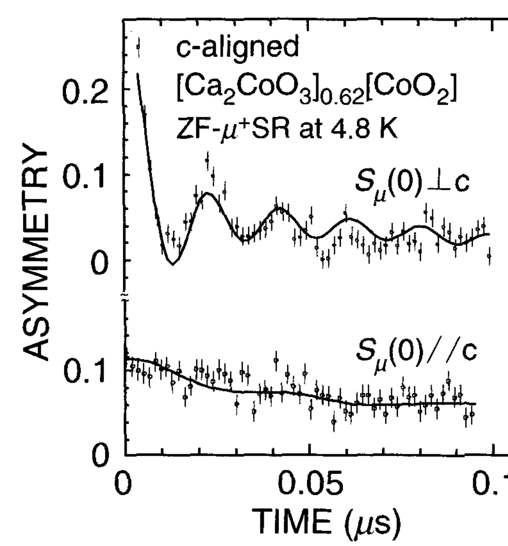

FIG. 2 ZF-μ^+SR time spectra of the c-aligned $[Ca_2CoO_3]_{0.62}[CoO_2]$ plate at 4.8 K. The configurations of the sample and the initial muon spin direction $S_\mu(0)$ are (top) $S_\mu(0)\perp c$ and (bottom) $S_\mu(0)//c$.

Δ is the static width of the distribution of local frequencies at the disordered sites and λ_{tail} is the slow relaxation rate of the "tail" (not shown in this Figure), and was impossible to fit using any other physically reasonable function. We therefore conclude that $[Ca_2CoO_3]_{0.62}[CoO_2]$ undergoes a magnetic transition from a paramagnetic state to an **IC-SDW** state (*i.e.* $T_c^{on}=T_{SDW}^{on}$). The absence of a clear oscillation in the bottom spectrum of Fig. 2 indicates that the internal magnetic field $\boldsymbol{H}_{int}$ is roughly parallel to the *c*-axis, since the muon spins do not precess in a parallel magnetic field. The **IC-SDW** is unlikely to propagate along the *c*-axis due both to the two-dimensionality and to the misfit between the two subsystems. The **IC-SDW** is therefore considered to propagate in the *a-b* plane, with oscillating moments directed along the *c*-axis. This suggests that the ferrimagnetic interaction is also parallel to the *c*-axis.

In order to determine the subsystem in which the **IC-SDW** exists, ZF-μ^+SR spectra were measured in doped samples: *c*-aligned polycrystalline $[Ca_{1.8}Sr_{0.2}CoO_3]_{0.62}[CoO_2]$, $[Ca_{1.8}Y_{0.2}CoO_3]_{0.62}[CoO_2]$ and $[Ca_{1.8}Bi_{0.2}CoO_3]_{0.62}[CoO_2]$. In each case, the dopant occupies the Ca site in the $[Ca_2CoO_3]$ subsystem. Nevertheless, a clear precession was observed in the ZF-μ^+SR spectrum in every sample below 30-80 K. In addition, all the samples show approximately the same precession frequency (~55 MHz) at zero temperature. Here, doping with Sr does not affect T_{SDW}^{on}, while Y or Bi-doping increases T_{SDW}^{on} by 30 K.[12] This suggests that the local magnetic field $H_{int}(0\ K)$ is independent of dopant. Since H_{int} in the doped $[Ca_2CoO_3]$ subsystem should be strongly affected by the dopant, it is concluded that the **IC-SDW** exists not in the $[Ca_2CoO_3]$ subsystem but in the $[CoO_2]$ subsystem.[18] Therefore, the **IC-SDW** is found to be caused by the spin-order of the conduction electrons in the $[CoO_2]$ subsystem.

It is worth noting that χ of polycrystalline samples exhibits no marked anomaly accompanying the **IC-SDW** transition detected by μ^+SR, whereas $\rho(T)$ is metallic above 80 K and semiconducting below 80 K. However, according to the recent χ measurements using single crystal platelets, a small shoulder in the $\chi(T)$ curve was observed at 27 K only for ***H*//*c***.[15] This temperature (27 K) corresponds to the end point of the **IC-SDW** transition observed by wTF-μ^+SR experiment. Thus, it is considered that a short-range order **IC-SDW** state appears below 100 K=T_{SDW}^{on}, while the long-range order is completed below 27 K; *i.e.*, $T_{SDW}= T_{SDW}^{end}$. This is in good agreement with the fact that a clear μ^+SR signal due to the **IC-SDW** was not observed above 30 K.

3-2. Spin State Transition

The high-temperature wTF-μ^+SR spectra in the *c*-aligned $[Ca_2CoO_3]_{0.62}[CoO_2]$ sample indicate the existence of a broad shoulder in the $\lambda_{para}(T)$ curve at 400-600 K, although such a shoulder seems to be ambiguous in the Y-doped sample [Fig. 3(a)]. This behavior is in good agreement with the results of $\chi(T)$ measurements. That is, the $\chi^{-1}(T)$ curve of the pure sample exhibits an obvious change in slope at T_{SS}^{χ}=380 K, while that of the Y-doped sample does not [Fig. 3(b)]. This change is attributed to the spin state transition of the Co^{3+} and Co^{4+} ions from the low temperature *LS*+*IS* to the high-temperature *IS*+*HS* or *HS*, as in the case of $LaCoO_3$.[19,20] Here *LS*, *IS* and *HS* are the low-spin (t_{2g}^6 and t_{2g}^5), intermediate-spin ($t_{2g}^5e_g^1$ and $t_{2g}^4e_g^1$) and high-spin ($t_{2g}^4e_g^2$ and $t_{2g}^3e_g^2$) states, respectively. At these temperatures muons are diffusing rapidly, so that the relaxation rate usually decreases monotonically with increasing temperature. Furthermore, above 150 K A_{para} levels off to its maximum value (~0.23); *i.e.* the sample volume is almost 100% paramagnetic. Hence we can conclude that this shoulder is induced by the spin state transition. Since H_{int} increases due to the spin state transition above T_{SS}, λ_{para} is expected to increase with increasing *T*. On the other hand, both the rapid muon diffusion and the fast exchange rate of electrons between Co^{3+} and Co^{4+} ions decrease λ_{para} with increasing *T*. The competition between these three factors is likely responsible for the broad shoulder in $\lambda_{para}(T)$ around 400-600 K.

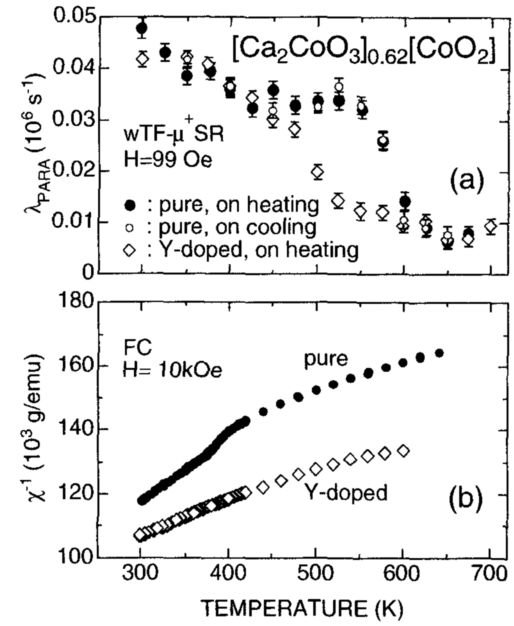

FIG. 3 Temperature dependences of (a) the muon spin relaxation rate λ_{para} and (b) the inverse susceptibility χ^{-1} in a *c*-aligned polycrystalline $[Ca_2CoO_3]_{0.62}[CoO_2]$ sample (● and ○) and a polycrystalline $[Ca_{1.8}Y_{0.2}CoO_3]_{0.62}[CoO_2]$ sample (◇); λ_{para} was obtained by fitting the wTF-μ^+SR spectrum in the time domain using a simple exponential relaxation function, $A_{para}\exp(-\lambda_{para}t)\cos(\omega_\mu t+\phi)$.

The broad shoulder also indicates that the spin state changes gradually in the temperature range between 400 and 600 K. In other words, the onset temperature of the transition T_{SS}^{on}~600 K and the endpoint $T_{SS}^{end}=T_{SS}^{\chi}$= 380 K. This is consistent with the observed $\rho\ (T)$ curve indicating a broad maximum between 400 and 600 K.[2] Furthermore, if the transition occurs abruptly at T_{SS}^{χ} as seen in the $\chi^{-1}(T)$ curve, then a calculation[21] using the degeneracy of spin and orbital degrees of freedom of Co ions predicts that the thermopower should show a dramatic change at T_{SS}^{χ}. Therefore, this gradual change in the spin state is apparently essential to the large thermoelectric power at elevated temperatures.

3-3. Magnetism and Thermoelectric Properties

Figure 4 summarizes the magnetic transitions in $[Ca_2CoO_3]_{0.62}[CoO_2]$. The two magnetic transitions detected by μ^+SR, i.e. the **IC-SDW** and the spin state transitions, are found to correlate closely with the transport properties of $[Ca_2CoO_3]_{0.62}[CoO_2]$. The existence of the **IC-SDW** transition indicates an enhancement of the effective mass of charge carriers (and thus the thermoelectric properties) by strong electron correlations. The existence of the spin state transition suggests that the crystal-field splitting between t_{2g} and e_g levels is comparable to ~400 K. Furthermore, the gradual change in the spin state prevents a decrease in thermoelectric power above T_{SS}^{end}. In other words, these transitions are likely to be key factors in achieving a good thermoelectric performance.

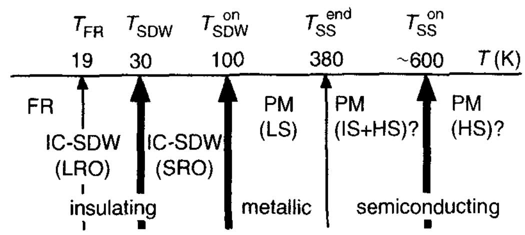

FIG. 4 Successive magnetic transitions in $[Ca_2CoO_3]_{0.62}[CoO_2]$. The bold arrows indicate the transitions found by the present μ^+SR experiment, while the narrow arrows show those detected by the previous susceptibility measurements [refs. 2,12,15]. An incommensurate (**IC**) spin density wave (**SDW**) is observed directly by ZF-μ^+SR below about 30 K, (see Fig. 2), and evidence for the onset of the **IC-SDW** state is seen below T_{SDW}^{on}~100 K, (see Fig. 1), while the muon spin relaxation is characteristic of a paramagnet (**PM**) above T_{SDW}^{on}. Below T_{FR}~19 K, the **IC-SDW** apparently coexists with ferrimagnetism (**FR**). The spin states above T_{SS}^{end}~380 K are not clear at present. A recent muonic Knight shift measurement indicates that T_{SS}^{on} ~580 K.[ref. 22]

ACKNOWLEDGEMENT

We thank Dr. S. R. Kreitzman, Dr. B. Hitti and Dr. D. J. Arseneau of TRIUMF for help with the μ^+SR experiments. Also, we thank Mr. A. Izadi-Najafabadi and Mr. S. D. LaRoy of University of British Columbia for help with the experiments. We appreciate useful discussions with Dr. R. Asahi of Toyota Central R&D Labs., Inc., Prof. U. Mizutani, Prof. H. Ikuta and Prof. T. Takeuchi of Nagoya. This work was supported at Toyota CRDL by joint research and development with International Center for Environmental Technology Transfer in 2002-2004, commissioned by the Ministry of Economy Trade and Industry of Japan, at UBC by the Canadian Institute for Advanced Research, the Natural Sciences and Engineering Research Council of Canada, and at TRIUMF by the National Research Council of Canada.

References

[1] R. Funahashi, I. Matsubara, H. Ikuta, T. Takeuchi, U. Mizutani, and S. Sodeoka. *Jpn. J. Appl. Phys.* **39**, L1127-L1129 (2000).

[2] A. C. Masset, C. Michel, A. Maignan, M. Hervieu, O. Toulemonde, F. Studer, B. Raveau, and J. Hejtmanek, *Phys. Rev. B* **62**, 166-175 (2000).

[3] Y. Miyazaki, K. Kudo, M. Akoshima, Y. Ono, Y. Koike, and T. Kajitani, *Jpn. J. Appl. Phys.* **39**, L531-L533 (2000).

[4] J. Molenda, C. Delmas, P. Dordor, and A. Stoklosa, *Solid State Ionics*, **12**, 473-477 (1989).

[5] H. Yakabe, K. Kikuchi, I. Terasaki, Y. Sasago, and K. Uchinokura, in *Proc. 16th Int. Conf. Thermoelectrics*, Dresden, 1997 (IEEE, Piscataway, 1997), pp.523-527.

[6] I. Terasaki, Y. Sasago, and K. Uchinokura, *Phys. Rev. B* **56**, R12685-R12687 (1997).

[7] T. Yamamoto, I. Tsukada, K. Uchinokura, M. Takagi, T. Tsubone, M. Ichihara, and K. Kobayashi, *Jpn. J. Appl. Phys.* **39**, L747-L750 (2000).

[8] I. Tsukada, T. Yamamoto, M. Takagi, T. Tsubone, S. Konno, and K. Uchinokura, *J. Phys. Soc. Jpn.* **70**, 834-840 (2001).

[9] Y. Miyazaki, T. Miura, Y. Ono, and T. Kajitani, *Jpn. J. Appl. Phys.* **41**, L849-L851 (2002).

[10] Y. Ando, N. Miyamoto, K. Segawa, T. Kawata, and I. Terasaki, *Phys. Rev. B* **60**, 10580-10583 (1999).

[11] Y. Miyazaki, M. Onoda, T. Oku, M. Kikuchi, Y. Ishii, Y. Ono, Y. Morii, and T. Kajitani, *J. Phys. Soc. Jpn.* **71**, 491-497 (2002).

[12] J. Sugiyama, H. Itahara, T. Tani, J. H. Brewer, and E. J. Ansaldo, *Phys. Rev. B* **66**, 134413-1-9 (2002).

[13] J. Sugiyama, J. H. Brewer, E. J. Ansaldo, M. Bayer, H. Itahara, and T. Tani, *Physica B* **326**, 518-521 (2003).

[14] T. Tani, H. Itahara, C. Xia, and J. Sugiyama, *J. Mater. Chem.* **13**, 1865-1867 (2003).

[15] J. Sugiyama, C. Xia, and T. Tani, *Phys. Rev. B* **67**, 104410-1-5 (2003).

[16] G. M. Kalvius, D. R. Noakes, and O. Hartmann, in *Handbook on the Physics and Chemistry of Rare Earths* **32**, edited by K. A. Gschneidner Jr. *et al.* (North-Holland, Amsterdam, 2001) pp. 55-451.

[17] Y. J. Uemura, in *Muon Science*, edited by S. L. Lee *et al.*, (Institute of Physics Publishing, Bristol, 1999) pp. 85-114.

[18] The latest μ^+SR experiment on $[Ca_2Co_{4/3}Cu_{2/3}O_3]_{0.62}[CoO_2]$, which consists of the quadruple rocksalt-type subsystem and the single $[CoO_2]$ subsystem, also indicates the existence of an **IC-SDW** state below ~200 K. The precession frequency due to an internal **IC-SDW** field is estimated as ~60 MHz at zero temperature. This strongly suggests that the **IC-SDW** exists in the $[CoO_2]$ subsystem, because one third of the Co ions in the rocksalt-type subsystem are replaced by Cu ions. J. Sugiyama *et al.*, (2003) unpublished.

[19] J. B. Goodenough, in *Magnetism and the chemical bond* (Wiley, New York, 1963).

[20] T. Saitoh, T. Mizokawa, A. Fujimori, M. Abbate, Y. Takeda, and M. Takano, *Phys. Rev. B* **55**, 4257-4266 (1997).

[21] W. Koshibae, K. Tsutsui, and S. Maekawa, *Phys. Rev. B* **62**, 6869-6872 (2000).

[22] J. Sugiyama *et al.*, (2003) unpublished.

(Received October 13, 2003; Accepted January 16, 2004)