Hidden magnetic transitions in thermoelectric layered cobaltite, \([\text{Ca}_2\text{CoO}_3]_{0.62}[\text{CoO}_2]\)

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A positive muon spin rotation and relaxation (\(\mu^+\)SR) experiment on \([\text{Ca}_2\text{CoO}_3]_{0.62}[\text{CoO}_2]\), (i.e., \(\text{Ca}_2\text{Co}_3\text{O}_9\), a layered thermoelectric cobaltite) indicates the existence of two magnetic transitions at \(\sim 100\) K and 400 - 600 K; the former is a transition from a paramagnetic state to an incommensurate (IC) spin density wave (SDW) state. The anisotropic behavior of zero-field \(\mu^+\)SR spectra at 5 K suggests that the IC-SDW propagates in the \(a\)-\(b\) plane, with oscillating moments directed along the \(c\)-axis; also the IC-SDW is found to exist not in the \([\text{Ca}_2\text{CoO}_3]\) subsystem but in the \([\text{CoO}_2]\) subsystem. In addition, it is found that the long-range IC-SDW order completes below \(\sim 30\) 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 above 400 K. These two magnetic transitions detected by \(\mu^+\)SR are found to correlate closely with the transport properties of \([\text{Ca}_2\text{CoO}_3]_{0.62}[\text{CoO}_2]\).

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I. 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, \([\text{Ca}_2\text{CoO}_3]_{0.62}[\text{CoO}_2]\), \(\text{Na}_x\text{CoO}_2\) with \(x \sim 0.6\), \(\text{Sr}_2\text{Bi}_2\text{O}_5\), \([\text{Sr}_2\text{Bi}_2\text{O}_5]_2[\text{CoO}_2]\), \(\text{Cd}_2\text{I}_3\), and \([\text{Ca}_2\text{CoO}_3]\), 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 \(\text{CoO}_2\) planes, in which a two-dimensional-triangular lattice of Co ions is formed by a network of edge-sharing \(\text{CoO}_6\) octahedra. Charge carrier transport in these materials is thought to be restricted mainly to these \(\text{CoO}_2\) planes, as in the case of the CuO planes for the high-\(T_c\) cuprates. Since specific heat measurements on \(\text{Na}_x\text{CoO}_2\) indicate a large thermal effective mass of carriers \(\text{[1]}\), all these cobaltites are believed to be strongly correlated electron systems.

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μ⁺SR time spectra in [Ca₂CoO₃]₀.₆₂[CoO₂] at temperatures below 700 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 quasi-static paramagnetic moments.

II. EXPERIMENT

A randomly oriented polycrystalline disk (≈ 20 mm diameter and ≈ 2 mm thick) of [Ca₂CoO₃]₀.₆₂[CoO₂] was synthesized by a conventional solid state reaction technique [13]. C-axis aligned polycrystalline [Ca₂CoO₃]₀.₆₂[CoO₂] and [Ca₁.₈M₀.₂CoO₃]₀.₆₂[CoO₂] (M = Sr, Y, Bi) plates (≈ 20 × 20 × 2 mm³) were synthesized by a reactive templated grain growth technique [17]. Single-crystal platelets of [Ca₂CoO₃]₀.₆₂[CoO₂] (≈ 5 × 5 × 0.1 mm³) were prepared by a SrCl₂ flux method [16]. Then, all the samples were annealed in an O₂ flow at 450 °C for 12 hours. The preparation and characterization of these samples were described in detail elsewhere [17, 18]. The μSR experiments were performed on the M20 and M15 surface muon beam line at TRIUMF. The experimental setup is described elsewhere [10].

III. RESULTS

A. IC-SDW transition

In all the [Ca₂CoO₃]₀.₆₂[CoO₂] 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:

\[
A_0 P(t) = A_{\text{PARA}} \exp(-\lambda_{\text{PARA}} t) \cos(\omega_m t + \phi) + A_{\text{fast}} \exp(-\lambda_{\text{fast}} t) + A_{\text{slow}} \exp(-\lambda_{\text{slow}} t),
\]

where \(A_0\) is the initial asymmetry, \(P(t)\) is the muon spin polarization function, \(\omega_m\) is the muon Larmor frequency, \(\phi\) is the initial phase of the precession and \(A_n\) and \(\lambda_n\) (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 \(T_{\text{SDW}}^{\text{on}} \approx 100\) K and probably suggest the existence of multiple muon sites in [Ca₂CoO₃]₀.₆₂[CoO₂].

Figures 1(a) and 1(b) show the temperature dependences of the paramagnetic asymmetry \(A_{\text{PARA}}\) (which is proportional to the volume fraction of a paramagnetic phase in the sample) and the corresponding relaxation rate \(A_{\text{PARA}}\) in three [Ca₂CoO₃]₀.₆₂[CoO₂] samples: a randomly oriented polycrystalline sample [15], a c-axis aligned polycrystalline plate (squares) and single crystal (sc) platelets (open circles). For the sc platelets, both the value of \(A_{\text{PARA}}\) above 100 K and the change in \(A_{\text{PARA}}\) 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.

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 \(\vec{S}_\mu(0)\) perpendicular to the c-axis and the bottom one with \(\vec{S}_\mu(0) \parallel \hat{c}\). A clear oscillation due to quasi-static internal fields is observed only when \(\vec{S}_\mu(0) \perp \hat{c}\). 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 [19, 20, 21].

Actually, the top oscillating spectrum was fitted using a combination of three signals:

$$A_0 P(t) = A_{SDW} J_0(\omega \mu t) \exp(-\lambda_{SDW} t) + A_{KT} G_{zz}^{KT}(t, \Delta) + A_{tail} \exp(-\lambda_{tail} t),$$  \hspace{1cm} (2)

$$\omega \mu \equiv 2\pi \nu \mu = \gamma \mu H_{int},$$  \hspace{1cm} (3)

$$G_{zz}^{KT}(t, \Delta) = \frac{1}{3} + \frac{2}{3} (1 - \Delta^2 t^2) \exp(-\Delta^2 t^2/2),$$  \hspace{1cm} (4)

where $A_0$ is the empirical maximum muon decay asymmetry, $A_{SDW}$, $A_{KT}$ and $A_{tail}$ are the asymmetries associated with the three signals, $G_{zz}^{KT}(t, \Delta)$ is the static Gaussian Kubo-Toyabe function, $\Delta$ is the static width of the distribution of local frequencies at the disordered sites and $\lambda_{tail}$ is the slow relaxation rate of the 'tail' (not shown in this Figure), and the fit using an exponential relaxed cosine oscillation, $\exp(-\Delta t) \cos(\omega \mu t + \phi)$, provides a phase angle $\phi \sim 90^\circ$, which is physically meaningless [22].

We therefore conclude that $[\text{Ca}_2\text{CoO}_3]_{0.62}[\text{CoO}_2]$ undergoes a magnetic transition from a paramagnetic state to an IC-SDW state (i.e. $T_{c}^{\text{on}} = T_{c}^{\text{on}_{\text{SDW}}}$). The absence of a clear oscillation in the bottom spectrum of Fig. 2 indicates that the internal magnetic field $\mathbf{H}_{\text{int}}$ 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, and is consistent with the results of our $\chi$ measurement on single crystals [22].

![Figure 2: ZF-$\mu^+$SR time spectra of the c-aligned $[\text{Ca}_2\text{CoO}_3]_{0.62}[\text{CoO}_2]$ plate at 4.8 K. The configurations of the sample and the initial muon spin direction $\hat{S}_\mu(0)$ are (top) $\hat{S}_\mu(0) \perp \hat{c}$ and (bottom) $\hat{S}_\mu(0) \parallel \hat{c}$.](image)

![Figure 3: Temperature dependences of (a) $A_{SDW}$ and $A_{PARA}$ (estimated by the wTF-$\mu^+$SR experiment), (b) $\nu_\mu$, and (c) $\lambda_{SDW}$ for the c-aligned $[\text{Ca}_2\text{CoO}_3]_{0.62}[\text{CoO}_2]$. The solid line in Fig. 3(b) represents the temperature dependence of the BCS gap energy. The deviation of the experimental data from the theory around 20 K is probably due to the effect of the ferrimagnetic transition at 19 K.](image)
Figures 3(a) - 3(c) show the temperature dependences of $A_{SDW}$, $\Delta_{SDW}$ and $\Delta$ for the c-aligned [Ca$_2$CoO$_3$]$_{0.62}$[CoO$_2$]. $\Delta$ for the c-aligned [Ca$_2$CoO$_3$]$_{0.62}$[CoO$_2$] samples. Doping with Y and Bi increase the magnitude of $\lambda_{SDW}$ rapidly with decreasing temperature, although $\lambda_{SDW}$ decreases rapidly with decreasing temperature. This strongly suggests that the IC-SDW exists not in the [Ca$_2$CoO$_3$]$_{0.62}$[CoO$_2$] subsystem but in the [CoO$_2$] subsystem, because one third of the Co ions in the rocksalt-type subsystem are replaced by Cu ions. Therefore, the IC-SDW is found to be caused by the spin-order of the conduction electrons in the [CoO$_2$] subsystem.

### B. Spin State Transition

The high-temperature wTF-$\mu^+$SR spectra were measured in an air flow to avoid the formation of oxygen deficiency in the sample, whereas the previous experiment in vacuum. The spectra in the c-aligned [Ca$_2$CoO$_3$]$_{0.62}$[CoO$_2$] sample were well fit using an exponential relaxed cosine oscillation, $A_{\text{PARA}} \exp(-\lambda_{\text{PARA}} t) \cos(\omega_{\mu} t + \phi)$. Figures 4(a) - 4(d) show the temperature dependences of $A_{\text{PARA}}$, $\lambda_{\text{PARA}}$, the shift of $\omega_{\mu}(\Delta\omega_{\mu})$ and the inverse susceptibility $\chi^{-1}$ in the c-aligned polycrystalline [Ca$_{2}$.M$_{0.2}$CoO$_{3}$.62][CoO$_{2}$] sample and a polycrystalline [Ca$_{1.8}$Y$_{0.2}$CoO$_{3}$.62][CoO$_{2}$] sample. Here, $\Delta\omega_{\mu}$ is defined as $(\omega_{\mu}(T)-\omega_{\mu}(300 \text{ K}))/\omega_{\mu}(300 \text{ K})$; since the oscillation of a reference was not measured, $\Delta\omega_{\mu}$ is inequivalent to the mosaic Knight shift.

A broad shoulder is clearly seen in the $\lambda_{\text{PARA}}(T)$ curve of the pure sample at 400 - 600 K, although such a
FIG. 5: Temperature dependences of (a) the asymmetry $A_{\text{PARA}}$, (b) the muon spin relaxation rate $\lambda_{\text{PARA}}$, (c) the shift of the muon precession frequency $\Delta\omega_{\mu}$, and (d) the inverse susceptibility $\chi^{-1}$ in a $c$-aligned polycrystalline [Ca$_2$CoO$_3$]$_{0.62}$[CoO$_2$] sample (circles) and a polycrystalline [Ca$_{1.8}$Y$_{0.2}$CoO$_3$]$_{0.62}$[CoO$_2$] sample (diamonds); $A_{\text{PARA}}$ and $\lambda_{\text{PARA}}$ was obtained by fitting the wTF-$\mu^+$SR spectrum in the time domain using a simple exponential relaxation function. 

$A_{\text{PARA}} \exp(-\lambda_{\text{PARA}} t) \cos(\omega_{\mu} t + \phi)$.

shoulder seems to be ambiguous in the Y-doped sample [Fig. 5b]. Moreover, as $T$ increases, the $\Delta\omega_{\mu}(T)$ curve exhibits a sudden decrease at $\sim 400$ K, while the $\Delta\omega_{\mu}(T)$ curve in the Y-doped sample is roughly independent of $T$. It should be noted that, as seen in Figs. 5a and 5a, above 150 K $A_{\text{PARA}}$ levels off to its maximum value ($\sim 0.26$) — i.e. the sample volume is almost 100% paramagnetic. In addition, there is no thermal hysteresis in the data for the $c$-aligned [Ca$_2$CoO$_3$]$_{0.62}$[CoO$_2$] sample obtained on heating and on cooling. This suggests that the changes in the $\lambda_{\text{PARA}}$ and the $\Delta\omega_{\mu}$ are not caused by the formation of oxygen deficiency but by a magnetic transition, as discussed later.

These behaviors are 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 $T^{\chi}_{SS} = 380$ K, while that of the Y-doped sample does not [Fig. 5d]. The change in the $\chi^{-1}(T)$ curve is considered to be attributed to the spin state transition of the Co$^{3+}$ and Co$^{4+}$ ions from the low temperature LS or LS+IS to the high-temperature $LS+IS$, IS, IS+HS or HS, as in the case of LaCoO$_3$. Here LS, IS and HS are the low-spin ($t_{2g}^6$, $S=0$ and $t_{2g}^5$)$_{g1}$, intermediate-spin ($t_{2g}^5$)$_{g2}$, $S=1$ and $t_{2g}^4$)$_{g3}$, $S=3/2$) and high-spin ($t_{2g}^4$)$_{t2}$, $S=2$ and $t_{2g}^3$)$_{t3}$, $S=5/2$) states, respectively.

At these temperatures muons are diffusing rapidly, so that the relaxation rate usually decreases monotonically with increasing temperature. Hence we can conclude that both the shoulder in the $\lambda_{\text{PARA}}(T)$ curve and the sudden decrease in the $\Delta\omega_{\mu}(T)$ curve are induced by the spin state transition, because there is no indications for the appearance of a magnetically ordered state (see Fig. 5a)). Therefore, the spin state transition from the low-temperature LS to the high-temperature $LS+HS$ or HS is most reasonable to explain the change in $H_{\text{int}}$ (suggested by the changes in $A_{\text{PARA}}(T)$ and $\Delta\omega_{\mu}(T)$ without the magnetic order, i.e., the temperature independent $A_{\text{PARA}}(T)$). On the other hand, both the rapid muon diffusion and the fast exchange rate of electrons between Co$^{3+}$ and Co$^{4+}$ ions decrease $\lambda_{\text{PARA}}$ with increasing $T$. The competition between these three factors is likely responsible for the broad shoulder in $\lambda_{\text{PARA}}(T)$ around 400 - 600 K.

In order to know the contribution from the latter two factors, Fig. 6 shows the relationship between $\lambda_{\text{PARA}}$ and $T^{-1}$ of the pure and Y-doped samples, because the latter two factors are expected to depend on $\exp(T^{-1})$. Nevertheless, the linear relationship is not observed even in the Y-doped sample; thus, it is difficult to separate the contribution from each factor at present, although the difference between both samples are clearly seen in Fig. 6.

Indeed, the $\lambda_{\text{PARA}}(T)$ curves of the pure and Y-doped samples seem to level off to a constant value ($\sim 0.01 \times 10^5$ sec$^{-1}$) above 650 K due to a rapid muon diffusion, as in the case of YBa$_2$Cu$_3$O$_{6.5}$. Therefore, we can not determine the onset temperature ($T^{\chi}_{SS}$) of the broad shoulder in the $\lambda_{\text{PARA}}(T)$ curve, based only on the present $\mu^+$SR result, although $T^{\chi}_{SS} \geq 600$ K. The broad shoulder also suggests the possibility that the spin state changes gradually above 400 K. In other words, $T^{\chi}_{SS} \geq 600$ K and the endpoint $T^{\chi}_{SS}$ ends at $T^{\chi}_{SS} = 380$ K. And at temperatures between $T^{\chi}_{SS}$ and $T^{\chi}_{SS}$, the populations
FIG. 6: Muon spin relaxation rate $\lambda_{\text{Para}}$ as a function of $T^{-1}$ in a c-aligned polycrystalline $[\text{Ca}_2\text{CoO}_3]_{0.62}$[CoO$_2$] sample (circles) and a polycrystalline $[\text{Ca}_2\text{CoO}_3]_{0.62}$[CoO$_2$] sample (diamonds). A discontinuous in data at 300 K was caused by the change in the experimental setup from a cryostat to an oven.

of the $\text{IS}$ and $\text{HS}$ states are likely to vary as a function of temperature, as in the case of LaCoO$_3$. The relationship between the spin state transition and the transport properties is discussed later.

IV. DISCUSSION

A. The nature of IC-SDW

There are two Co sites in the $[\text{Ca}_2\text{CoO}_3]_{0.62}$[CoO$_2$] lattice; thus, it is difficult to determine the Co valence in the [CoO$_2$] plane by a $\chi$ measurement or a chemical titration technique, although both Co$^{3+}$ and Co$^{4+}$ ions are mainly in the $\text{LS}$ state below $T_{SS}^{\text{nd}}$, according to the photo-emission and x-ray absorption studies on the related cobaltites, $[\text{Sr}_2\text{Bi}_{2-y}\text{Pb}_y\text{O}_{4}]_x[\text{CoO}_2]$ and $\chi$ measurements on several cobaltites. If we assume that only Co$^{3+}$ and Co$^{4+}$ ions exist in $[\text{Ca}_2\text{CoO}_3]_{0.62}$[CoO$_2$] the average valence of the Co ions in the [CoO$_2$] plane is calculated as +3.38. This value is similar to the nominal valence of Co ions in Na$_2$CoO$_2$. Hence, the Co spins with $S = 1/2$ are considered to occupy 40% corners in the two dimensional triangular lattice to minimize an electric repulsion and a geometrical frustration in the IC-SDW state.

It is worth noting that the $\mu^+$ sites are bound to the O ions in the [CoO$_2$] plane. This means that the $\mu^+$ mainly feel the magnetic field in the [CoO$_2$] plane. Thus, the IC-SDW is most unlikely to be caused by the misfit between the two subsystems, but to be an intrinsic behavior of the [CoO$_2$] plane. Nevertheless, the structure of the IC-SDW order is still unknown at present, because the current $\mu^+$SR experiments provide no information on the incommensurate wave vector. In order to obtain such information, it is necessary to carry out both $^{59}$Co-NMR and neutron scattering experiments on these cobaltites.

B. Calculation and other experiments on IC-SDW

The IC-SDW order in $[\text{Ca}_2\text{CoO}_3]_{0.62}$[CoO$_2$] is assigned to be a spin ($S=1/2$) order on the two-dimensional triangular lattice at non-half filling. Such a problem was investigated by several workers using the Hubbard model within a mean field approximation; $[32, 33, 34, 35]$

$$H = -t \sum_{<ij>,\sigma} c_{i\sigma}^\dagger c_{j\sigma} + U \sum_{i} n_{i\uparrow} n_{i\downarrow},$$

where $c_{i\sigma}^\dagger(c_{j\sigma})$ creates (destroys) an electron with spin $\sigma$ on site $i$, $n_{i\sigma} = c_{i\sigma}^\dagger c_{i\sigma}$ is the number operator, $t$ is the nearest-neighbor hopping amplitude and $U$ is the Hubbard on-site repulsion. The electron filling $n$ is defined as $n = (1/2N)\sum_{i} n_{i\sigma}$, where $N$ is the total number of sites. At $T=0$ and $n=0.5$ (i.e., the average valence of the Co ions in the [CoO$_2$] plane is +4), as $U$ increased from 0, the system is paramagnetic metal up to $U/t \sim 3.97$, and changes into a metal with a spiral IC-SDW, and then at $U/t \sim 5.27$, a first-order metal-insulator transition occurs. $[32]$ On the other hand, at $n=0.81$ (i.e., the average valence of the Co ions in the [CoO$_2$] plane is +3.38), a spiral SDW state is stable below $U/t \sim 3$. $[33, 34]$ These calculations suggest that the IC-SDW state is stable for a weak-to-moderate coupling ($U/t \leq 5$). Also, the IC-SDW phase boundary was reported to depend on $n$; that is, in the $n$ range between 0.75 and 1, the largest $U/t$ for the IC-SDW phase increased monotonically with increasing $n$. $[33]$ Since larger $U/t$ stabilize the energy gap at higher temperature, the calculations are consistent with the present $\mu^+$SR results, i.e., the large increase in $T_{SDW}$ due to the Y- or Bi-doping into $[\text{Ca}_2\text{CoO}_3]_{0.62}$[CoO$_2$].

On the other hand, our preliminary heat capacity measurements using single crystal and c-aligned polycrystal $[\text{Ca}_2\text{CoO}_3]_{0.62}$[CoO$_2$] samples indicate that the electronic specific heat parameter $\gamma$ ranges from 60 to 90 mJ/K$^{-2}$ per mol [CoO$_2$], if we ignore the magnetic contribution. This value is higher than that for Na$_2$CoO$_2$ with $x \sim 0.5$ ($\gamma \sim 24$ mJ/K$^{-2}$ per mol Co). $[11]$ Thus, $[\text{Ca}_2\text{CoO}_3]_{0.62}$[CoO$_2$] seems to be a strongly correlated electron system, as well as Na$_2$CoO$_2$. As a result, it is expected that $U \gg t$, although the above calculations suggest $U/t \leq 5$. In order to solve this puzzle, it is necessary to determine the IC-SDW structure at first.

According to the recent photoelectron spectroscopic study on $[\text{Ca}_2\text{CoO}_3]_{0.62}$[CoO$_2$] below ambient temperature, the density of states DOS at the Fermi level $E_F$ de-
creased with decreasing $T$ and disappeared at 10 K. Thus, the energy gap was clearly observed at 10 K. This also supports our conclusion; that is, both the broad minimum at $\sim 80$ K in the $\rho(T)$ curve and the rapid increase in $\rho$ below 80 K with decreasing $T$ are caused by the IC-SDW order between the spins of the conduction electrons and not by a magnetic scattering, such as, the Kondo effect.

### C. Effect of Oxygen Deficiency on Spin State Transition

In order to know the effect of atmosphere during the measurement, Fig. 7 shows the comparison of the previous [2] and the present $\lambda_{\text{PARA}}(T)$ curve; the former was measured in vacuum and the latter in an air flow. There is a clear thermal hysteresis in the $\lambda_{\text{PARA}}(T)$ curve obtained in vacuum. In addition, the broad maximum between 400 and 600 K looks very ambiguous in the data obtained in vacuum compared with that in an air flow. Recently, it was reported that oxygens are removed from [Ca$_2$CoO$_3$]$_{0.62}$[CoO$_2$] above 723 K ($= 450 \degree$C) even in an oxygen flow. Therefore, both the clear thermal hysteresis and the suppression of the broad maximum in the $\lambda_{\text{PARA}}(T)$ curve obtained in vacuum are induced by the formation of oxygen deficiency. As well as the oxygen deficiency, the substitution of Ca by Y decreases the average Co valence; as a result, the $\lambda_{\text{PARA}}(T)$ curve of the Y-doped sample looks quite similar to that of [Ca$_2$CoO$_3$]$_{0.62}$[CoO$_2$] obtained in vacuum on cooling (see Fig. 7(b) and Fig. 7(a)).

### D. Relationship between Spin State Transition and Transport Properties

The broad shoulder in the $\lambda_{\text{PARA}}(T)$ curve at 400 - 600 K is in good agreement with the behavior of the $\rho(T)$ curve, because the $\rho(T)$ curve shows a broad maximum between 400 and 600 K, and above 600 K $\rho$ decreases monotonically with increasing $T$ up to 1000 K. On the other hand, the $S(T)$ curve exhibits a small change in slope around $T_{SS}$; that is, as $T$ increases from 0 K, $S$ increases monotonically up to $\sim 100$ K and seems to level off a constant value ($\sim 130 \mu$VK$^{-1}$) up to $\sim 400$ K, then $S$ again increases linearly ($dS/dT \sim 80$ nVK$^{-2}$) up to 1000 K. Therefore, above $T_{\text{SS}}$, the $\rho(T)$ curve exhibits a semiconducting behavior, whereas the $S(T)$ curve metallic.

The two Co sites in the [Ca$_2$CoO$_3$]$^{\text{RS}}$[CoO$_2$] lattice leads to a question which is responsible for the spin state transition, as in the case of IC-SDW order. Both the change in slope of $S(T)$ at $\sim 400$ K and the broad maximum of $\rho(T)$ at 400 - 600 K suggest that the Co ions in the [CoO$_2$] plane play a significant role on the spin state transition. Indeed, the related cobaltites, Na$_{0.9}$[CoO$_2$] and Na$_2$Ca$_2$[CoO$_3$], were reported to exhibit a small magnetic anomaly around 300 K, probably indicating the existence of a spin state transition, although the [CoO$_2$] plane was considered to be rigid due to a network of edge-sharing CoO$_6$ octahedra. Hence, the Co ions in the [CoO$_2$] planes are most likely to change their spin state at 400 - 600 K.

The existence of the spin state transition suggests that the crystal-field splitting between $t_{2g}$ and $e_g$ levels is comparable to $\sim 400$ K. Thus, above $T_{\text{SS}}$, charge carrier transport in the [CoO$_2$] plane is considered to be dominated by not only the direct hopping of the $t_{2g}$ electrons between the Co ions but also the hybridization between Co-$e_g$ levels and O-2$p$ levels, as in the case of the perovskite LaCoO$_3$. Indeed, $\rho$ of LaCoO$_3$ decreased with increasing $T$ above 500 K, which is the temperature of the apparent spin state transition from $LS$ to $IS$ accompanied with an insulator-to-metal transition.

If we employ the modified Heikes formula using the degeneracy of spin and orbital degrees of freedom of Co ions, the value of $S_{T \to \infty}$ is calculated as $154 \mu$VK$^{-1}$, when the concentration of Co$^{4+}$ is equivalent to that of Co$^{3+}$ and both Co$^{3+}$ and Co$^{4+}$ are in the $LS$ state. In order to explain the observed $S(T)$ curve above $T_{\text{SS}}$, it is necessary to assume that Co$^{3+}$ is in the $LS$ state and Co$^{4+}$ in the $LS + IS$ state; under this assumption, we obtain $S_{T \to \infty} = 293 \mu$VK$^{-1}$, although such inequivalent spin state is unlikely to exist at elevated temperatures.
In Fig. 8, FR means ferrimagnetic, PM paramagnetic and LS, IS and HS low-, intermediate- and high-spin state, respectively; and IC-SDW incommensurate spin density wave state, LRO and SRO long-range and short-range order. The spin states above $T_{SS}^{end} \approx 380$ K are not clear at present.

Our $\chi$ measurements using single crystal platelets of [Ca$_2$CoO$_3$]$_{0.62}$[CoO$_2$] showed a clear thermal hysteresis with a width of $\sim 25$ K for the spin state transition at $T_{SS}^{end}$. The thermal hysteresis was also confirmed by a heat capacity measurement. These indicate that the spin state transition accompanies a structural change, as well as the case of LaCoO$_3$ around 100 K and 500 K detected by neutron diffraction measurements.  

Hence, in order to elucidate the mechanism of the spin state transition, further $\mu^+$ SR experiments on the related cobaltites, such as Na$_{0.9}$[CoO$_2$] and Na$_2$Ca$_y$[CoO$_2$], are necessary; in particular, a precise muonic Knight shift measurement would provide a significant information on the change in $H_{int}$ during the spin state transition. In addition, we need an x-ray and/or neutron diffraction analysis for [Ca$_2$CoO$_3$]$_{0.62}$[CoO$_2$] as a function of temperature, to obtain the information on structural change, which would affect the magnitude and distribution of $H_{int}$ above $T_{SS}^{end}$. Furthermore, the photo-emission and x-ray absorption studies on [Ca$_2$CoO$_3$]$_{0.62}$[CoO$_2$] at elevated temperatures are needed to determine the spin state for understanding the transport properties above $T_{SS}^{end}$.

V. SUMMARY

We investigated the magnetism of the misfit layered cobaltite, [Ca$_2$CoO$_3$]$_{0.62}$[CoO$_2$], by a positive muon spin rotation and relaxation experiment. It is found that [Ca$_2$CoO$_3$]$_{0.62}$[CoO$_2$] exhibits the successive magnetic transitions, as summarized in Fig. 8. An incommensurate (IC) spin density wave (SDW) is observed directly by ZF-$\mu^+$SR below about 30 K, and evidence for the onset of the IC-SDW state is seen below $T_{SS}^{SDW} \approx 100$ K, while the muon spin relaxation is characteristic of a paramagnet (PM) above $T_{SS}^{SDW}$. Therefore, we conclude that the long-range IC-SDW order completes below $\sim 30$ K, whereas the short-range order appears below 100 K. Also the IC-SDW is found to propagate in the [CoO$_2$] plane, with oscillating moments directed along the c-axis. Below $T_{FR} \approx 19$ K, the IC-SDW apparently coexists with ferrimagnetism (FR).

At 400 - 600 K, the spin state of Co ions changes; that is, the populations of the low-, intermediate- and high-spin states are most likely to vary gradually with increasing temperature above 380 K ($= T_{SS}^{end}$). Also, this transition is found to be sensitive to the Co valence, which is controlled by doping and/or oxygen deficiency.

These two magnetic transitions detected by $\mu^+$SR are found to correlate closely with the transport properties of [Ca$_2$CoO$_3$]$_{0.62}$[CoO$_2$]; in particular, both a broad minimum at around 80 K and a broad maximum between 400 and 600 K in the $\rho(T)$ curve.

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