A Mystery in Thermoelectric Layered Cobaltites; the Correlation between Magnetism and Transport Properties on the Two-Dimensional Triangular Lattice

Jun Sugiyama

Abstract

Using muon spin spectroscopy we have found that, for both Na$_{0.6}$CoO$_2$ ($0.6 \leq x \leq 0.9$) and 3- and 4-layer cobaltites, a common low temperature magnetic state (which in some cases is manifest as an incommensurate spin density wave) forms in the CoO$_2$ planes. Here we summarize those results and report an almost dome-shaped relation between the transition temperature into the low-$T$ magnetic state and the composition $x$ for Na$_x$CoO$_2$ and/or the high-temperature asymptotic limit of thermopower in the more complex 3- and 4-layer cobaltites. This behavior is explained using the Hubbard model on two-dimensional triangular lattice in the CoO$_2$ plane.

Keywords

Muon spin rotation/relaxation, Spin density wave, Thermoelectrics, Cobaltites, Two-dimensional triangular lattice

要旨

良好な熱電性能を示す一連の層状コバルト酸化物の磁性を、ミュオンスピン回転・緩和法により調べた。最も単純な構造のNa$_x$CoO$_2$のみならず3重あるいは4重岩塩型を含む全ての層状コバルト酸化物で、低温では薄膜の磁性相がCoO$_2$面に形成されることを見出した（この磁性相の構造は多くの場合、非整合スピン密度波状態だった）。ここではこれらの測定結果をまとめ、転移温度とCoO$_2$面のCo価数との間に共通のドーム型の関係があることを示す。この挙動は、スピンが半導体近傍にある2次元3角格子（つまりCoO$_2$面）へハバード模型を適用することにより統一的に説明された。

キーワード

ミュオンスピン回転・緩和、スピン密度波、熱電体、コバルト酸化物、2次元3角格子
1. Introduction

Although the widespread current interest in the layered cobaltites (i.e., 5 K superconductivity in Na_{0.35}CoO_2*2H_2O)^1,2) was originally due mainly to their unique combination of high thermopower $S$ with metallic transport properties,^3–10) which makes them one of the most promising systems for power applications, we have shown that they also display interesting and complex magnetic orderings, directly correlated with the enhanced $S$. The richness of behavior of the layered cobaltites is due to their intrinsic structure, namely: electrically active triangular planes of CoO$_2$, which are separated by a variety of intermediate structures; their relatively strong electronic correlations; and the fact that the structures between the CoO$_2$ planes can be modified in a variety of ways to vary their dimensionality, ionic states, carrier doping in the CoO$_2$ planes and the relevant interaction strengths.

At present, the following three groups of cobaltites are known to be good thermoelectrics, because they display metallic conductivities as well as high thermoelectric powers $S$, for reasons which are currently not fully understood.

1. Na$_x$[CoO$_2$],^3–5)
2. [Ca$_2$CoO$_3$]$_{0.62}$[CoO$_2$],^6–8)
3. [Sr$_2$Bi$_2$O$_4$]$_{0.5}$[CoO$_2$].^9, 10)

Here, RS stands for a rocksalt-type block; a triple rocksalt-type block for the group No. 2 and a quadruple group for No. 3. All 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 (see Fig. 1). Charge carrier transport in these cobaltites is thought to be restricted mainly to the CoO$_2$ planes, as in the case of the CuO$_2$ planes for the high-$T_c$ cuprates. Since specific heat measurements on Na$_x$CoO$_2$ indicate a large thermal effective mass of carriers,^11) all these cobaltites are believed to be strongly correlated electron systems.

In order to elucidate the magnetism in the CoO$_2$ planes and the mechanism of the good thermoelectric properties, we have carried out positive muon spin rotation and relaxation ($\mu^+$SR) experiments on the layered cobaltites. As a result, we found the transition from a high-temperature paramagnetic to a low-$T$ commensurate or incommensurate spin density wave (C- or IC-SDW) state for [Ca$_2$CoO$_3$]$_{0.62}$[CoO$_2$] below $\sim$100 K,^12, 13) Na$_{0.75}$CoO$_2$ at 22 K^14) and [Ca$_2$Co$_4$/3Cu$_{2}$/3O$_4$]$_{0.62}$[CoO$_2$] below $\sim$200 K.^15) The common magnetic ordering is thus not always that of a classic frustrated AF (triangular planar arrangement of spins) system but rather a variety of states including disordered AF and (most common) an IC-SDW, arising in parallel with other effects in the triangular lattice such as effective mass enhancement and the enhanced $S$ in the Na$_x$CoO$_2$ case. The more complex cobaltites exhibit, in addition, other magnetic orderings and even higher $S$.

Nevertheless, the transition temperature was scattered in the wide $T$ range (22 - 200 K), and there was no clear relationship between $T_{SDW}$ and structural properties and/or carrier concentration of the layered cobaltites. We back therefore to the basic system, Na$_x$CoO$_2$, to investigate the dependence of $T_{SDW}$ on $x$ by $\mu^+$SR. Also, for the multilayer systems, we clarify the magnitude of $T_{SDW}$ as a function of the Co valence varied by the change in composition of the rocksalt-type subsystem. For the Na$_x$CoO$_2$ case, we show that a calculation based on the Hubbard model for a triangular lattice of $S=1/2$ Co ions with occupancy given by $x$ (correlated with band filling) is able to explain the dome shaped magnetic phase diagram.

![Fig. 1 Schematic crystal structures of layered cobaltites; (a) Na$_x$CoO$_2$, (b) 3-layer cobaltites, and (c) 4-layer cobaltites.](image-url)
shown below. Similar behavior is observed for the multilayer systems, where the increased two dimensionality due to the extra layers leads to higher \( T_{SDW} \) and is correlated with higher \( S \).

### 2. Experiment

#### 2.1 \( \mu^+ \)SR

Muon spin rotation and relaxation (\( \mu \)SR) is an important tool for probing local static and dynamic magnetic properties, especially for detecting magnetic order/disorder and determining a magnetic phase diagram in magnetic materials.\(^{24, 25}\) Actually, the magnetic phase diagram of the superconducting cuprates were clarified by \( \mu \)SR experiments.\(^{26}\)

Since \( \mu \)SR requires low energy muons in order to stop the beam in samples of convenient thickness (below 1 cm), the required intensities are available only from ordinary two-body pion decay, from which the muon emerges (in the rest frame of the pion) with a momentum of 29.79 MeV/c and a kinetic energy of 4.119 MeV (i.e., surface muon). The lifetime of a free charged pion is 26.03 ns.

\[
\pi^+ \rightarrow \mu^+ + \nu_\mu, \quad \cdots \cdots \cdots \cdots \cdots \cdots (1)
\]

where \( \nu_\mu \) is muon neutrino and pions in turn are produced in medium energy nucleon-nucleon collisions as,

\[
p + p \rightarrow \pi^+ + p + n. \quad \cdots \cdots \cdots \cdots \cdots \cdots (2)
\]

Typically, one directs a beam of proton \( p \) with a kinetic energy in the range 0.5-1 GeV onto a target of light nuclei such as Be or C.

The most remarkable feature of positive \( \pi \) decay is that it maximally violates Parity symmetry, causing the \( \mu \) to be emitted with perfect spin polarization.

This is the greatest advantage of \( \mu \)SR as a magnetic resonance technique: whereas NMR and ESR rely upon a thermal equilibrium spin polarization, usually achieved at low temperatures in strong magnetic fields, \( \mu \)SR begins with a perfectly polarized probe, regardless of conditions in the medium to be studied. It also implies that muon spin degrees of freedom usually start their evolution as far from thermal equilibrium as conceivable.

Once the muons are implanted within a sample and stopped usually at interstitial sites much less than 1 nsec, their local magnetic environment dictates the subsequent evolution of their spin vectors. If the muons experience a unique off-axis magnetic field (either internal or applied), the spins precess coherently around the filed at their Larmor frequency. However any spatial or temporal, site to site, variation of the magnetic field results in dephasing or depolarization of the muon spin ensemble. This precessional motion and/or depolarization of the muon spins can be monitored because of the propensity of the muon decay positron \( e^- \) to be emitted preferentially along the spin direction of muon, a further consequence of Parity-violation in the weak interaction. In a \( \mu \)SR experiment, the information on the distribution of local magnetic environments over all muon sites is thus delivered to the observer in the form of relatively high energy (up to 53 MeV) decay \( e^- \) which readily penetrate sample holders, cryostats or ovens and the detectors used to established the time and direction of the muon spin at the instant decay.

\[
\mu^+ \rightarrow e^- + \nu_e + \nu_\mu, \quad \cdots \cdots \cdots \cdots \cdots \cdots (3)
\]

Here, we have measured both weak (~100 Oe) transverse-field positive muon spin rotation and relaxation (wTF-\( \mu \) SR) and zero field (ZF-) \( \mu \)SR time spectra. The former method is sensitive to local magnetic order via the shift of the \( \mu^+ \) spin precession frequency and the enhanced \( \mu^+ \) spin relaxation, while ZF-\( \mu \)SR is sensitive to weak local magnetic [dis]order in samples exhibiting quasi-static paramagnetic moments.

#### 2.2 Sample preparation

Single-crystal platelets of Na\(_x\)CoO\(_2\) were prepared by a flux method.\(^{27}\) Polycrystalline 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.\(^{28}\) Polycrystalline 3- and 4-layer cobaltites listed in Table 1 (see p.10) were synthesized by a
3. Results

3.1 Na$_{x}$CoO$_2$

Polycrystalline Na$_{0.75}$CoO$_2$ exhibited a magnetic transition at 22 K accompanying the increase in the slope of the resistivity-$vs.-T$ ($\rho(T)$) curve and the appearance of the large positive magnetoresistance effect, while no transitions were found in Na$_{0.65}$CoO$_2$ down to 2 K.31 Interestingly, both $\rho(T)$ and $S$ of Na$_{0.75}$CoO$_2$ were significantly larger than those of Na$_{0.65}$CoO$_2$.28 In other words, the thermoelectric properties of Na$_x$CoO$_2$ seem to be enhanced by the magnetic interaction between 3$d$ electrons which induces the magnetic transition. On the other hand, Na$_{0.9}$CoO$_2$ was reported to exhibit a magnetic transition at 19 K, although $\rho$ (300 K) in Na$_{0.9}$CoO$_2$ was higher by one order of magnitude than that of Na$_{0.65}$CoO$_2$.27 Therefore, to investigate the magnetism of Na$_{0.9}$CoO$_2$ in greater detail, we have measured $\mu^+$SR spectra in Na$_x$CoO$_2$ with $x = 0.6 - 0.9$ at temperatures below 300 K.

Figure 2 shows zero-field (ZF-)$\mu^+$SR time spectra at 1.8 K for single crystal platelets of Na$_{0.9}$CoO$_2$. The top spectrum was obtained with the initial $\mu^+$ spin direction $S_\mu(0)$ perpendicular to the c-axis and the bottom one with $S_\mu(0)$ parallel to c. A clear oscillation due to quasistatic internal fields is observed only for the $S_\mu(0) \perp c$ case. The oscillation in the top spectrum is characteristic of a zeroth-order Bessel function of the first kind $J_0(\omega_\mu t)$ that describes the muon polarization evolution in an IC-SDW field distribution.32 Actually, the top oscillating spectrum was fitted using a combination of three signals:

$$
A_0 \rho(t) = A_{\text{SDW}} J_0(\omega_\mu t) \exp(-\lambda_{\text{SDW}} t^2) + A_K G_{ZZ}^K(t, \Delta) \exp(-\Delta t^2/2) + A_x \exp(-\lambda_x t^2/2),
$$

where $A_0$ is the empirical maximum muon decay asymmetry, $A_{\text{SDW}}$, $A_K$, and $A_x$ are the asymmetries associated with the three signals, $G_{ZZ}^K(t, \Delta)$ is the static Gaussian Kubo-Toyabe function, $\Delta$ is the static width of the distribution of local frequencies at the disordered sites, $\lambda_i$ is the slow relaxation rate and $\lambda_{\text{SDW}}$ and $\lambda_x$ are the power of the exponential relaxation. Fits using just an exponentially damped cosine oscillation, $\exp(-\lambda t) \cos(\omega_\mu t + \phi)$, provides a phase angle $\phi \approx -42^\circ$, which is physically meaningless.24

We therefore conclude that Na$_{0.9}$CoO$_2$ undergoes a transition from a paramagnetic to an IC-SDW state at $T_{\text{SDW}} = 19$ K. The absence of a clear oscillation for the $S_\mu(0) \parallel c$ case indicates that the internal field $H_{\text{int}}$ is roughly parallel to the c-axis. Due to the strong anisotropy, the IC-SDW is thus considered to localize in the CoO$_2$ plane, with oscillating moments directed along the c-axis, as in the case of [Ca$_2$CoO$_3$)$_{30.62}$][CoO$_2$].14 Moreover, this anisotropic result is consistent with $\chi$ measurements. That is, the cusp at 19 K was observed, when $H$ was applied parallel to the c-axis, whereas the cusp was undetected if $H \perp c$.27

Figure 3 shows the $T$ dependence of the muon precession frequency $f_\mu = \omega_\mu / 2\pi$ for the single crystal platelets of Na$_{0.9}$CoO$_2$. Here $f_\mu$ is the order parameter of the transition and its $T$ dependence is well described by the BCS weak coupling expression for such order parameters, as expected for the IC-SDW state.33 The magnetic phase diagram (Fig. 4) of Na$_x$CoO$_2$ can thus be sketched.
from the $\mu^s$SR results for polycrystalline samples with $x = 0.65$ and $0.75^{14}$ and the present $x = 0.6$ and 0.9 crystals. According to recent compositional and chemical titration analyses, the oxygen deficiency $\delta$ in Na$_{x}$CoO$_2$ is negligibly small even for the $x = 0.9$ sample. Hence, the average Co valence is directly calculated from $x$. As $x$ increases from 0.6 (i.e. the Co valence decreases from 3.4), the magnitude of $T_{SDW}$ increases up to around $x = 0.8$, then decreases with further increasing $x$. As a result, we obtain the dome-shaped relationship of Fig. 4 between $T_{SDW}$ and $x$, viz. the Co valence for Na$_{x}$CoO$_2$.  

Although a fully occupied Na$_{x}$CoO$_2$ phase cannot be prepared by conventional solid state reaction and/or flux techniques, the related compound LiCoO$_2$ is easily obtained. The structure of LiCoO$_2$ is almost the same as that of Na$_{x}$CoO$_2$, and it is reported to be diamagnetic down to 4.2 K. $^{34}$ indicating the Co$^{3+}$ in LiCoO$_2$ are in a low-spin state $t_{2g}^6$, as for Na$_{x}$CoO$_2$. Therefore, Na$_{x}$CoO$_2$ is also expected to lack magnetically ordered states.  

The occupancy of Co$^{4+}$ spins ($S = 1/2$) in the two-dimensional triangular lattice (2DTL) increases with decreasing $x$. A fully Na deficient Na$_{x}$CoO$_2$ would be a half filled 2DTL; that is, every lattice site is occupied by an $S = 1/2$ spin. The Hubbard model within a mean field approximation can be used for explaining the magnetism of such a system, with the Hamiltonian $H$ $^{19\sim21}$:

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

where $c_{i\sigma}^\dagger (c_{i\sigma})$ 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 $n = (1/2N) \sum_{i} n_{i}$, where $N$ is the total number of sites.  

At $T = 0$ and $n = 0.5$ (i.e., Na$_{0.5}$CoO$_2$), as $U$ increases from 0, the system is a paramagnetic (PM) metal up to $U/t = 3.97$ due to geometrical frustration, then changes into a metal with a spiral IC-SDW, and then at $U/t = 5.27$ a first-order metal-insulator transition occurs. $^{19}$ The lack of magnetic transitions for Na$_{x}$CoO$_2$ with $x = 0.6$ and 0.65 suggests that $U/t \leq 3.97$. This means that Na$_{x}$CoO$_2$ is unlikely to be a typical strongly correlated electron system, because $U \gg t$ for such a system. The calculations $^{20}$ also predict that, as $n$ increases from 0, the value of $U/t$ at the boundary between the PM and SDW phases decreases, with increasing slope $(d(U/t)/dn)$ up to $n = 0.75$. Even for $U/t = 0$, the SDW phase is stable at $n = 0.75$. The value of $U/t$ then increases with further increasing $n$, with decreasing slope. Therefore, the dome-shaped phase diagram of Fig. 4 is qualitatively explained by the calculations, although the measured maximum of the dome is located around $x = 0.8$ (i.e. $n = 0.9$). This is likely due to the simple band structure assumed in the above calculation, while calculations for Na$_{x}$CoO$_2$ determined by the $\mu^s$SR experiments. Solid and open circles represent the present results on single crystals and polycrystalline samples, respectively. The point at $x = 1$ is extrapolated from the data on the related compound LiCoO$_2$. $^{34}$
suggest more complicated one.\textsuperscript{35)

3.2 \([\text{Ca}_2\text{CoO}_3]_{0.62}[\text{CoO}_2]\)\textsuperscript{12,13} and  
\([\text{Ca}_2\text{Co}_{4/3}\text{Cu}_{2/3}\text{O}_3]_{0.62}[\text{CoO}_2]\)\textsuperscript{15}

The crystal structure of \([\text{Ca}_2\text{CoO}_3]_{0.62}[\text{CoO}_2]\) consists of alternating layers of the triple rocksalt-type \([\text{Ca}_2\text{CoO}_3]\) subsystem and the single Cdl$_2$-type \([\text{CoO}_2]\) subsystem stacked along the \(c\)-axis.\textsuperscript{7,8} There is a misfit between these subsystems along the \(b\)-axis. Susceptibility (\(\chi\)) measurements\textsuperscript{5,12} indicate two magnetic transitions at 19 K and 380 K; the former is a ferrimagnetic transition (\(T_{\text{fr}}\)) and the latter is probably a spin-state transition (\(T_{\text{SS}}\)). The temperature dependence of the resistivity \(\rho\) exhibits a broad minimum around 80 K\textsuperscript{7,8,12} and a broad maximum between 400 and 600 K.\textsuperscript{7} Although \(\rho\) appears to diverge with decreasing temperature below \(T_{\text{fr}}\), it is worth noting that \(\chi(T)\) shows no clear anomalies near 80 K or 600 K.

In all the \([\text{Ca}_2\text{CoO}_3]_{0.62}[\text{CoO}_2]\) samples, the wTF-\(\mu^+\)SR spectra in a magnetic field of \(H \sim 100\) Oe exhibit a clear reduction of the \(\mu^+\) precession amplitude below 100 K. The data were obtained by fitting the wTF-\(\mu^+\)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:

\[
A_0 P(t) = A_{\text{para}} \exp\left(-\lambda_{\text{para}} t\right) \cos \left(\omega_{\text{L}} t + \phi\right) \\
+ A_{\text{fast}} \exp\left(-\lambda_{\text{fast}} t\right) \\
+ A_{\text{slow}} \exp\left(-\lambda_{\text{slow}} t\right), \quad \cdots \cdots \cdots \cdots (8)
\]

where \(\omega_{\text{L}}\) is the muon Larmor frequency, \(\phi\) is the initial phase of the precession and \(A_{\text{para}}, A_{\text{fast}}\) and \(A_{\text{slow}}\) are the asymmetries and exponential relaxation rates of the three signals. The latter two signals (\(A_{\text{fast}}\) and \(A_{\text{slow}}\)) have finite amplitudes below \(T_{\text{SDW}} \approx 100\) K and probably suggest the existence of multiple muon sites in \([\text{Ca}_2\text{CoO}_3]_{0.62}[\text{CoO}_2]\).

Figures 5(a)-(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 \(\lambda_{\text{para}}\) in three \([\text{Ca}_2\text{CoO}_3]_{0.62}[\text{CoO}_2]\) samples: a randomly oriented polycrystalline sample,\textsuperscript{12} a \(c\)-aligned polycrystalline sample, and single crystal platelets. The large decrease in \(A_{\text{para}}\) below 100 K (and the accompanying increase in \(\lambda_{\text{para}}\)) indicate the existence of a magnetic transition with an onset temperature \(T_{\text{SDW}} \approx 100\) K and a transition width \(\Delta T \approx 70\) K. The single crystal data suggest that the large \(\Delta T\) is not caused by inhomogeneity of the sample but is an intrinsic property of this compound.

Figure 6 shows ZF-\(\mu^+\)SR time spectra at 4.8 K in the \(c\)-aligned sample; the top spectrum was obtained with the initial \(\mu^+\) spin direction \(S_\mu(0)\) perpendicular to the \(c\)-axis and the bottom one with \(S_\mu(0) \parallel c\). A clear oscillation due to quasi-static internal fields is observed only when \(S_\mu(0) \perp c\). The top oscillating spectrum is a characteristic of \(J_0(\omega_{\text{L}} t)\) that describes the muon polarization evolution in an IC-SDW field distribution,\textsuperscript{24,32} and was fitted using a combination of three signals, as in the case of \(\text{Na}_0.9\text{CoO}_2\):

\[
A_0 P(t) = A_{\text{SDW}} J_0(\omega_{\text{L}} t) \exp\left(-\lambda_{\text{SDW}} t\right) \\
+ A_{\text{KT}} G^{KT} (t, \Delta) \\
+ A_{\text{tail}} \exp\left(-\lambda_{\text{tail}} t\right), \quad \cdots \cdots \cdots \cdots (9)
\]
where $A_{SDW}$, $A_{KT}$ and $A_{tail}$ are the asymmetries associated with the three signals and $\lambda_{tail}$ is the slow relaxation rate of the "tail" (not shown in this Figure).

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. $T_{c}^{\text{on}} = T_{fr}^{\text{on}}$). The absence of a clear oscillation in the bottom spectrum of Fig. 6 indicates that the internal magnetic field $H_{int}$ 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, and is consistent with the results of our $\chi$ measurement on single crystals.\(^{36}\)

**Figures 7(a)-(b) show the temperature dependences of $A_{SDW}$, $A_{KT}$ and $A_{para}$ (same in Fig. 5), $f_{\mu}$ and $\lambda_{SDW}$ and $\lambda$ for the $c$-aligned $[Ca_2CoO_3]_{0.62}[CoO_2]$. $A_{SDW}$ increases with decreasing $T$ below 30 K, although $A_{para}$ obtained by the wTF-$\mu$SR measurement exhibits a rapid decrease below 100 K and levels off to almost 0 below 30 K (see Fig. 7(a)). According to the recent $\chi$ measurements using single crystal platelets,\(^{36}\) a small shoulder in the $\chi(T)$ curve was observed at 27 K only for $H \perp ab$. This temperature (27 K) corresponds to the highest temperature that

![Fig. 6](image_url)  
**Fig. 6** ZF-$\mu$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) $S_{\mu}(0) \parallel c$. 

![Fig. 7](image_url)  
**Fig. 7** Temperature dependences of (a) $A_{SDW}$ and $A_{para}$ (estimated by the wTF-$\mu$SR experiment) and (b) $f_{\mu}$ for the $c$-aligned $[Ca_2CoO_3]_{0.62}[CoO_2]$. The solid line in Fig. 7(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 ($= T_{fr}$). Here, the ferrimagnetism is considered to be caused by an interlayer coupling between Co spins in the $[Ca_2CoO_3]$ and $[CoO_2]$ subsystems,\(^{36}\) while the IC-SDW order completes below 27 K. This means that the IC-SDW is affected by the ferrimagnetic coupling via the Co spins in the $[Ca_2CoO_3]$ subsystem. Therefore, the enhancement of the internal magnetic field at $T_{fr}$ is likely to be
caused by a critical phenomenon around the ferrimagnetic transition. In addition, the magnitude of $\lambda_{SDW}$ decreases rapidly with decreasing $T$ and levels off to a constant value below 20 K. This suggests that the broadening of the IC-SDW field distribution at the $\mu^+$ sites mainly occurs in the temperature range between $T_{SDW}$ and $T_{FR}$.

In order to determine the subsystem in which the IC-SDW exists, ZF-$\mu^+$SR spectra were measured in doped samples: $c$-aligned polycrystalline $[\text{Ca}_{1.8}M_{0.2}\text{CoO}_3]_{0.62}[\text{CoO}_2]$ ($M = \text{Sr}, \text{Y}$ and Bi). A clear precession was observed in the ZF-$\mu^+$SR spectrum with $S_{\mu}(0) \perp c$ in every sample, although $T_{SDW}$ depended on dopant. Figure 8 shows the temperature dependences of $f_{\mu}$ for the $c$-aligned pure and doped $[\text{Ca}_{2}\text{CoO}_3]_{0.62}[\text{CoO}_2]$ samples. Doping with Y and Bi increase $T_{SDW}$ by $\sim 40$ K and Sr-doping by $\sim 20$ K, although Sr-doping did not affect $T_{FR}$ by the previous wTF-$\mu^+$SR experiment. $T_{FR}$ is found to be caused by the spin-order of the conduction electrons in the [CoO$_2$] subsystem.

### 3.3 Other 3-layer cobaltites

For the cobaltites with triple rocksalt-type subsystem, a new way to control the Co valence was proposed by the analogy of the high-$T_c$ cuprates. That is, the partial substitution of Co in the rocksalt-type subsystem by Ti, Hg, Tl or Pb, as seen in Table 1. The systematic change in $S$ suggests that the charge carrier concentration in the CoO$_2$ planes is successfully controlled in a wider range than the case of $[\text{Ca}_{2-z}M_z\text{CoO}_3]_{RS}[\text{CoO}_2]$. The crystal structure of these cobaltites is essentially the same as that of $[\text{Ca}_2\text{CoO}_3]_{RS}[\text{CoO}_2]$, i.e., alternating layers of the triple rocksalt-type subsystem and the single CdI$_2$-type [CoO$_2$] subsystem stacked along the $c$-axis. There is also a misfit between these two subsystems along the $b$-axis.

Figures 9(a)-(c) show the temperature dependences of $A_{\mu^+}$, $\lambda_{\mu^+}$ ($\mu = \text{para}$ and fast) estimated from the wTF-$\mu^+$SR spectrum using Eq. (8) and $\chi$ and $\chi'$ in $[\text{Ca}_{2-z}\text{Pb}_x\text{Co}_{0.6}\text{O}_3]_{0.62}[\text{CoO}_2]$. As $T$ decreases from 250 K, the magnitude of $A_{\mu^+}$ is nearly independent of temperature down to 150 K, then decreases as $T$ is lowered further. Finally $A_{\mu^+}$ seems to level off to a constant value below about 40 K. The decrease in $A_{\mu^+}$ below 120 K (and the accompanying increase in $\lambda_{\mu^+}$) indicate the existence of a magnetic transition with an onset temperature $T_c = 130 \pm 20$ K, a transition width $\Delta T \sim 80$ K and an endpoint $T_c^\text{end} \sim 40$ K, respectively. Since $A_{\mu^+}$ is roughly proportional to the volume of a paramagnetic phase, the volume fraction $V_p$ of the magnetic phase at the lowest temperature measured is estimated to be $\sim 30\%$. 

![Fig. 8](image-url)  
**Fig. 8** Temperature dependences of $f_{\mu}$ for the $c$-aligned $[\text{Ca}_{1.8}M_{0.2}\text{CoO}_3]_{0.62}[\text{CoO}_2]$ ($M = \text{Sr}, \text{Y}$ and Bi) and $c$-aligned $[\text{Ca}_2\text{CoO}_3\text{Cu}_{0.3}\text{O}]_{0.462}[\text{CoO}_2]$. The dotted lines represent the temperature dependence of the BCS gap energy.
On the other hand, the $A_{\text{fast}}(T)$ curve exhibits a broad maximum at about 50 K, probably due to the onset of even stronger local fields (resulting in unobservably fast muon spin depolarization) below 50 K. Both the $\lambda_{\text{para}}(T)$ and the $\lambda_{\text{fast}}(T)$ curves exhibit a broad maximum around 80 K. That is, $\lambda_{\text{para}}$ increases with decreasing $T$ from 250 K to 80 K, then decreases below 80 K, and finally levels off to a constant value below 40 K. Meanwhile, $\lambda_{\text{fast}}$ increases with decreasing $T$ from about 120 K (where it is first detected) down to 80 K, after which it decreases down to the lowest temperature measured. It is noteworthy that the highest value of $\lambda_{\text{fast}}$ ($\sim 12 \times 10^6$ s$^{-1}$) is 220 times larger than that of $\lambda_{\text{para}}$ ($\sim 0.05 \times 10^6$ s$^{-1}$).

Nevertheless, the $\chi(T)$ curve exhibit anomalies neither at $T_{\text{c}}^\text{on}$ nor at $T_{\text{c}}^\text{end}$, although a rapid increase in $\chi$ with decreasing $T$ was observed below $\sim 20$ K (Fig. 9(c)).

This behavior is very similar to the cases of $[\text{Ca}_2\text{CoO}_3]_{0.62}[\text{CoO}_2]$ and $[\text{Ca}_2\text{Co}_{4/3}\text{Cu}_{2/3}\text{O}_4]_{0.62}[\text{CoO}_2]$. Figure 10 shows ZF-$\mu$SR time spectra at $\sim 1.8$ K for polycrystalline $[\text{Ca}_2\text{Pb}_{0.4}\text{Co}_{0.6}\text{O}_3]_{0.62}[\text{CoO}_2]$, $[\text{Ca}_2\text{Ti}_{0.4}\text{Co}_{0.6}\text{O}_3]_{0.62}[\text{CoO}_2]$, and $[\text{Sr}_2\text{Hg}_{0.4}\text{Co}_{0.6}\text{O}_3]_{0.56}[\text{CoO}_2]$ samples. The top spectrum is reasonably well fitted with Eq. (9) for IC-SDW. Furthermore the IC-SDW frequency is estimated as 59.6 MHz at 1.9 K for $[\text{Pb}_{0.4}\text{Co}_{0.6}\text{Ca}_2\text{O}_3]_{0.62}[\text{CoO}_2]$; this value is very close to that of the other 3- and 4-layer cobaltites (see Fig. 8).

The absence of a clear oscillation in the middle and bottom spectrum indicates an inhomogeneous or a fast fluctuating distribution of internal magnetic fields in the Ti- and Hg-substituted samples, although the origin of the changes in the wTF-$\mu$SR spectra below $T_{\text{c}}^\text{on}$ is considered to be essentially the same as those for the Pb-substituted sample and $[\text{Ca}_2\text{CoO}_3]_{0.62}[\text{CoO}_2]$, i.e., the formation of the IC-SDW order.
4. Discussion

4.1 Magnetic phase diagram

For the 3- and 4-layer cobaltites, \([\text{Ca}_2\text{CoO}_3]_{0.62}[\text{CoO}_2]\) and \([\text{Ca}_2\text{Co}_{4/3}\text{Cu}_{2/3}\text{O}_4]_{0.62}[\text{CoO}_2]_2\), the IC-SDW transition was also observed as a common behavior in the CoO2 planes.\(^{12, 15}\) We have studied by \(\mu^+\)SR the dependence of the IC-SDW transition on the Co valence for the variety of layered cobaltites shown in Table 1. It should be noted that the magnetic susceptibility \(\chi(T)\) curves for the 3- and 4-layer samples lacked a marked change at either the \(T_{\text{SDW, on}}\) or \(T_{\text{SDW, end}}\) detected by \(\mu^+\)SR. The volume fraction \(V_F\) of the SDW phase in Na\(_{x}\)CoO2 is smaller than those of the 3- and 4-layer cobaltites, due to the reaction of excess Na with humidity and the resulting disorder in the sandwich layers.\(^{14, 27}\) Thus, the SDW order is intrinsic, while the other fractions (disorder) are not. Because of the two Co sites in the 3- and 4-layer cobaltite lattices (one in the rocksalt-type subsystem and the other in the CoO2 plane), it is difficult to determine the Co valence in the CoO2 plane by \(\chi\) measurements or chemical titration techniques. Also, a large \(T\) dependence of the Hall coefficient of the cobaltites\(^{27}\) makes difficult to estimate the carrier concentration in the CoO2 plane. On the other hand, the magnitude of \(S\) in the layered cobaltites is almost independent of \(T\) above 200 K.\(^{7, 9, 16-18, 37}\) Therefore, we use the value of \(S\) at 300 K as an indicator of the Co valence in the CoO2 plane for these cobaltites. The modified Heikes formula gives \(S\) at the high-temperature limit \((S_{T\to\infty})\) as Ref. 38

\[
S_{T\to\infty} = -\frac{k_B}{e} \ln \left( \frac{g_3}{g_4} \frac{y}{1-y} \right), \quad \text{(10)}
\]

where \(k_B\) is the Boltzmann constant, \(e\) is the elementary charge and \(g_3\) and \(g_4\) are the numbers

*Table 1* Parameters of the magnetic transition and reported thermopower \(S\) of several cobaltites; the number of the layers between the two adjacent [CoO2] planes \((N)\), the onset and endpoint temperature of the magnetic transition detected by the \(\mu^+\)SR experiments, the volume fraction of the magnetic phase \((V_F)\) and \(S\) at 300 K.

<table>
<thead>
<tr>
<th>cobaltite</th>
<th>(N)</th>
<th>(T_{\text{SDW, on}}) (K)</th>
<th>(T_{\text{SDW, end}}) (K)</th>
<th>(V_F) (%)</th>
<th>(S) (300 K) ((\mu)VK(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Ca}_2\text{CoO}<em>3]</em>{0.62}[\text{CoO}_2])</td>
<td>3</td>
<td>100 ± 5</td>
<td>30 ± 5*</td>
<td>84</td>
<td>130</td>
</tr>
<tr>
<td>([\text{Ca}_2\text{Bi}_0.5\text{CoO}<em>3]</em>{0.62}[\text{CoO}_2])</td>
<td>3</td>
<td>120 ± 20</td>
<td>70 ± 10*</td>
<td>78</td>
<td>140</td>
</tr>
<tr>
<td>([\text{Ca}<em>2\text{Co}</em>{0.5}\text{Y}_{0.5}\text{O}<em>4]</em>{0.62}[\text{CoO}_2])</td>
<td>3</td>
<td>120 ± 20</td>
<td>70 ± 10*</td>
<td>92</td>
<td>140</td>
</tr>
<tr>
<td>([\text{Ca}<em>2\text{Sr}</em>{0.5}\text{CoO}<em>3]</em>{0.62}[\text{CoO}_2])</td>
<td>3</td>
<td>100 ± 10</td>
<td>45 ± 10*</td>
<td>80</td>
<td>118</td>
</tr>
<tr>
<td>([\text{Ca}<em>2\text{Pb}</em>{0.5}\text{CoO}<em>3]</em>{0.62}[\text{CoO}_2])</td>
<td>3</td>
<td>130 ± 20</td>
<td>40 ± 10*</td>
<td>58</td>
<td>165</td>
</tr>
<tr>
<td>([\text{Sr}<em>2\text{Ca}</em>{0.5}\text{Pb}_{0.5}\text{CoO}<em>3]</em>{0.62}[\text{CoO}_2])</td>
<td>3</td>
<td>90 ± 10</td>
<td>10 ± 10</td>
<td>~39*</td>
<td>130</td>
</tr>
<tr>
<td>([\text{Sr}<em>2\text{Co}</em>{0.5}\text{Pb}_{0.5}\text{CoO}<em>3]</em>{0.62}[\text{CoO}_2])</td>
<td>3</td>
<td>80 ± 10</td>
<td>nd ≥ 3.3</td>
<td>~40*</td>
<td>120</td>
</tr>
<tr>
<td>([\text{Sr}<em>2\text{Ti}</em>{0.5}\text{CoO}<em>3]</em>{0.62}[\text{CoO}_2])</td>
<td>3</td>
<td>10 ± 40</td>
<td>nd ≥ 5.1</td>
<td>~10*</td>
<td>90</td>
</tr>
<tr>
<td>([\text{Sr}<em>2\text{Bi}</em>{0.5}\text{CoO}<em>3]</em>{0.62}[\text{CoO}_2])</td>
<td>3</td>
<td>25 ± 5</td>
<td>nd ≥ 1.7</td>
<td>~18*</td>
<td>90</td>
</tr>
<tr>
<td>([\text{Sr}<em>2\text{Ti}</em>{0.5}\text{CoO}<em>3]</em>{0.62}[\text{CoO}_2])</td>
<td>3</td>
<td>nd ≥ 2.5</td>
<td>nd ≥ 2.5</td>
<td>-</td>
<td>90</td>
</tr>
<tr>
<td>([\text{Sr}<em>2\text{Hg}</em>{0.5}\text{CoO}<em>3]</em>{0.62}[\text{CoO}_2])</td>
<td>3</td>
<td>40 ± 25</td>
<td>5 ± 5</td>
<td>~88*</td>
<td>100</td>
</tr>
<tr>
<td>([\text{Ca}<em>2\text{Ti}</em>{0.5}\text{CoO}<em>3]</em>{0.62}[\text{CoO}_2])</td>
<td>3</td>
<td>150 ± 10</td>
<td>15 ± 5</td>
<td>~92*</td>
<td>150</td>
</tr>
<tr>
<td>([\text{Ca}<em>2\text{Co}</em>{0.5}\text{Cu}_{0.5}\text{O}<em>4]</em>{0.62}[\text{CoO}_2])</td>
<td>4</td>
<td>190 ± 10</td>
<td>145 ± 10*</td>
<td>98</td>
<td>150</td>
</tr>
<tr>
<td>([\text{Ca}<em>2\text{Bi}</em>{0.5}\text{CoO}<em>3]</em>{0.62}[\text{CoO}_2])</td>
<td>4</td>
<td>60 ± 20</td>
<td>nd ≥ 5</td>
<td>~12*</td>
<td>140</td>
</tr>
<tr>
<td>([\text{Sr}<em>2\text{Bi}</em>{0.5}\text{CoO}<em>3]</em>{0.62}[\text{CoO}_2])</td>
<td>4</td>
<td>nd ≥ 2.3</td>
<td>nd ≥ 2.3</td>
<td>-</td>
<td>134</td>
</tr>
<tr>
<td>([\text{Ba}<em>2\text{Bi}</em>{0.5}\text{CoO}<em>3]</em>{0.62}[\text{CoO}_2])</td>
<td>4</td>
<td>nd ≥ 1.8</td>
<td>nd ≥ 1.8</td>
<td>-</td>
<td>100</td>
</tr>
<tr>
<td>(\text{Na}_{0.9}\text{CoO}_2)</td>
<td>1</td>
<td>19 ± 0.5</td>
<td>19 ± 3*</td>
<td>50</td>
<td>150</td>
</tr>
<tr>
<td>(\text{Na}_{0.75}\text{CoO}_2)</td>
<td>1</td>
<td>22 ± 0.5</td>
<td>22 ± 1**</td>
<td>21</td>
<td>120</td>
</tr>
<tr>
<td>(\text{Na}_{0.65}\text{CoO}_2)</td>
<td>1</td>
<td>nd ≥ 2.5</td>
<td>nd ≥ 2.5</td>
<td>-</td>
<td>100</td>
</tr>
<tr>
<td>(\text{Na}_{0.6}\text{CoO}_2)</td>
<td>1</td>
<td>nd ≥ 4.3</td>
<td>nd ≥ 4.3</td>
<td>-</td>
<td>100</td>
</tr>
</tbody>
</table>
of the spin configurations of Co$^{3+}$ and Co$^{4+}$, and $y$ is the ratio Co$^{4+}/$(Co$^{3+}$ + Co$^{4+}$). Since both Co$^{3+}$ and Co$^{4+}$ are in the low-spin state and $g_3 = 1$ and $g_4 = 6$, we can convert $S(300 \text{ K})$ to $y$, assuming that $S(300 \text{ K}) = S_T$. 

**Figure 11** shows $T_{\text{SDW}}^{\text{on}}$ as a function of $S(300 \text{ K})$ for the all cobaltites listed in Table 1. A clear dome-shaped relation is observed for all the available cobaltites with a variable number of layers ($N$) between the two adjacent CoO$_2$ planes. As $N$ increases from 1, the $T_{\text{SDW}}^{\text{on}}$ - $S(300 \text{ K})$ curve shifts towards higher $T_c$, due to the increased two-dimensionality induced by the increase in the interlayer distance between CoO$_2$ planes. Also, the large observed transition widths (50-130 K) are consistent with enhanced two-dimensionality and resulting spin fluctuations. Phenomenologically, the phase diagram is very similar to the well-known dome-shaped relation observed for all the cobaltites listed in Table 1. A clear dome-shaped relation is observed for all the available cobaltites with a variable number of layers ($N$) between the two adjacent CoO$_2$ planes. As $N$ increases from 1, the $T_{\text{SDW}}^{\text{on}}$ - $S(300 \text{ K})$ curve shifts towards higher $T_c$, due to the increased two-dimensionality induced by the increase in the interlayer distance between CoO$_2$ planes. Also, the large observed transition widths (50-130 K) are consistent with enhanced two-dimensionality and resulting spin fluctuations. Phenomenologically, the phase diagram is very similar to the well-known dome-shaped relation observed for all the cobaltites listed in Table 1. A clear dome-shaped relation is observed for all the available cobaltites with a variable number of layers ($N$) between the two adjacent CoO$_2$ planes. As $N$ increases from 1, the $T_{\text{SDW}}^{\text{on}}$ - $S(300 \text{ K})$ curve shifts towards higher $T_c$, due to the increased two-dimensionality induced by the increase in the interlayer distance between CoO$_2$ planes. Also, the large observed transition widths (50-130 K) are consistent with enhanced two-dimensionality and resulting spin fluctuations. Phenomenologically, the phase diagram is very similar to the well-known dome-shaped relation observed for all the cobaltites listed in Table 1. A clear dome-shaped relation is observed for all the available cobaltites with a variable number of layers ($N$) between the two adjacent CoO$_2$ planes. As $N$ increases from 1, the $T_{\text{SDW}}^{\text{on}}$ - $S(300 \text{ K})$ curve shifts towards higher $T_c$, due to the increased two-dimensionality induced by the increase in the interlayer distance between CoO$_2$ planes.

**4.2 Magnitude of internal magnetic field**

If the SDW state is induced by the competition between $U/t$ and $n$ in the CoO$_2$ 2DTL, the nature of the SDW state is considered to be essentially same in all the cobaltites. However, the internal magnetic field of the ordered state, $f_{\mu}(0 \text{ K})$, is found to be $\sim 3$ MHz for Na$_x$CoO$_2$, while it is $\sim 60$ MHz for [Ca$_2$CoO$_3$]$_{0.62}$[CoO$_2$] and [Ca$_2$Co$_{4/3}$Cu$_{2/3}$O$_4$]$_{0.62}$[CoO$_2$]. This discrepancy is difficult to explain only by differences in the $\mu^+$ site experiencing the SDW field. That is, even if the $\mu^+$’s in Na$_x$CoO$_2$ locate in the vacant sites in the Na plane and those in the latter two cobaltites are bound to oxygen in the CoO$_2$ plane, the ratio between the bond length $d$ of Na-Co and O-Co is about 1.65. Assuming that $f_{\mu}(0 \text{ K}) = 60$ MHz at the oxygen site in the CoO$_2$ plane, $f_{\mu}(0 \text{ K})$ at the Na site would be roughly $\sim 13$ MHz, because the dipolar field is proportional to $d^{-3}$. This is still four times larger than the experimental result.

Hence, there should be the other reasons for the lower $f_{\mu}(0 \text{ K})$ found in Na$_x$CoO$_2$. Considering the crystal structure of these cobaltites, the distance between adjacent CoO$_2$ planes in Na$_x$CoO$_2$ is significantly smaller than those in [Ca$_2$CoO$_3$]$_{0.62}$[CoO$_2$] and [Ca$_2$Co$_{4/3}$Cu$_{2/3}$O$_4$]$_{0.62}$[CoO$_2$] and [Ca$_2$Co$_{4/3}$Cu$_{2/3}$O$_4$]$_{0.62}$[CoO$_2$]. Thus, the interlayer interaction between the CoO$_2$ planes in Na$_x$CoO$_2$ is considerably larger than in the other layered cobaltites. Such interaction is thought to weaken the two dimensionality of the CoO$_2$ plane. As a result, the magnitude of $f_{\mu}(0 \text{ K})$ in Na$_x$CoO$_2$ may be smaller than those in the other layered cobaltites. Indeed, large transition widths, $\Delta T \approx 70 \text{ K}$, were observed in [Ca$_2$CoO$_3$]$_{0.62}$[CoO$_2$] and [Ca$_2$Co$_{4/3}$Cu$_{2/3}$O$_4$]$_{0.62}$[CoO$_2$], while $\Delta T \approx 0 \text{ K}$ for Na$_x$CoO$_2$. This suggests an increase in spin

![Image of Figure 11](image_url)
frustration, reflecting the decrease in the two-dimensionality in Na$_x$CoO$_2$.

5. Summary

In order to elucidate the magnetism in 'good' thermoelectric layered cobaltites, $\mu$SR spectroscopy has been used on all known cobaltites at temperatures below 300 K. It was found that a common low temperature magnetic state (which in some cases is manifest as an incommensurate spin density wave IC-SDW) forms in the CoO$_2$ planes. The magnitude of the transition temperature to the IC-SDW state $T_{SDW}$ is found to be sensitive both to the Co valence in the CoO$_2$ plane, i.e., the occupancy of the Co spin ($S=1/2$) in the triangular lattice, and to the structure of the subsystem sandwiched by the two CoO$_2$ planes.

A tentative magnetic phase diagram was obtained for Na$_x$CoO$_2$ with $x \geq 0.6$. The relationship between $T_{SDW}$ and $x$ changed dome-shaped, as well as the change in the high-$T_c$ cuprates. Since this relationship was explained using the Hubbard model within a mean field approximation for two-dimensional triangular lattice of the CoO$_2$ plane, which is a common structural component for the all known thermoelectric layered cobaltites, this dome-shaped relationship is concluded to be a common behavior for the layered cobaltites.

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References