Two dimensionality in quasi one-dimensional cobalt oxides

J. Sugiyama1†, H. Nozaki1, J. J. Brewer2, E. J. Ansalldo3, T. Takami4, H. Ikuta4, and U. Mizutani4

1Toyota Central Research and Development Labs. Inc., Nagakute, Aichi 480-1192, Japan
2TRIUMF, CIAR and Department of Physics and Astronomy, University of British Columbia, Vancouver, BC, V6T 1Z1 Canada
3University of Saskatchewan 1 and TRIUMF, 4004 Wesbrook Mall, Vancouver, BC, V6T 2A3 Canada and
4Department of Crystalline Materials Science, Nagoya University, Faro-cho, Chikusa-ku, Nagoya, 464-8603 Japan

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By means of muon spin rotation and relaxation ($\mu^+\text{SR}$) techniques, we have investigated the magnetism of quasi one-dimensional (1D) cobalt oxides $AE_{n+2}B_O\text{O}_{3n+3}$ ($AE=$Ca, Sr and Ba, $n=1, 2, 3, 5$ and $\infty$), in which the 1D CoO$_3$ chain is surrounded by six equally spaced chains forming a triangular lattice in the $ab$-plane, using polycrystalline samples, from room temperature down to 1.8 K. For the compounds with $n=1 - 5$, transverse field $\mu^+\text{SR}$ experiments showed the existence of a magnetic transition below $\sim 100$ K. The onset temperature of the transition ($T_{\mu^+\text{SR}}$) was found to decrease with $n$; from 100 K for $n=1$ to 60 K for $n=5$. A damped muon spin oscillation was observed only in the sample with $n=1$ (Ca$_3$Co$_2$O$_6$), whereas only a fast relaxation obtained even at 1.8 K in the other three samples. In combination with the results of susceptibility measurements, this indicates that a two-dimensional short-range antiferromagnetic (AF) order appears below $T_{\mu^+\text{SR}}$ for all compounds with $n=1 - 5$; but quasi-static long-range AF order formed only in Ca$_3$Co$_2$O$_6$, below 25 K. For BaCoO$_3$ ($n=\infty$), as $T$ decreased from 300 K, 1D ferromagnetic (F) order appeared below 53 K, and a sharp 2D AF transition occurred at 15 K.

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I. INTRODUCTION

In the two-dimensional (2D) layered cobalt oxides, $Na_xCoO_2$, [Ca$_2CoO_3$]$_{0.62}$[CoO$_2$] and [Ca$_2CoO_4$]$_{0.62}$[CoO$_2$], a long-range magnetic order — which is clearly incommensurate spin density wave in single crystalline samples — was previously found at low temperatures by positive muon spin rotation and relaxation ($\mu^+\text{SR}$) experiments. Several researchers reconfirmed later the existence of long-range magnetic order in the layered cobaltites by not only $\mu^+\text{SR}$ but also neutron diffraction experiments. These cobaltites share a common structural component as a conduction path, i.e., 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.

This leads naturally to the question of the (cause and effect) interrelationship between magnetism and dimensionality. That is, the most stable spin configuration as a function of a spin density in low dimensional systems. Recently, a homologous series of $A_{n+2}B'_xB_0\text{O}_{3n+3}$ ($A=$ Ca, Sr, Ba, $B'$ and $B=$Co) was discovered, in which charge carrier transport is restricted mainly to a one-dimensional (1D) [$B'_3B_0\text{O}_{3n+3}$] chain. Each chain is surrounded by six equally spaced chains forming a triangular lattice in the $ab$-plane. As seen in Fig. 1, the [$B'_3BO_6$] chain in the $n=1$ compound consists of alternating face-sharing $B'_3O_6$ trigonal prisms and $BO_6$ octahedra. As $n$ increases, only the number of $[BO_6]$ octahedra increases so as to build the chain with $n$ $[BO_6]$ octahedra and one $B'_3O_6$ trigonal prism.

The $n=1$ compound, Ca$_3$Co$_2$O$_6$, in particular, has attracted much attention for the past eight years, because it is considered to be a typical quasi-1D system. It was found that Ca$_3$Co$_2$O$_6$ exhibits a transition from a paramagnetic to an antiferromagnetic state below 24 K ($=T_N$) although the magnetic structure is not fully understood even after neutron scattering studies, probably due to the competition between the intra-chain ferromagnetic (F) and inter-chain antiferromagnetic (AF) interactions. The valence state of the Co ions was assigned to be +3; also, the spin configuration of Co$^{3+}$ ions in the CoO$_6$ octahedra is the low-spin (LS) state with $S=0$ and in the CoO$_6$ prism the high-spin (HS) state with $S=2$. At lower temperatures, magnetization and $^{59}$Co-NMR measurements suggested the existence of a ferrimagnetic transition around 10 K, which, however, was not seen in the specific heat ($C_p$). Furthermore, the $C_p$ measurement revealed an indication of either a short-range magnetic order or a gradual change in the spin state of Co ions at higher temperatures (100 - 200 K).

The other end member, BaCoO$_3$ ($n=\infty$), crystallizes in the hexagonal perovskite structure, in which the face sharing CoO$_6$ octahedra form a 1D CoO$_3$ chain. The chains locate on a corner of the two-dimensional triangular lattice separated by Ba ions. Although a weak ferromagnetic, ferrimagnetic or spin-glass-like behavior was observed below $\sim 100$ K in the susceptibility,
predicted a ferromagnetic ground state as the most stable ally, a recent electronic structural calculation (LDA+U) predicted a ferromagnetic ground state as the most stable configuration. The structure of BaCoO$_3$ is the same to that of CsCoCl$_3$ and/or BaVS$_3$, which are known as typical 1D systems with $S=1/2$. The electronic configuration (t$_{2g}^2$) of Co$^{4+}$ ions in BaCoO$_3$ suggests that the nature of BaCoO$_3$ is more like that of BaVS$_3$ (with t$_{2g}^3$ for V$^{4+}$) than that of CsCoCl$_3$ (t$_{2g}^3$e$_g^1$ for Co$^{3+}$). In other words, the interaction between t$_{2g}$ orbitals presumably plays the dominant role for magnetism in both BaCoO$_3$ and BaVS$_3$. Also, BaVS$_3$ exhibits a structural phase transition at 240 K, a metal-insulator transition at 69 K and an AF transition at ~30 K. However, a ZF-$\mu^+$SR experiment on BaVS$_3$ did not detect muon spin oscillations, even at 2.2 K, but only a fluctuating random field well described by a dynamic Kubo-Toyabe relaxation function.

For the compounds with $2 \leq n < \infty$, there are very limited data on physical properties, except for the structural data. Very recently, Takami et al. reported transport and magnetic properties for the compounds with $n=2$ - 5. According to their susceptibility ($\chi$) measurements, there are no drastic changes in the ($\chi(T)$) curve below 300 K for all these compounds, while the slope of $\chi^{-1}$ changes at around 180 K for the compounds with $n=2$ and 3.

As $n$ increases from 1, the Co valence increases from +3 and approaches +4 with increasing $n$ up to ~i.e., BaCoO$_3$. Also the ratio between prism and octahedron in the 1D CoO$_3$ chain reduces from 1/1 for $n=1$ to 0 for $n=\infty$. Further systematic research on $A_{n+2}B'_nB_3O_{3n+3}$ is therefore needed to provide more significant information concerning the dilution effect of HS Co$^{3+}$ in the 1D chain on magnetism. In particular, muon spin spectroscopy, as it is very sensitive to the local magnetic environment, is expected to yield crucial data in frustrated low-dimensional system, as was the case for the 2D layered cobaltites.

### TABLE I: Composition and lattice parameters for quasi-one-dimensional cobalt oxides, $A_{n+2}B'_nB_3O_{3n+3}$ ($A=$ Ca, Sr, Ba, $B'$ and $B=$Co). Here, $b=a$, $\alpha=\beta=90^\circ$ and $\gamma=120^\circ$.

| $n$ | composition | $a$(Å) | $c$(Å) | space group |
|-----|-------------|--------|--------|-------------|
| 1   | Ca$_3$Co$_2$O$_6$ | 9.07   | 10.38  | $R3c$      |
| 2   | Sr$_3$Co$_3$O$_9$ | 9.35   | 10.57  | $P321$     |
| 3   | Sr$_3$Co$_4$O$_{12}$ | 9.4   | 20.2   | $P3c1$     |
| 5   | (Sr$_{1/2}$Ba$_{1/2}$)$_7$Co$_6$O$_{18}$ | 9.7  | 30.7   | $P3c1$     |
| $\infty$ | BaCoO$_3$ | 5.65   | 4.75   | $P6_{3}/mmc$ |

Here we report on a series of measurements at both weak (relative to the spontaneous internal fields in the ordered state) transverse-field, ($w$TF-) $\mu^+$SR, and zero field, (ZF-) $\mu^+$SR, for polycrystalline $n=1$, 2, 3, 5 and $\infty$ compounds at temperatures between 1.8 and 300 K. The former method is sensitive to local magnetic order via the shift of the $\mu^+$ spin precession frequency in the applied field and the enhanced $\mu^+$ spin relaxation, while ZF-$\mu^+$SR is uniquely sensitive to weak local magnetic [dis]order in samples exhibiting quasi-static paramagnetic moments.

### II. EXPERIMENT

Polycrystalline samples of quasi-1D cobalt oxides were synthesized at Nagoya University by a conventional solid state reaction technique, using reagent grade Co$_3$O$_4$, CaCO$_3$, SrCO$_3$ and BaCO$_3$ powders as starting materials. For BaCoO$_3$, a sintered pellet was annealed at 650°C for 150 h in oxygen under pressure of 1 MPa. Powder X-ray diffraction (XRD) studies indicated that the samples were single-phase of hexagonal structure. The composition and lattice parameters of the five samples are summarized in Table I. The preparation and characterization of the samples with $n=1$ - 5 were reported in detail elsewhere.

Magnetic susceptibility ($\chi$) was measured using a superconducting quantum interference device (SQUID) magnetometer (mpms, Quantum Design) at temperatures between 2 - 600 K with magnetic field $H \leq 55$ kOe. Heat capacity ($C_p$) was measured using a relaxation technique (ppms, Quantum Design) in the temperature range between 300 and 1.9 K. The $\mu^+$SR experiments were performed on the M20 surface muon beam line at TRIUMF. The experimental setup and techniques were described elsewhere.
III. RESULTS

A. n=1 compound, \( \text{Ca}_3\text{Co}_2\text{O}_6 \)

The wTF-\( \mu^+ \)SR spectra in a magnetic field of \( H \sim 90 \text{ Oe} \) in the \( \text{Ca}_3\text{Co}_2\text{O}_6 \) \((n=1)\) sample, exhibit a clear reduction of the \( \mu^+ \) precession amplitude below \( \sim 100 \text{ K} \). The wTF-\( \mu^+ \)SR spectrum below \( \sim 100 \text{ K} \) was well fitted in the time domain with a combination of four signals; a slowly relaxing precessing signal caused by the applied field, a fast relaxing precessing signal induced by quasi-static internal fields, a slowly non-oscillatory and a fast non-oscillatory background signals, namely:

\[
A_0 \, P(t) = A_{\text{TF}} \exp(-\lambda_{\text{TF}} t) \cos(\omega_{\mu,\text{TF}} t + \phi_{\text{TF}})
+ A_{\text{AF}} \exp(-\lambda_{\text{AF}} t) \cos(\omega_{\mu,\text{AF}} t + \phi_{\text{AF}})
+ A_{\text{fast}} \exp(-\lambda_{\text{fast}} t),
\]

where \( A_0 \) is the initial \( (t=0) \) asymmetry, \( P(t) \) is the muon spin polarization function, \( \omega_{\mu,\text{TF}} \) and \( \omega_{\mu,\text{AF}} \) are the muon Larmor frequencies corresponding to the applied weak transverse field and the internal antiferromagnetic field, \( \phi_{\text{TF}} \) and \( \phi_{\text{AF}} \) are the initial phases of the two precessing signals and \( A_n \) and \( \lambda_n \) \((n = \text{TF, AF, fast and slow})\) are the asymmetries and exponential relaxation rates of the four signals. The fast relaxing precessing signal has a finite amplitude below \( \sim 30 \text{ K} \) and the two non-oscillatory signals \((n=\text{fast and slow})\) below \( \sim 80 \text{ K} \).

Figures 2(a) - 2(c) show the temperature dependences of \( A_n, \lambda_n \) \((n = \text{TF, AF, fast and slow})\), and inverse susceptibility \( \chi^{-1} \) measured in field cooling mode with \( H = 10 \text{ kOe} \) in the \( \text{Ca}_3\text{Co}_2\text{O}_6 \) sample \((n=1)\). As \( T \) decreases from 200 K, the magnitude of \( A_{\text{TF}} \) is nearly independent of temperature down to 100 K; then \( A_{\text{TF}} \) decreases rapidly as \( T \) is lowered further. Finally \( A_{\text{TF}} \) levels off to zero at temperatures below about 30 K. This indicates the existence of a magnetic transition below around 100 K. Since \( A_{\text{TF}} \) is proportional to the volume of a paramagnetic phase, the volume fraction \( V_{\text{p}} \) of the magnetic phase below 30 K is estimated to be \( \sim 100\% \). On the other hand, the \( A_{\text{fast}}(T) \) curve exhibits a maximum at around 30 K, probably due to the onset of even stronger local fields (resulting in unobservably fast muon spin depolarization) below 30 K. The magnitude of \( A_{\text{fast}} \) reaches the full asymmetry of \( \sim 0.22 \) at the maximum. The two other signals, \( A_{\text{AF}} \) and \( A_{\text{slow}} \), appear below around 20 K, whereas \( A_{\text{fast}} \) seems to disappear below 20 K.

Both the \( \lambda_{\text{TF}}(T) \) and the \( \lambda_{\text{fast}}(T) \) curves exhibit a broad maximum around 60 K and 30 K, respectively. That is, \( \lambda_{\text{TF}} \) increases with decreasing \( T \) from 200 K to 60 K, then decreases below 60 K. Meanwhile, \( \lambda_{\text{fast}} \) increases with decreasing \( T \) from about 80 K (where it is first detected) down to 30 K, after which it decreases down to the lowest temperature measured. It is noteworthy that the highest value of \( \lambda_{\text{fast}} \) \((\sim 60 \times 10^6 \text{ s}^{-1})\) is 20 times larger than that of \( \lambda_{\text{TF}} \) \((\sim 3 \times 10^6 \text{ s}^{-1})\).

In order to elucidate magnetism below 30 K in greater detail, Fig. 3 shows ZF-\( \mu^+ \)SR time spectra for \( \text{Ca}_3\text{Co}_2\text{O}_6 \) below 36.7 K. The spectrum at 36.7 K consists mainly of a fast relaxed non-oscillatory signal, while below 23.2 K a first minimum and maximum are clearly seen, indicative of a fast relaxing oscillation. Indeed, this spectrum is reasonably well fitted with a combination of an exponentially relaxed cosine oscillation (for a quasi-static internal field) and fast and slow exponential relaxation functions (for fluctuating moments), given by the last three terms in eq. (1). Moreover, it was very difficult to fit using Kubo-Toyabe functions, which describe a random field distribution. We therefore conclude that \( \text{Ca}_3\text{Co}_2\text{O}_6 \) undergoes a magnetic transition to a long-range ordered state below \( \sim 30 \text{ K} \). Only the first minimum and maximum can be observed in the spectra even at 1.8 K, indicating that the formation of the long-range order is
strongly suppressed probably due to geometrical frustration in the triangular lattice.

Figures 4(a) - 4(d) show the temperature dependences of $A_n$, $\lambda_n$ ($n=$AF, fast and slow) and muon precession frequency $\nu_{\text{AF}}(=\omega_{\mu,\text{AF}}/2\pi)$ in $\text{Ca}_3\text{Co}_2\text{O}_6$. The oscillating signal has a finite intensity below 27 K, while the slow exponential relaxed signal disappears below around 30 K. This means that the magnetic moment fluctuating at high temperatures slows down with decreasing $T$ and then orders below 27 K, and becomes quasi-static (within the experimental time scale). The $T$ dependence of $\nu_{\text{AF}}$, which is an order parameter of the transition, is in good agreement with the $\chi$ and neutron diffraction measurements ($T_N=24$ K). These results confirm that muons experience the internal magnetic field due to the long-range 2D AF order. It should be noted that this provides $\nu_{\text{AF}}(0\text{K})=14.6\pm0.8$ MHz, $\beta=0.18\pm0.12$, and $T_N=29\pm5$ K (see, Fig. 4c)). In spite of the low accuracy of the fitting, the critical exponent ($\beta$) obtained lies between the predictions for the 2D and 3D Ising models ($\beta=0.125$ and 0.3125).
there are no marked anomalies in the ZF-\(\mu^+\)SR results around 10 K corresponding to the ferrimagnetic transition temperature.\[12\] This is very reasonable because the ferrimagnetism is induced by the external field.

There are two probable explanations for the decrease in \(A_{TF}\) below 100 K. One is a conventional scenario, in which a short-range 1D F order appears below 100 K as proposed by Aasland et al.\[11\] and probably completes below \(\sim 40\) K, because both \(A_{TF}\) (Fig. 2) and \(A_{slow}\) (Fig. 4) seem to level off to their minimum value \((\sim 0)\) below around 40 K. The long-range 2D AF order then appears below 27 K. The other scenario is more ambiguous; that is, a short-range 2D AF order appears below 100 K and completes below 27 K. This means that the 1D F order should exist above 100 K, which is not supported by the present \(\mu^+\)SR experiments. Based only on the result in Ca\(_3\)Co\(_2\)O\(_6\), it is difficult to determine which scenario is more probable. We will therefore discuss this problem later.

\[\text{B. } n=2, 3 \text{ and 5 compounds}\]

Figure 5(a) - 5(c) show the temperature dependences of (a) normalized \(A_{TF}\) (\(n\cdot A_{TF}\)), (b) \(\lambda_{TF}\), and (c) \(\chi^{-1}\) in Ca\(_3\)Co\(_2\)O\(_6\) \((n=1)\), Sr\(_4\)Co\(_2\)O\(_9\) \((n=2)\), Sr\(_5\)Co\(_4\)O\(_{12}\) \((n=3)\), and (Ba\(_{0.5}\)Sr\(_{0.5}\))\(\tau\)Co\(_6\)O\(_{18}\) \((n=5)\). The data were obtained by fitting the wTF-\(\mu^+\)SR spectra using eq. (1) without the oscillatory signal due to a static internal antiferromagnetic magnetic field (the \(A_{AF}\) signal). In order to compare the value of \(A_{TF}\) for these samples, \(N_{ATF}\) is defined as:

\[
N_{ATF} = \frac{A_{TF}(T)}{A_{TF,\text{max}}},
\]

in which \(A_{TF,\text{max}}\) is the maximum value of \(A_{TF}\). Since \(A_{TF,\text{max}}\) corresponds to \(A_{TF}\) for the paramagnetic state, \(N_{ATF}\) is roughly equivalent to the volume fraction of the paramagnetic phase in the sample.

All four samples show the magnetic transition below 100 K; the onset temperatures of the transition \((T^\text{on})\) are estimated as 100\(\pm\)25 K for \(n=1\), 90\(\pm\)10 K for \(n=2\), 85\(\pm\)10 K for \(n=3\) and 50\(\pm\)10 K for \(n=5\), respectively. The magnitude of \(T^\text{on}\) is thus found to decrease with \(n\). It should be noted that there are no marked anomalies in the \(\chi^{-1}(T)\) curve measured with \(H=10\) kOe at \(T^\text{on}\) for the four compounds. Although \(N_{ATF}\) for the \(n=1\) compound levels off to its minimum value \((\sim 0)\) below 30 K, the \(N_{ATF}(T)\) curve for the other three compounds never reaches their minimum even at 1.8 K, indicating that the internal magnetic field is still fluctuating. Indeed, \(\lambda_{TF}\) for the samples with \(n=2\), 3 & 5 increases monotonically with decreasing \(T\), whereas the \(\lambda_{TF}(T)\) curve for Ca\(_3\)Co\(_2\)O\(_6\) \((n=1)\) exhibits a sharp maximum around 55 K.

\[\text{FIG. 5}: \text{Temperature dependences of (a) normalized } A_{TF}, \text{(b) } \lambda_{TF}, \text{and (c) inverse susceptibility } \chi^{-1} \text{ in Ca}_{3}\text{Co}_{2}\text{O}_{6} \text{ (}n=1\text{), Sr}_{4}\text{Co}_{2}\text{O}_{9} \text{ (}n=2\text{), Sr}_{5}\text{Co}_{4}\text{O}_{12} \text{ (}n=3\text{), and (Ba}_{0.5}\text{Sr}_{0.5}\text{)}\tau\text{Co}_{6}\text{O}_{18} \text{ (}n=5\text{). } \chi \text{ was measured with magnetic field } H=10 \text{ kOe in field cooling mode. }\text{[31]}\]

In spite of the large decrease in \(A_{TF}\) below 100 K for the samples with \(n=2, 3\) and 5, the ZF-\(\mu^+\)SR spectra exhibit no oscillations even at 1.8 K as seen in Fig. 6. This indicates that the magnetic moment appears below \(T^\text{on}\), but is still fluctuating at 1.8 K. The ZF-\(\mu^+\)SR spectra are well fitted by a combination of fast and slow exponential relaxation functions (for fluctuating moments) and a dynamical Kubo-Toyabe function \(G^\text{DGKT}\) (for a fluctuating random moment component).

\[
A_0 P(t) = A_{\text{fast}} \exp(-\lambda_{\text{fast}}t) + A_{\text{slow}} \exp(-\lambda_{\text{slow}}t) + A_{\text{KT}} \exp(-\lambda_{\text{KT}}t) G^\text{DGKT}.
\]

The fast exponentially relaxed signal, which corresponds to the initial decay of the ZF-spectrum in Fig. 6 appears below \(\sim 80\) K for the samples with \(n=2\) and 3. The \(A_{\text{fast}}(T)\) and \(\lambda_{\text{fast}}(T)\) curves increase monotonically with decreasing \(T\), as expected from the wTF-\(\mu^+\)SR measurement. The fitted values of \(\lambda_{\text{fast}}\) at the lowest \(T\)
indicating the existence of a magnetic transition. How-

Also, the $C_{\mu}$ for ferrimagnetic behavior below 53 K with $H_T$ and its temperature derivative $dC_{\mu}/dT$ for $n=1$ is most likely caused by an inter-chain 2D AF interaction. It should be noted that $\lambda_{AF}(1.8 \, K)$ decreases with $n$, suggesting that the magnitude of the 2D AF interaction is weakened with decreasing $n$.

C. $n=\infty$ compound, BaCoO$_3$

Figures 6(a)-6(c) show the temperature dependences of (a) $A_{fast}$, (b) $\lambda_{TF}$, (c) $\chi^{-1}$, (d) specific heat $C_p$, and (e) its temperature derivative $dC_p/dT$ for BaCoO$_3$ ($n=\infty$). Both $A_{TF}$ and $\lambda_{TF}$ were obtained by fitting the wTF-\mu$^+SR$ spectra, the same way as the compounds with $n=2$ - 5. The $\chi^{-1}(T)$ curve indicates the existence of an AF transition at 14 K ($=T_N$) with $H=10$ kOe, but a weak F or ferrimagnetic behavior below 53 K with $H=100$ Oe. Also, the $C_p(T)$ curve shows a sharp maximum at 15 K, indicating the existence of a magnetic transition. However, at around 53 K, there are no clear anomalies in the $C_p(T)$ curve, although the slope $(dC_p/dT)$ increases slightly around 50 K with decreasing $T$. The lack of a clear anomaly around 50 K in the $C_p(T)$ curve suggests that the transition at 53 K is induced by the 1D F order, as in the case for the 1D F order in Ca$_3$Co$_2$O$_6$.

The wTF-\mu$^+SR$ experiment with 90 Oe show that, as $T$ decreases from 100 K, $A_{TF}$ drops suddenly down to $\sim 0$ at $T_N$, indicating that the whole sample enters into an AF state. Such abrupt change in $A_{TF}$ is very different from those for the other quasi-1D cobalt oxides with $n=1$ - 5, which typically show a large transition width of 50 - 80 K. On the other hand, the $\lambda_{TF}(T)$ curve exhibits a small increase below $\sim 50$ K with decreasing $T$, probably associated with the complicated magnetism observed in $\chi$ with low magnetic fields. As $T$ decreases further from 50 K, $\lambda_{TF}$ increases rapidly below 17 K, showing typical critical behavior towards $T_N$.

The ZF-\mu$^+SR$ spectrum at 1.7 K exhibits a clear but complex muon spin oscillation, displayed in Fig. 6(a). The Fourier transform of the ZF-\mu$^+SR$ time spectrum (Fig. 6(b)) indicates that the ZF-\mu$^+SR$ spectrum has five frequency components ($\nu_p = 14.4, 13.5, 6.4, 5.1$ and $3.5$ MHz), even though the sample is structurally single phase at room temperature and there is no indication of any structural phase transition down to 77 K in resistivity ($\rho$) and thermopower (TEP) measurements, nor are there any anomalies in the $\chi(T)$ curve down to 4 K, except around $T_N$. The ZF-spectra were well fitted by...
FIG. 8: Temperature dependences of (a) weak transverse field asymmetry $A_{TF}$, (b) exponential relaxation rate $\lambda_{TF}$, (c) inverse susceptibility $\chi^{-1}$, (d) specific heat $C_p$, and (e) its temperature derivative $dC_p/dT$ for BaCoO$_3$ ($n=\infty$). $A_{TF}$ and $\lambda_{TF}$ were obtained by fitting the wTF-$\mu$SR spectra with $A_{TF}(t) = \sum_{i=1}^{5} A_{AF,i} \exp(-\lambda_{AF,i} t) \cos(\omega_{\mu,i} t + \phi_{TF})$. $\chi$ was measured with magnetic field $H=10$ kOe and 100 Oe in both zero-field cooling (ZFC) and field cooling (FC) mode.

FIG. 9: (a) ZF-$\mu$SR spectrum for BaCoO$_3$ ($n=\infty$) at 1.7 K and (b) Fourier transform of (a). The solid line in Fig. 7 represents the result of fitting using eq. (5).

The following equation:

$$A_0 P(t) = \sum_{i=1}^{5} A_{AF,i} \exp(-\lambda_{AF,i} t) \cos(\omega_{\mu,i} t + \phi) + \sum_{i=1}^{2} A_i \exp(-\lambda_i t),$$  

where $A_0$ is the empirical maximum experimental muon decay asymmetry, $A_{AF,i}$ and $\lambda_{AF,i}$ ($i = 1 - 5$) are the asymmetries and exponential relaxation rates associated with the five oscillating signals, and $A_i$ and $\lambda_i$ ($i = 1$ and 2) are the asymmetries and exponential relaxation rates of the two non-oscillating signals (for the muon sites experiencing fluctuating magnetic fields).

The internal magnetic fields of the five signals, i.e., $\nu_{\mu,i}$ with $i = 1 - 5$, exhibit a similar temperature dependence, as seen in Fig. 10(a). That is, as $T$ decreases from 20 K, each $\nu_{\mu,i}$ suddenly appears below 15 K, at which the $C_p(T)$ curve shows a typical behavior for the AF transition (Fig. 10(b)), and increases with a decreasing slope $d\nu_{\mu,i}/dT$, then levels 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 rapid temperature dependence of $\nu_{\mu,i}$...
the experimental data. The $C_p(T)$ curve also supports that the transition at $15 \text{ K}$ is continuous. Actually, the $C_p/T$ decreases roughly in proportion to $T^2$ below $T^*_N$, the magnetic contribution should not be ignored even at the lowest $T$ measured. This means that the temperature is extremely difficult to determine the Debye temperature and/or subtract the lattice contribution from the experimental data.

just below $T_N$ suggests that the transition is likely to be continuous. Actually, the $C_p(T)$ curve also supports that the transition at $15 \text{ K}$ is continuous. The five frequencies are therefore unlikely to be caused by inequivalent muon sites in the crystal lattice (compositional inhomogeneities), but most likely reflect the intrinsic behavior of BaCoO$_3$.

**IV. DISCUSSION**

**A. $T^n_c$ for the compounds with $n=1-5$**

In order to understand the common features of the macroscopic magnetism of the quasi-1D compounds taken collectively, Fig. 11 shows the average valence of Co $(\bar{V}_{Co})$ ions, the effective magnetic moment of Co ions $(M_{eff})$ and the paramagnetic Curie temperature $(\Theta_p)$ as a function of $n$. The $\bar{V}_{Co}(n)$ curve is calculated from the nominal composition of the 1D system; that is, we ignored a possible oxygen deficiency in the samples. The values of $M_{eff}$ and $\Theta_p$ were obtained by fitting the $\chi(T)$ curve between 300 - 600 K using the Curie-Weiss law. The solid line in Fig. 11(b) represents the $M_{eff}(n)$ curve for the charge and spin distribution on the CoO$_3$ chain in Table II that is, one Co$^{3+}$ in the CoO$_6$ prism (Co$^{3+}_{prism}$) with the HS state $(S=2)$ and one Co$^{3+}$ and $(n-1)$Co$^{4+}$ in the CoO$_6$ octahedra (Co$^{3+}_{oct}$ and Co$^{4+}_{oct}$) with the LS state $(S=0$ and $1/2)$. The relationship between $M_{eff}$ and $n$ is given by:

$$
M_{eff}^2 = \left( \frac{1}{n+1} M_{eff,S=2}^2 + \frac{n-1}{n+1} M_{eff,S=1/2}^2 \right),
$$

where $M_{eff,S=2}$ and $M_{eff,S=1/2}$ are $M_{eff}$ for Co ions with $S=2$ and $S=1/2$ (Co$^{3+}_{prism}$ and Co$^{4+}_{oct}$). Since the variation of measured $M_{eff}$ below $n=5$ is well explained by eq. 11, the above spin and charge configuration in the CoO$_3$ chain is the most probable one. This also suggests that the oxygen deficiency in the samples with $n \leq 5$ is very small. For BaCoO$_3$ $(n=\infty)$, $M_{eff}$ is estimated as 2.45 $\mu_B$, whereas it is $M_{eff} = 1.73 \mu_B$ for Co$^{3+}_{oct}$, with $S=1/2$. This discrepancy was also reported by another group $(M_{eff} \sim 2.3 \mu_B)$ and was explained using a large $g$ factor (=2.2) for the Co ions, 22 although $g=2.0$ for Fe-doped Ca$_3$Co$_2$O$_6$ was found in an ESR study. 37

For Ca$_3$Co$_2$O$_6$ $(n=1)$, $\Theta_p = 36.1 \pm 0.8 \text{ K}$, and this is consistent with past work. 12, 13 As $n$ increases from 1 to 3, $\Theta_p$ changes its sign from positive to negative and rapidly decreases down to -180 K, then increases with further increasing $n$ and approaches $-0$ at $n=\infty$. A large negative paramagnetic Curie temperature for the samples with $n=2$ and 3 obviously indicates that the transition at $T^n_c$ is caused by an inter-chain 2D AF interaction. Considering the structural similarity among the quasi 1D cobalt oxides, $T^n_c$ for the samples with $n=1$ and 4 are therefore most likely due to the appearance of the short-range 2D AF order. The magnitude of the 1D F interaction would be strongly affected by $n$, because not only the structure of the chain but also the Co valence are altered by $n$ (see Table II). Compared with the the intra-chain 1D F interaction, the inter-chain 2D AF interaction is expected to be insensitive to $n$, as the geometrical arrangement of the chains in the $ab$ plane is essentially the same for all the compounds with $n=1\text{ - }\infty$. This indicates that the inter-chain AF interaction plays a significant role for determining the magnetism detected by the current $\mu^+\text{SR}$ measurements. Here we wish to emphasize that $T^n_c$ is not caused by the change in the spin state of Co ions proposed by Hardy et al., 26 because the decrease in $A_{2\text{FF}}$ confirms the appearance of a magnetically ordered phase. On the contrary, it was found that not $A_{2\text{FF}}$ but $A_{1\text{FF}}$ exhibit an anomaly at the spin state transition in the layered cobaltites. 26

Since each chain is considered to act as a single spin, we ignore the intra-chain 1D F interaction. Within the mean field theory, $T_N$ is expressed by:

$$
T_N = \frac{1}{2} 2z | J_{AF} | \frac{S(S+1)}{3k_B},
$$

where $\lambda_{crit}$ is the magnetic ordering temperature at the critical magnetic field $H_{crit}$, and $\lambda_{AF}$ is the magnetic ordering temperature at the critical magnetic field $H_{AF}$.
TABLE II: Composition and nominal charge and spin distribution in the CoO₃ chain for quasi-one-dimensional cobalt oxides, \(A_{n+2}Co_{n+1}O_{3n+3}\) (\(A=\text{Ca, Sr, Ba}\)). Here, Co_{pri} and Co_{oct} denote the Co ion in a CoO₆ prism and in a CoO₆ octahedron. For the compounds with \(n=2-5\), mixed valence state would exist in the neighboring CoO₆ octahedra to minimize electronic repulsion.

| \(n\) | composition | charge distribution | spin distribution |
|-------|-------------|---------------------|------------------|
| 1     | Ca₃Co₂O₆   | Co³⁺, Co⁺⁺       | 2, 0             |
| 2     | Sr₄Co₃O₉   | Co³⁺, Co⁺⁺, Co⁺⁺⁺ | 2, 0, 1/2        |
| 3     | Sr₅Co₂O₁₂  | Co³⁺, Co⁺⁺⁺, Co⁺⁺⁺ | 2, 0, 1/2, 1/2   |
| 5     | (Sr₁/₂Ba₁/₂)CoO₁₈ | Co³⁺, Co⁺⁺⁺, Co⁺⁺⁺, Co⁺⁺⁺⁺ | 2, 0, 1/2, 1/2, 1/2 |
| ∞     | BaCoO₄      | Co⁺⁺⁺⁺, Co⁺⁺⁺⁺     | 1/2              |

FIG. 11: (a) Average Co valence, (b) effective magnetic moment of Co ions (\(M_{eff}\)) and (c) paramagnetic Curie temperature (\(\Theta_p\)) as a function of \(n\) in the 1D system, \(A_{n+2}Co_{n+1}O_{3n+3}\).

where \(z\) is the number of the nearest neighboring spins, \(J_{AF}\) is the 2D AF coupling constant and \(k_B\) is the Boltzmann constant. Although \(T_N=29\pm5\) K for Ca₃Co₂O₆ from the ZF-µSR measurement, we introduce a virtual \(T_N'(T_N')\) to explain the behavior of the \(A_{TF}(T)\) curve, indicating the appearance of the short-range 2D AF order. Assuming that \(T_c^{on}\) (or \(T_c^{mid}\) = \(T_N'\)) and \(z=6\), we can estimate \(J_{AF}\) for the current samples using the spin distribution in Table II. Here, \(T_c^{mid}\) denotes the temperature at which \(NA_{TF}=0.5\). Figures [12(a) and 12(b)] show the variation of \(T_c\) and \(J_{AF}\) as a function of the inter-chain distance \(d_{inter-chain}\) in \(A_{n+2}Co_{n+1}O_{3n+3}\). Although \(T_c\) decreases with \(d_{inter-chain}\) (and/or \(n\)), the magnitude of \(J_{AF}/k_B\) is roughly the same (~20 K or 10 K) for all the samples. This suggests that \(T_c^{on}\) is induced by the 2D AF interaction not only for the compounds with \(n \geq 2\) but also for Ca₃Co₂O₆.

For BaCoO₄, the lowest \(T_c^{on}\) and the sharp transition
width are characteristic features compared with those for the compounds with \( n \leq 5 \) (see Figs. 5 and 6). Also, a clear muon oscillation is observed only in BaCoO\(_3\) below 15 K. These suggest a smaller fluctuation and/or distribution of the internal magnetic field in BaCoO\(_3\) than in the compounds with \( n \leq 5 \). As seen in Table II, Co\(^{4+}\) ions with \( S=1/2 \) (Co\(_{\text{oct}}^{4+}\)) are stable in BaCoO\(_3\), while both Co\(^{3+}\) ions with \( S=2 \) and \( S=0 \) (Co\(_{\text{pri}}^{3+}\) and Co\(_{\text{oct}}^{3+}\)) coexist in Ca\(_3\)Co\(_2\)O\(_6\) and Co\(_{\text{pri}}^{3+}\), Co\(_{\text{oct}}^{3+}\) and Co\(_{\text{oct}}^{4+}\) in the compounds with \( n=2-5 \). A mixed valence state is expected in the neighboring Co\(_{\text{oct}}^{3+}\) and Co\(_{\text{oct}}^{4+}\) ions for minimizing electronic repulsion, indicating the existence of a fluctuating magnetic field. Also, the spin and charge distribution in the compounds with \( n \leq 5 \) would induce a large distribution in the internal magnetic field. These are most likely to be the reasons for the difference between BaCoO\(_3\) and the compounds with \( n=1-5 \).

**B. Ferromagnetic order along the chain**

As seen in Fig. 8 the \( \chi^{-1}(T) \) curve for BaCoO\(_3\) exhibits a weak F or ferrimagnetic behavior below 53 K only under low magnetic fields. Reflecting this change, \( \lambda_{TF} \) increases slightly below \( \sim 50 \) K with decreasing \( T \), while there are no anomalies in the \( A_{TF} \) curve down to 15 K. It is therefore most reasonable to conclude that, as \( T \) decreases, the 1D F order completes below 53 K, then the 2D AF order becomes stable below 15 K. In other words, the F order in the chain is easily observed by \( \chi \) measurements but looks very complex in \( \mu^+ \)SR. This situation is similar to the case for the typical 1D antiferromagnet CsCoCl\(_3\), in which the short-range 1D AF order appears below 75 K. This corresponds to the maximum in the \( \chi(T) \) curve. Nevertheless, moving solitons along the chain induce a large fluctuation of the internal field at the muon sites. As a result, \( \mu^+ \)SR was able to detect the 2D AF order but unable to observe the short-range 1D AF order.

For the compounds with \( n=1-5 \), we propose that \( T_{c}^{-\text{en}} \) (or \( T_{c}^{-\text{mid}} \)=\( T_{N}^{\text{SR}} \)) is caused by the 2D AF interaction. Hence, there should exist a transition into the short-range 1D F ordered state above \( T_{c}^{-\text{en}} \). For Ca\(_3\)Co\(_2\)O\(_6\), this requirement is very consistent with the indication of a short-range magnetic order below \( \sim 200 \) K detected by a specific heat measurement. The \( \chi^{-1}(T) \) curve for the current Ca\(_3\)Co\(_2\)O\(_6\) also exhibits a deviation from the linear relationship below \( \sim 150 \) K (see Fig. 10). Presumably indicating the appearance of the 1D F order. Furthermore, recent \( \chi \) measurements for the compounds with \( n=2-5 \) showed a field dependence even at 300 K. This may be due to the appearance of short-range 1D F order along the chain. The overall scenario for the quasi-1D systems is therefore that the 1D F ordered state exists even at \( \sim 200 \) K, while the 2D AF ordered state appears below \( \sim 100 \) K. The former is very difficult to detect by \( \mu^+ \)SR and neutron diffraction measurements, but the latter can be relatively easily observed by \( \mu^+ \)SR.

**C. Multi-frequency components in BaCoO\(_3\)**

In order to evaluate the critical exponent (\( \beta \)) for the AF transition, Fig. 14 shows the relationship between the normalized oscillation frequency \( \nu_{\mu,i}/\nu_{\mu,i}(0K) \) and the reduced temperature \( (T_N-T)/T_N \). Here, \( \nu_{\mu,i}(0K) \) and \( T_N \) are obtained by fitting the \( \nu_{\mu,i}(T) \) curve (Fig. 10) with eq. \( 2 \). We obtain \( \beta=0.191\pm0.009 \) and \( T_N=14.5\pm0.2 \). The evaluated \( \beta \) for BaCoO\(_3\) also ranges between the predictions for the 2D and 3D Ising model (\( \beta=0.125 \) and 0.3125) , and is roughly the same as that for Ca\(_3\)Co\(_2\)O\(_6\) (\( \beta=0.18\pm0.12 \)). This indicates a strong 2D character of the AF transition in BaCoO\(_3\), in contrast to \( \beta=0.31 \) for the 1D antiferromagnet CsCoBr\(_3\). Here \( \beta \) of CsCoBr\(_3\) was evaluated using the neutron diffraction data in the vicinity of \( T_N \) (5\( \times \)10\(^{-4} \) \( \leq (T_N-T)/T_N \) \( \leq 0.08 \)), whereas \( \beta \) of BaCoO\(_3\) \( \mu \)SR data at 0.03 \( \leq (T_N-T)/T_N \) \( \leq 0.9 \). According to Ref. [40], however \( \beta \) of CsCoBr\(_3\) looks almost the same value (0.31) even using the data at 0.03 \( \leq (T_N-T)/T_N \). The result that \( \beta_{[\text{BaCoO}_3]} < \beta_{[\text{CsCoBr}_3]} \) is therefore reliable. This discrepancy is probably due to the difference of the d orbitals contributing to the magnetism; that is, \( t_{2g} \) for Co\(^{3+}\) in BaCoO\(_3\) and \( e_g \) for Co\(^{2+}\) in CsCoBr\(_3\). The overlap of the former between the neighboring chains is expected to be smaller than that of the latter.

The simple hexagonal structure of BaCoO\(_3\) (and the lack of structural phase transitions at low \( T \)) and good quality of our sample suggest the difficulty for explaining five frequencies by multi-muon sites and/or inhomogeneity of the sample. In addition the fact that the five frequencies show a sharp transition at the same temperature indicates that these are the intrinsic behavior in
BaCoO$_3$. We consider the following two hypotheses:

1. coexistence of 2D AF and 1D F interaction

According to the $\chi$ measurement at high $T$, the paramagnetic Curie temperature $\Theta_p$ was found to be almost 0 K. This indicates that the magnitude of the inter-chain 2D AF interaction is roughly the same as that of the intra-chain 1D F interaction. The highest frequency in Fig. 14 (14.4 MHz) is comparable to the AF oscillation frequency in Ca$_3$Co$_2$O$_6$ (15 MHz at 1.8 K). The signals with $\sim$5 MHz would correspond to the magnetic fields of the intra-chain 1D F order.

2. AF domain structure

One CoO$_3$ chain (at (0,0)) is surrounded by six nearest neighboring CoO$_3$ chains in the 2D triangular lattice. We ignore the effect of the second nearest neighboring chains. If the dipole field from the nearest neighboring chain is defined as $h$ at (0,0), the total field at (0,0) can be represented by: $H_0$, $H_0 \pm 2h$, $H_0 \pm 4h$ and $H_0 \pm 6h$, in which $H_0$ is the field from the chain at (0,0). This could be consistent with a roughly symmetrical distribution of $\nu_{\mu,i}$ at 1.8 K (see Fig. 4(b)). In this case, $\gamma_{\mu}/2\pi \times H_0 \sim 10$ MHz, where $\gamma_{\mu}/2\pi = 18.55342$ kHz/Oe. Furthermore, the electronic structural calculation suggested almost a similar stability for the two type of AF configuration, although the F configuration was predicted to be most stable.\textsuperscript{24}

In order for further understanding the nature of the AF phase in BaCoO$_3$, more precise $\mu^+\text{SR}$ measurements on pure and doped BaCoO$_3$ are necessary; in particular, the change in the inter-chain distance by chemical and/or physical pressure is crucial to distinguish the two hypothesis above through the shift of the balance between the 1D F and 2D AF interactions.

V. SUMMARY

Magnetism of quasi one-dimensional (1D) cobalt oxides $AE_{n+2}Co_{n+1}O_{3n+3}$ ($AE=$Ca, Sr and Ba, $n=1$, 2, 3, 5 and $\infty$) was investigated by susceptibility ($\chi$) and $\mu^+\text{SR}$ measurements using polycrystalline samples, at temperatures from 300 K down to 1.8 K. The $\chi$ measurement confirmed a systematic change in the charge and spin distribution in the 1D CoO$_3$ chain with $n$. The weak transverse field (wTF-) $\mu^+\text{SR}$ experiments showed the existence of a magnetic transition in all five samples investigated. The onset temperature of the transition ($T_{c\text{m}}^n$) was found to decrease with $n$; that is, 100±25 K, 90±10 K, 85±10 K, 50±10 K, and 15±1 K for $n=1$, 2, 3, 5, and $\infty$, respectively. In particular, for the samples with $n=2$, 5, $T_{c\text{m}}^n$ was detected only by the present $\mu^+\text{SR}$ experiments. A muon spin oscillation was clearly observed in both Ca$_3$Co$_2$O$_6$ ($n=1$) and BaCoO$_3$ ($n=\infty$), whereas only a fast relaxation is apparent even at 1.8 K in the other three samples ($n=2$, 3 and 5).

A large negative paramagnetic Curie temperature for the samples with $n=2$ and 3 indicated that the transition at $T_{c\text{m}}^n$ is caused by an inter-chain two-dimensional (2D) antiferromagnetic (AF) interaction. Considering the structural similarity among the quasi 1D cobalt oxides, the transitions at $T_{c\text{m}}^n$ for the samples with $n=1$ and 5 were therefore most likely due to the appearance of the short-range 2D AF order. This suggested that the 1D ferromagnetic order in the CoO$_3$ chain of Ca$_3$Co$_2$O$_6$ ($n=1$) would occur at higher temperatures ($\sim 200$ K) than proposed previously ($\sim 80$ K).

For BaCoO$_3$ ($n=\infty$), the $\chi$ measurement confirmed that $T_{c\text{m}}^\infty=T_N(=15$ K) and $T_C=53$ K, which corresponds to the ferromagnetic (F) transition caused by an intra-chain 1D interaction. Nevertheless, the wTF-asymmetry ($A_{TF}$) did not exhibit a marked anomaly at $T_C$, while $A_{TF}$ is very sensitive to the formation of magnetic order. This is likely to be caused by a domain motion in the 1D chain, as in the case for CsCoCl$_3$. In spite of the fact that the sample is structurally homogeneous, the ZF-$\mu^+\text{SR}$ spectrum showed a complex of at least five frequency components below $T_N$, which require further detailed studies.

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