

Evidence of Two Dimensionality in Quasi-One-Dimensional Cobalt Oxides

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The quasi-one-dimensional (Q1D) cobalt oxides $A_{n+2}Co_{n+1}O_{3n+3}$ ($A = Ca, Sr, \text{ and } Ba, n = 1 - \infty$) were investigated by muon-spin spectroscopy under applied pressures of up to 1.1 GPa. The relationship between the onset Néel temperature T_N^{on} and the interchain distance (d_{ic}), which increases monotonically with n , is well fitted by the formula $T_N/T_{N,0} = (1 - d_{\text{ic}}/d_{\text{ic},0})^\beta$; here $T_N^{\text{on}} \sim 100$ K for $Ca_3Co_2O_6$ ($n = 1$) and ~ 15 K for $BaCoO_3$ ($n = \infty$) at ambient P . The $T_N^{\text{on}} - d_{\text{ic}}$ curve also predicts a large P dependence of T_N for the compounds with $n \geq 5$, i.e., in the vicinity of $d_{\text{ic},0}$, while the $n = 1-4$ compounds show only a very small effect. Indeed, our high-pressure μ^+ SR results show that T_N of $BaCoO_3$ is enhanced by P with a slope of 2.2 K/GPa, whereas no detectable changes by P for both $Ca_3Co_2O_6$ and $Sr_4Co_3O_9$ ($n = 2$). This clearly confirms the role of the 2D-antiferromagnetic interaction on T_N^{on} in the Q1D cobalt oxides.

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Pressure is one of the crucial parameters for changing macroscopic magnetism in solids, mainly through the change in distance between magnetic ions and the resulting enhancement of the interaction between magnetic moments. Although there are a huge number of works concerning pressure dependences of magnetism [1], here we wish to add a very unique example; namely, the pressure dependence of the Néel temperature (T_N) for quasi-one-dimensional (Q1D) cobalt oxides $A_{n+2}Co_{n+1}O_{3n+3}$ ($A = Ca, Sr, \text{ and } Ba, n = 1-\infty$) [2–4], in which a two-dimensional (2D) triangular lattice is formed by CoO_3 chains. The CoO_3 chain in the $n = 1$ compound consists of alternating face-sharing CoO_6 trigonal prisms and CoO_6 octahedra [5]. As n increases, the number of CoO_6 octahedra increases so as to build the chain with n CoO_6 octahedra and one CoO_6 trigonal prism. The average Co valence also increases from +3 to +4 with increasing n from 1 to ∞ . The magnetic interaction is thought to be ferromagnetic (F) along the CoO_3 chain (1D-F) and antiferromagnetic (AF) in the 2D triangular lattices (2D-AF) [6–8].

For the compounds with $n = 1-5$, earlier μ^+ SR experiments showed the existence of a magnetic transition below 100 K [9], although there were no clear anomalies in the susceptibility- T curve. The onset temperature of the transition (T_N^{on}) was found to decrease with increasing n , from 100 K for $n = 1$ to 55 K for $n = 5$. In combination with the fact that the paramagnetic Curie temperature ranges from -150 to -200 K for the compound with $n = 2$ and 3, the μ^+ SR results indicate that a short-range 2D-AF order, which had been thought to be unlikely to exist at high T due to a relatively strong 1D-F interaction, appears below T_N^{on} for all compounds with $n = 1-5$. For $BaCoO_3$ ($n = \infty$), a 1D-F order appeared below 53 K, and a sharp 2D-AF transition occurred at 15 K.

The relationship between T_N^{on} and the interchain distance d_{ic} in $A_{n+2}Co_{n+1}O_{3n+3}$ is well fitted by a formula $T_N/T_{N,0} = (1 - d_{\text{ic}}/d_{\text{ic},0})^\beta$, similarly to the T dependence of the order parameter (i.e., ν , muon-spin precession frequency) below T_N (see Fig. 1). This strongly supports that T_N^{on} is induced by the 2D-AF interaction for all the Q1D cobalt oxides. The T_N^{on} -vs- d_{ic} curve also indicates a significant role of pressure (P) on T_N via the shrinkage of d_{ic} , in particular, in the vicinity of $d_{\text{ic},0}$. We have therefore measured the high-pressure μ^+ SR spectrum to study the change in T_N for the samples with $n = 1, 2$, and ∞ down to 5 K. As a result, we found a very clear P dependence of T_N for $BaCoO_3$ but an absence of measurable P effects in $Ca_3Co_2O_6$ and $Sr_4Co_3O_9$, confirming the role of the 2D-AF interaction in magnetism of the Q1D cobalt oxides.

The following seven polycrystalline samples of Q1D cobalt oxides were synthesized at Nagoya University by a conventional solid state reaction technique, using reagent grade Co_3O_4 , $CaCO_3$, $SrCO_3$, and $BaCO_3$ powders as starting materials: $Ca_3Co_2O_6$ ($n = 1$), $Sr_4Co_3O_9$ ($n = 2$), $Sr_5Co_4O_{12}$ ($n = 3$), $Sr_6Co_5O_{15}$ ($n = 4 - 1$), $(Sr_{3/4}Ba_{1/4})_6Co_5O_{15}$ ($n = 4 - 2$), $(Sr_{1/2}Ba_{1/2})_7Co_6O_{18}$ ($n = 5$), and $BaCoO_3$ ($n = \infty$). 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 studies indicated that the samples were single-phase of hexagonal structure. The preparation and characterization of the samples with $n = 1-5$ were reported in detail elsewhere [10].

The shape of the sample for the high-pressure μ^+ SR experiment was a disk with 5 mm diameter and ~ 3 mm thickness. The μ^+ SR experiments were performed on the $\mu E1$ decay muon beam line at Paul Scherrer Institut (PSI). A piston cylindrical cell made of Cu-Be25 alloy was used

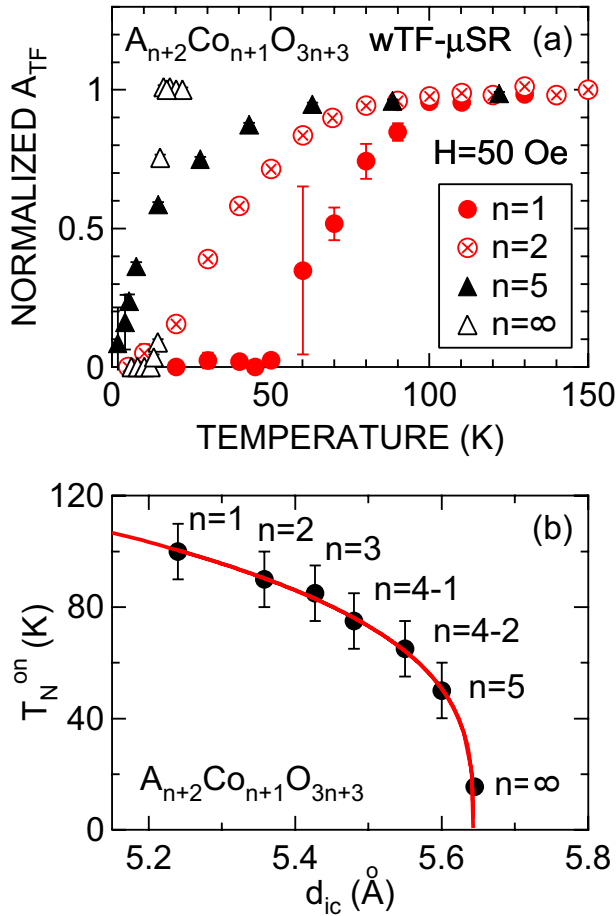


FIG. 1 (color online). (a) Temperature dependence of the normalized transverse field asymmetry ($N_{A_{TF}}$) for the samples with $n = 1, 2, 5$, and ∞ for $A_{n+2}Co_{n+1}O_{3n+3}$ and (b) the relationship between T_N^{on} and the interchain distance d_{ic} . The data in (a) were obtained by fitting the weak transverse field μ^+ SR spectrum using mainly a simple exponential relaxation signal. The solid line in (b) was obtained fitting to $T_N/T_{N,0} = (1 - d_{ic}/d_{ic,0})^\beta$, $\beta = 0.307$. The detailed composition of the samples is described in the text.

to apply pressure up to 1.1 GPa. Six disks of the sample were stacked in the sample space (5.2 mm diameter and 20 mm length) of the cell. In order to apply hydrostatic pressure to the sample, a 1:1 mixture of n -pentane and isoamyl alcohols was used as a pressure medium. The actual pressure at low temperatures was estimated by measuring the superconducting transition temperature of a piece of an indium wire placed at the bottom of the sample space, by ac susceptibility measurements. The μ^+ SR spectrum naturally consists of signals from both the sample and the body of the high-pressure cell. The ratio of the former signal to the latter is 15%–25%. The experimental setup and techniques are described elsewhere [11].

Figure 2 shows the T dependence of the normalized transverse field asymmetry ($N_{A_{TF}}$) at 0.1 M, 0.58 G, and 1.1 GPa for $BaCoO_3$. Since $N_{A_{TF}}$ is roughly proportional to the paramagnetic volume fraction in the sample, it is

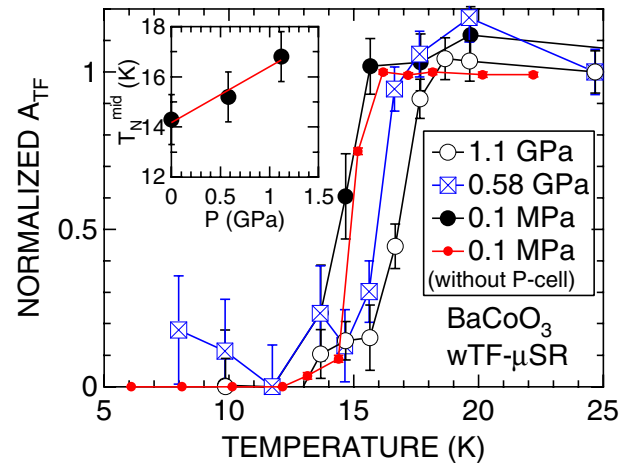


FIG. 2 (color online). $N_{A_{TF}}$ as a function of T at $P = 0.1$ MPa, 0.58 GPa, and 1.1 GPa for $BaCoO_3$ ($n = \infty$). The $N_{A_{TF}}(T)$ curve without the pressure cell at ambient P is also plotted for comparison. The data were obtained by fitting the wTF- μ^+ SR spectrum using a simple exponentially relaxed cosine oscillation. The inset shows the relationship between T_N^{mid} and P ; T_N^{mid} is defined as the temperature at which $N_{A_{TF}} = 0.5$.

clearly found that T_N is enhanced by increasing P . Interestingly, as P increases, the $N_{A_{TF}}(T)$ curve simply shifts towards the higher T side, suggesting a homogeneous P effect on the AF transition. As seen in the inset in Fig. 2, a linear relationship between T_N and P is found with a slope (dT_N/dP) of 2.2 K/GPa. On the contrary, for both $Ca_3Co_2O_6$ and $Sr_4Co_3O_9$, there are no detectable changes between the $N_{A_{TF}}(T)$ curves obtained at ambient pressure and 1.0 GPa (see Fig. 3). This is very consistent with the T_N^{on} -vs- d_{ic} curve [see Fig. 1(b)]. That is, the slope (dT_N^{on}/dd_{ic}) is steeper in the vicinity of $d_{ic,0} = 5.65$ Å than in the range of $d_{ic,0} \leq 5.5$ Å; in other words, a large P dependence of T_N is naturally expected for the samples with $n = \infty$ and probably also $n = 5$, whereas a very small effect for the samples with $n = 1-4$. Although the ferromagnetic transition temperature of $Ca_3Co_2O_6$ ($T_{ferri} = 12.5$ K) was found to increase with P by χ measurement ($dT_{ferri}/dP = 0.73$ K/GPa) [12], we wish to emphasize again that T_N^{on} has been measured only by μ^+ SR since, albeit not impossible, it is very difficult to investigate the P dependence of T_N^{on} with other techniques.

In order to know the changes in the internal magnetic field for $BaCoO_3$ induced by external pressure, we measured the P dependence of its zero field μ^+ SR spectrum, which was found to exhibit clear but complex muon-spin oscillations below T_N at ambient pressure [9]; that is, it has at least five frequency components ($\nu_\mu = 14.4, 13.5, 6.4, 5.1, \text{ and } 3.5$ MHz), even though the sample is structurally single-phase at room temperature and there is no indication of any structural phase transition down to 4 K. This implies that there is only one μ^+ site in the $BaCoO_3$ lattice, because every oxygen is equivalent for the simple hexagonal lattice. The internal magnetic fields of the five signals,

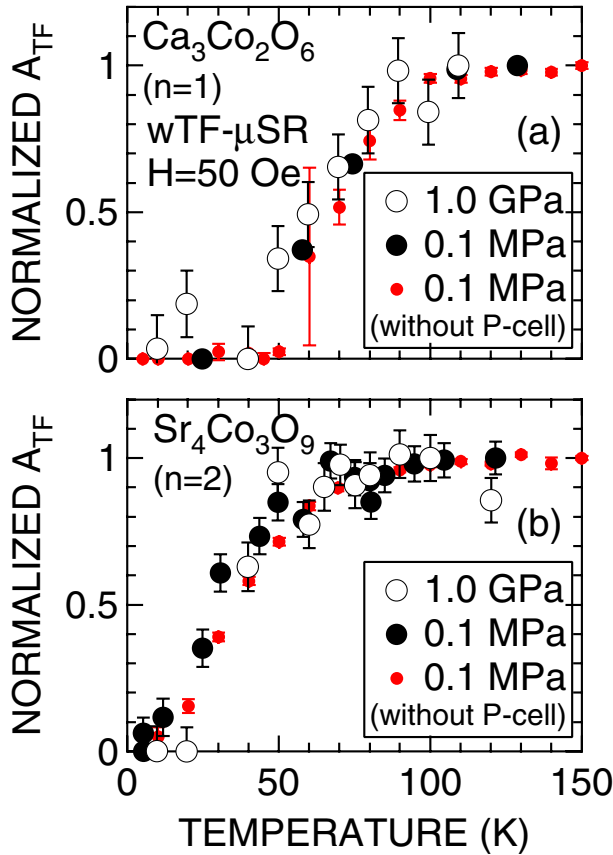


FIG. 3 (color online). T dependence of $N_{A_{TF}}$ at $P = 0.1$ MPa (solid circles) and 1.0 GPa (open circles) for (a) $\text{Ca}_3\text{Co}_2\text{O}_6$ ($n = 1$) and (b) $\text{Sr}_4\text{Co}_3\text{O}_9$ ($n = 2$). The small solid circles represent the data obtained at ambient pressure without the pressure cell [same as shown in Fig. 1(a)].

i.e., $\nu_{\mu,i}$ with $i = 1-5$, exhibit a similar temperature dependence, indicating that the five frequencies are unlikely to be caused by compositional inhomogeneities, but most likely reflect the intrinsic behavior of BaCoO_3 .

Figures 4(a) and 4(b) show the ZF- μ^+ SR spectrum and its Fourier transform of BaCoO_3 at 5 K under pressures of 0.1 M and 1.1 GPa. Each Fourier spectrum consists mainly of two components at around 3 and 14 MHz. As P increases, the higher F component clearly shifts towards higher values, whereas the lower one seems to be almost independent of P . In order to explain the origin of the multi- F components and their P dependence [see Fig. 4(c)], we assume that the muons locate near the corner of the triangular lattice, because the site 1.39 Å away from the Co position in the Ba plane is the most stable for μ^+ according to the distribution of the electrostatic potential calculated using a point-charge model (see Fig. 5).

The Co spins are thought to align ferromagnetically in the CoO_3 chain [5–9,13]. Depending on the relative local alignment of the Co chains, and by considering solely the effect of the nearest seven CoO_3 chains within the nearest four Co planes, one can estimate the local magnetic field at the μ^+ site to be restricted between 780 and 1900 Oe, if the

magnitude of each Co moment is $1\mu_B$. From the observed precession frequency of 14 MHz (=1033 Oe) and considering the above discussed muon site, the maximum Co moment can be ranged between 1.3 and $0.5\mu_B$ at 5 K. The effective magnetic moment of the Co^{4+} ions is, however, reported to be $2.1\mu_B$ from χ measurements at high T [8,9]. The geometrical AF frustration in the 2D triangular lattice is likely to induce a canted spin structure, resulting

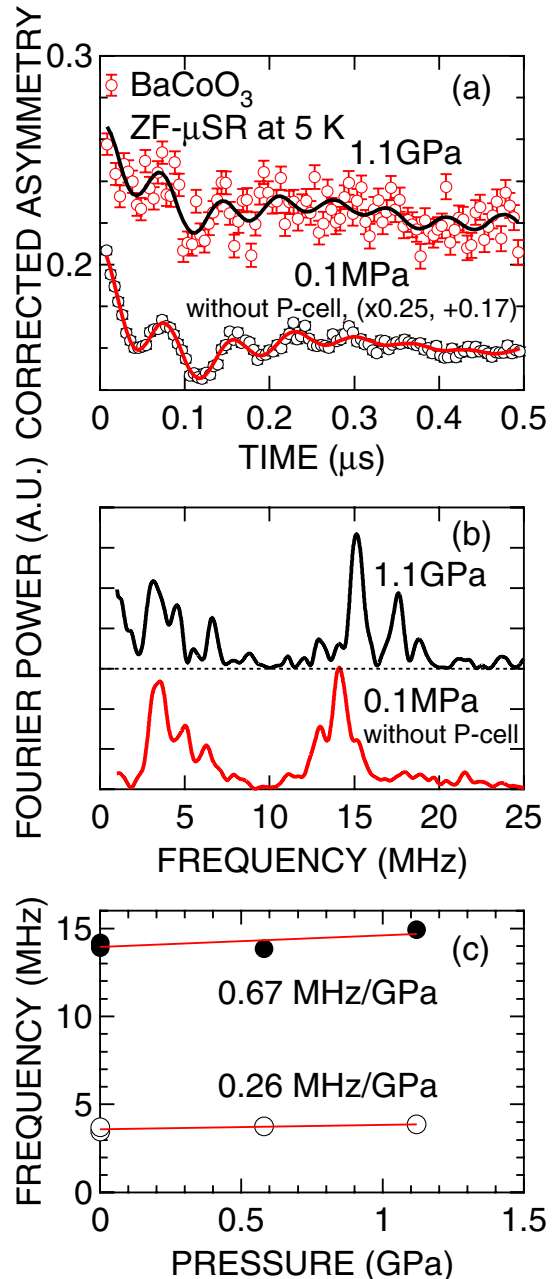


FIG. 4 (color online). (a) ZF- μ^+ SR spectrum and (b) its Fourier transform for BaCoO_3 at 5 K under $P = 0.1$ MPa (without the pressure cell) and 1.1 GPa and (c) P dependence of the muon precession frequency for the main two components around 3 and 14 MHz, estimated by fitting the zero field spectrum using a combination of five cosine oscillations with a fixed initial phase.

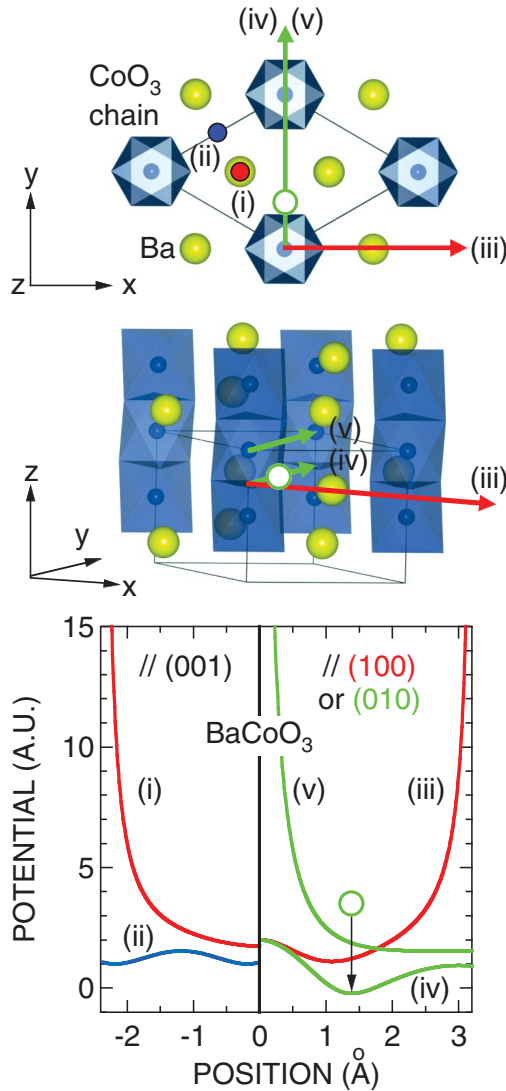


FIG. 5 (color). Crystal structure and distribution of electrostatic potential for BaCoO₃. The left half of the bottom panel shows the potential at (i) the center of the triangle and (ii) the middle of the edge of the triangle as a function of the position along the (001) direction, where $(x, y, 0)$ corresponds to the Ba plane. The right half shows the potential (iii) along the (100) direction and (iv) along the (010) direction in the Ba plane, while (v) along the (010) direction in the Co plane. Here Co ions locate at $(0, 0, \pm 4.75/4 \text{ \AA})$. The lowest potential is obtained at 1.39 \AA away from the Co position in the Ba plane along the (010) direction.

in a qualitatively more reasonable explanation for the magnitude of the internal magnetic field, but neutron diffraction experiments are necessary to better determine the correct magnetic structure for BaCoO₃, and the work is in progress.

It should be noted that the current results definitely confirm the role of the 2D-AF interaction on magnetism

in the Q1D cobalt oxides. This naturally leads to the question on the transition temperature to the 1D-F ordered state, which should appear above T_N^{on} . This is because the distance between the adjacent Co ions along the CoO₃ chain is smaller than d_{ic} —i.e., the former is 2.38 \AA , whereas the latter 5.65 \AA for BaCoO₃. Although the 1D-F order for BaCoO₃ was easily observed by both susceptibility and μ^+ SR measurements, those for the compounds with $n = 1-5$ have so far not been so clearly detected [9,10]. We wish to mention finally the possibility to detect the 1D-F order by muonic Knight shift (K) measurements using high transverse field μ^+ SR techniques, because the $K(T)$ curve on the 2D cobalt oxides exhibits a clear change in the slope at the spin state transition of Co ions [14], at which there are no crucial changes in asymmetry and relaxation rate.

This work was performed mainly at the Swiss Muon Source, Paul Scherrer Institut, Villigen, Switzerland, while a part of the data at ambient pressure was obtained at TRIUMF, Vancouver, Canada. We thank the LMU staff of PSI and the μ SR facility staff of TRIUMF for help with the μ^+ SR experiments.

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