

Frustrated magnetism in the two-dimensional triangular lattice of Li_xCoO_2

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(Received 9 June 2005; revised manuscript received 9 September 2005; published 27 October 2005)

Magnetism of the simplest layered cobaltite Li_xCoO_2 with $x=1.0, 0.95,$ and 0.7 has been investigated by positive muon spin rotation and relaxation ($\mu^+\text{SR}$) spectroscopy together with magnetic susceptibility measurements, using polycrystalline samples in the temperature range between 300 and 1.8 K. Weak transverse field $\mu^+\text{SR}$ showed the appearance of magnetism below ~ 65 K ($=T_c^{\text{on}}$) for the sample with $x=1.0$. The volume fraction of the magnetic phase at 1.8 K is determined to be $\sim 20\%$ for LiCoO_2 , strongly suggesting that the observed magnetism is not induced by impurities but is an intrinsic behavior. This indicates that either a charge disproportionation ($2\text{Co}^{3+} \rightarrow \text{Co}^{2+} + \text{Co}^{4+}$), a spin state transition ($t_{2g}^6 \rightarrow t_{2g}^5 e_g^1$), or an appearance of magnetic Co^{3+} at surface occurs below 65 K. Zero field $\mu^+\text{SR}$ spectra of LiCoO_2 consist mainly of a slow relaxing signal due to random fields even at 1.8 K plus a small amount of a fast relaxing signal and an oscillating component, implying the presence of an antiferromagnetic order, as in the case of Na_xCoO_2 with $x \geq 0.75$. For Li-deficient Li_xCoO_2 samples, T_c^{on} decreases with decreasing x from 50 K for $x=0.95$ to 25 K for $x=0.7$. The volume fraction of the magnetic phase is however almost independent of x and is estimated as 20% at 1.8 K, but no oscillations were observed in the zero field spectrum.

DOI: [10.1103/PhysRevB.72.144424](https://doi.org/10.1103/PhysRevB.72.144424)

PACS number(s): 76.75.+i, 75.30.Fv, 72.15.Jf, 75.30.Kz

I. INTRODUCTION

Layered cobaltites with CoO_2 planes, in which Co ions form the two-dimensional triangular lattice 2DTL by the connection of edge-sharing CoO_6 octahedra, have been intensively investigated originally due to reversible insertion and extraction of Li^+ in LiCoO_2 ,¹ then due to good thermoelectric properties in Na_xCoO_2 (Refs. 2–4) and $[\text{Ca}_2\text{CoO}_3]_{0.62}[\text{CoO}_2]$,^{5–7} and very recently due to superconductivity in $\text{Na}_{0.35}\text{CoO}_2 \cdot 1.3\text{H}_2\text{O}$.^{8–10} Among several layered cobaltites, LiCoO_2 is doubtlessly the most basic compound, because Li^+ is the smallest alkali ion. LiCoO_2 belongs to the rhombohedral system (space group $R\bar{3}m$) with the layered $\alpha\text{-NaFeO}_2$ structure, similarly to $\gamma\text{-Na}_x\text{CoO}_2$.

For stoichiometric LiCoO_2 , magnetic susceptibility (χ) measurements,¹¹ x-ray photoelectron spectroscopic (XPS) analysis,¹² and band-structural calculations¹³ indicate that Co^{3+} ions are in a low spin state (t_{2g}^6) with $S=0$ at ambient temperature. It is thus believed that LiCoO_2 does not exhibit magnetic transitions at low T . This was also confirmed by χ and NMR experiment down to 4.2 K.¹⁴ Although LiCoO_2 is known to be an insulator, Li deficient Li_xCoO_2 with $x=0.7\text{--}0.55$, in which Li was removed/deintercalated by an electrochemical reaction similar to Li batteries, exhibits metallic behavior above 50 K.¹⁵ In other words, as x decreases from 1, an insulator-to-metal transition was found at around $x=0.95$ by resistivity (ρ) measurements; $\rho(275\text{ K}) \sim 2000\ \Omega\text{ cm}$ for LiCoO_2 , $\sim 6\ \Omega\text{ cm}$ for $\text{Li}_{0.96}\text{CoO}_2$, and $\sim 1\ \Omega\text{ cm}$ for $\text{Li}_{0.94}\text{CoO}_2$. The lowest $\rho(275\text{ K})$ was observed in $\text{Li}_{0.7}\text{CoO}_2$ to be $\sim 33\ \text{m}\Omega\text{ cm}$. The value of $\rho(275\text{ K})$ increased with further lowering x , such as $\sim 80\ \text{m}\Omega\text{ cm}$ for $\text{Li}_{0.55}\text{CoO}_2$, although the $\rho(T)$ curve was

almost independent of T for Li_xCoO_2 with $x \leq 0.7$.¹⁵

This behavior is well explained by hole doping in the triple degenerate t_{2g} states with decreasing x , because Li deintercalation increases Co valence, i.e., the population of Co^{4+} ions. This is also consistent with the thermopower (Π) measurements,¹⁵ that is, at ambient temperature, $\Pi \sim 190\ \mu\text{VK}^{-1}$ for LiCoO_2 , $\sim 80\ \mu\text{V K}^{-1}$ for $\text{Li}_{0.7}\text{CoO}_2$ and $\sim 40\ \mu\text{V K}^{-1}$ for $\text{Li}_{0.6}\text{CoO}_2$. Considering that ρ was measured using polycrystalline pellets, the transport properties of $\text{Li}_{0.7}\text{CoO}_2$ seem to be almost comparable to those of $\gamma\text{-Na}_{0.7}\text{CoO}_2$, which is known to be a good thermoelectric material.^{8–10}

In Na_xCoO_2 with $x \geq 0.75$, a long-range magnetic order—which is clearly incommensurate (IC) spin density wave (SDW) in single crystalline samples—was found at low temperatures by positive muon spin rotation and relaxation ($\mu^+\text{SR}$) experiments.^{17,18} The existence of long-range magnetic order in Na_xCoO_2 was reconfirmed later by not only $\mu^+\text{SR}$ (Ref. 19) but also neutron diffraction experiments.²⁰ This leads the question of magnetism of Li_xCoO_2 , in particular for Li-deficient phases. Nevertheless, magnetism of Li_xCoO_2 is, to the authors' knowledge, not fully investigated, in particular, there are no systematic studies of microscopic magnetism for Li-deficient phases at low temperatures.

Muon spin spectroscopy, as it is very sensitive to the local magnetic environment, yields crucial data in frustrated 2D layered cobaltites.^{16–18,21,22} That is, only $\mu^+\text{SR}$ detected the appearance of a short-range magnetic order (IC-SDW state) in $[\text{Ca}_2\text{CoO}_3]_{0.62}[\text{CoO}_2]$ below $\sim 100\text{ K}$,^{21,22} at which the $\rho(T)$ curve exhibited a broad minimum, whereas susceptibility²³ and neutron diffraction experiments did not. This is because the μ^+ only feels the magnetic fields due to

its nearest neighbors and is specially sensitive to short-range magnetic order which sometimes appears in low-dimensional systems, while both neutron scattering and χ measurements mainly detect long-range magnetic order; if the correlation length is very short, neutron-diffraction peaks broaden and eventually disappear.

Here, we report on both weak (relative to the spontaneous internal fields in the ordered state) transverse-field (wTF) μ^+ SR and zero field (ZF) μ^+ SR, for polycrystalline Li_xCoO_2 samples with $x=1.0, 0.95$ and 0.7 at temperatures between 1.8 and 300 K. The former method is sensitive to local magnetic order via the shift of the μ^+ spin precession frequency in the applied field and the enhanced μ^+ spin relaxation, while ZF- μ^+ SR is uniquely sensitive to weak local magnetic [dis]order in samples exhibiting quasistatic paramagnetic moments.

II. EXPERIMENT

Polycrystalline LiCoO_2 was synthesized by a conventional solid state reaction technique using reagent grade Li_2CO_3 and Co_3O_4 powders as starting materials. The powders were thoroughly mixed in a ball mill using ethanol as solvent. After drying, the mixtures were calcined at 450 °C for 12 h in an air flow. After grinding, the calcined powder was pressed into a disk with 18 mm in diameter and 2 mm thick. The disk was sintered at 900 °C for 24 h in an O_2 gas flow and then furnace cooled to room temperature at a rate of 1 °C/min.

The Li-deficient samples of Li_xCoO_2 with $x=0.95$ and 0.7 were prepared by an electrochemical reaction at the University of Bordeaux using $\text{Li}|\text{LiClO}_4\text{-ethylene carbonate-dimethyl carbonate}|\text{Li}_x\text{CoO}_2$ cells. Powder x-ray diffraction (XRD) studies indicated that the samples of Li_xCoO_2 with $x=1.0, 0.95$, and 0.7 were single phase with a rhombohedral system of space group $R\bar{3}m$. The preparation and characterization of the Li-deficient samples were reported in detail elsewhere.¹⁵ An induction coupled plasma (ICP) analysis showed that the compositions (Li/Co ratio) of the samples were 1.034, 0.955, and 0.671, respectively.

Susceptibility (χ) was measured using a superconducting quantum interference device (SQUID) magnetometer (mpms, Quantum Design) in the temperature range between 400 and 5 K under magnetic field $H \leq 55$ kOe. The μ^+ SR experiments were performed on the M20 surface muon beam line at TRIUMF. The experimental setup and techniques were described elsewhere.²⁴

III. RESULTS

A. Susceptibility

Figure 1 shows the susceptibility χ and inverse susceptibility χ^{-1} of the present Li_xCoO_2 powders as a function of temperature, measured in field-cooling (FC) mode with $H=10$ kOe. The $\chi(T)$ curve in LiCoO_2 indicates a paramagnetic behavior down to 5 K, while the rapid increase in χ below ~ 50 K suggests the existence of localized moments, usually explained due to an undetected magnetic impurity (such as Co_3O_4) and/or an imperfection of the crystal lattice.

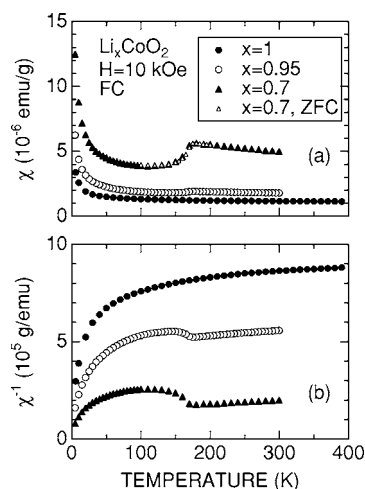


FIG. 1. Temperature dependences of (a) magnetic susceptibility χ and (b) χ^{-1} for Li_xCoO_2 with $x=1, 0.95$, and 0.7 . χ was measured in field-cooling FC mode with $H=10$ kOe. In order to know the nature of the anomaly around 175 K, the $\chi(T)$ curve in $\text{Li}_{0.7}\text{CoO}_2$ measured in zero field cooling ZFC mode is also plotted in Fig. 1(a).

The origin of localized moments is discussed later.

On the other hand, for $\text{Li}_{0.7}\text{CoO}_2$, as T decreases from 300 K, χ increases monotonically down to ~ 175 K and suddenly drops; then χ decreases with decreasing the slope ($d\chi/dT$) down to ~ 100 K, and then χ increases rapidly with further decreasing T . This behavior clearly indicates the existence of a magnetic transition around 175 K ($=T_m$). Since there is no marked difference between the data obtained in zero field-cooling (ZFC) and FC mode, this is unlikely due to a transition to a ferromagnetic, ferrimagnetic or spin-glass state.

The $\chi(T)$ curve in $\text{Li}_{0.95}\text{CoO}_2$ is located between those in LiCoO_2 and $\text{Li}_{0.7}\text{CoO}_2$. It should be noted that the value of T_m in $\text{Li}_{0.95}\text{CoO}_2$ is almost the same as for $\text{Li}_{0.7}\text{CoO}_2$, although the change in χ at T_m of $\text{Li}_{0.95}\text{CoO}_2$ is rather small compared with that of $\text{Li}_{0.7}\text{CoO}_2$. According to XRD and electrochemical analyses at room temperature, both $\text{Li}_{0.95}\text{CoO}_2$ and $\text{Li}_{0.7}\text{CoO}_2$ are a single phase. The present χ measurement therefore may suggest a magnetic phase separation below T_m in the Li deficient samples.

Assuming that only Co^{3+} and Co^{4+} moments are responsible for the paramagnetic behavior of χ at temperatures above T_m , the Curie-Weiss law in the general form is written as

$$\chi = \frac{N\mu_{\text{eff}}^2}{3k_B(T - \Theta_p)} + \chi_0, \quad (1)$$

where N is the number density of Co ions (per unit gram), μ_{eff} is the effective magnetic moment of Co ions, k_B is the Boltzmann's constant, T is the absolute temperature, Θ_p is the paramagnetic Curie temperature, and χ_0 is the temperature-independent susceptibility. Using Eq. (1) over the temperature range above 70 K for LiCoO_2 and above 180 K for $\text{Li}_{0.95}\text{CoO}_2$ and $\text{Li}_{0.7}\text{CoO}_2$, we obtain the values for μ_{eff} and Θ_p for the Li_xCoO_2 samples given in Fig. 2.

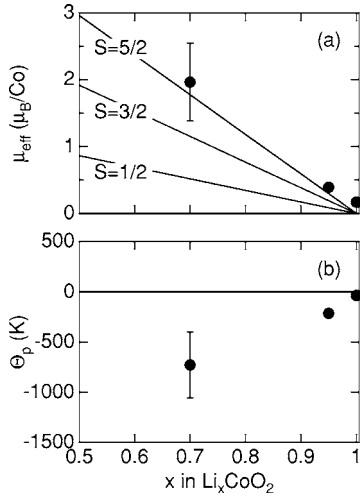


FIG. 2. (a) Effective magnetic moment of Co ions (μ_{eff}) and (b) paramagnetic Curie temperature (Θ_p) as a function of Li content x in Li_xCoO_2 . Three solid lines in Fig. 2(a) represent the change in μ_{eff} [$=g\sqrt{S(S+1)}\mu_B$ and $g=2$] caused by the increase in Co^{4+} ions with $S=5/2$, $3/2$, and $1/2$, respectively.

The values of μ_{eff} and Θ_p are found to be approximately 0 for LiCoO_2 . This is in good agreement with the results of several studies on LiCoO_2 ; that is, Co^{3+} ions in LiCoO_2 are in a low spin state ($t_{2g}^6e_g^0, S=0$). For the Li deficient samples, as x decreases from 1, μ_{eff} increases almost linearly, while Θ_p decreases. If we assume $S=0$ for Co^{3+} in Li_xCoO_2 , the slope of the μ_{eff} vs x curve is well explained by the increase in Co^{4+} ions in a high spin state ($t_{2g}^3e_g^2, S=5/2$), and is difficult to fit by Co^{4+} ions in an intermediate ($t_{2g}^4e_g^1, S=3/2$) and/or low spin state ($t_{2g}^5, S=1/2$). The transition at T_m is therefore likely due to a spin state transition of Co^{4+} ions in the Li deficient samples. This could indicate the possibility that the Co^{4+}O_6 octahedra are locally distorted into prisms, as in the case of the one-dimensional CoO_3 chains in $\text{Ca}_3\text{Co}_2\text{O}_6$.²⁵ On the other hand, the magnitude of Θ_p for the $\text{Li}_{0.7}\text{CoO}_2$ sample indicates a strong AF interaction between Co spins in 2DTL, suggesting large geometrical frustration in $\text{Li}_{0.7}\text{CoO}_2$ at low T .

B. wTF- μ^+ SR

The wTF- μ^+ SR spectra in a magnetic field of $H \sim 90$ Oe in the three Li_xCoO_2 samples exhibit a clear reduction of the μ^+ precession paramagnetic amplitude below ~ 50 K. The wTF- μ^+ SR spectra below ~ 50 K were well fitted in the time domain with a combination of a slowly relaxing precessing signal due to the external field and a fast nonoscillatory signal inferring either a fluctuating field or a static random field, as in the case of the other layered cobaltites:^{16,18,21,22}

$$A_0P(t) = A_{\text{TF}} \exp(-(\lambda_{\text{TF}}t)^{\beta_{\text{TF}}}) \cos(\omega_{\mu}t + \phi) + A_{\text{fast}} \exp(-\lambda_{\text{fast}}t), \quad (2)$$

where A_0 is the initial asymmetry, $P(t)$ is the muon spin polarization function, ω_{μ} is the muon Larmor frequency, ϕ is the initial phase of the precession, A_n and λ_n ($n=\text{TF}$ and fast)

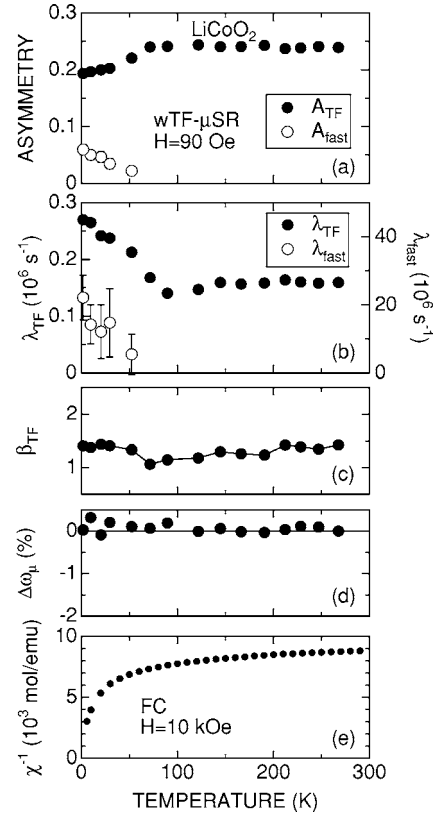


FIG. 3. Temperature dependences of (a) A_{TF} and A_{fast} , (b) λ_{TF} and λ_{fast} , and (c) the power of the exponential relaxation β_{TF} , (d) the shift of the muon precession frequency $\Delta\omega_{\mu}$, and (e) the inverse susceptibility χ^{-1} in a polycrystalline LiCoO_2 sample. The data were obtained by fitting the wTF- μ^+ SR spectra with Eq. (2).

are the asymmetries and exponential relaxation rates of the two signals, and β_{TF} is the power of the exponential relaxation. The power exponential (or stretched exponential) function suggests wide distribution of the relaxation rate, if $\beta_{\text{TF}} \neq 1$. The nonoscillatory signal ($n=\text{fast}$) has finite amplitudes below ~ 50 K.

Figures 3, 4, and 5 show the temperature dependences of A_n , λ_n ($n=\text{TF}$ and fast), β_{TF} , the shift of ω_{μ} ($\Delta\omega_{\mu}$) and χ^{-1} in the polycrystalline LiCoO_2 , $\text{Li}_{0.95}\text{CoO}_2$, and $\text{Li}_{0.7}\text{CoO}_2$ samples. Here, $\Delta\omega_{\mu}$ is defined as $[\omega_{\mu}(T) - \omega_{\mu}(300 \text{ K})]/\omega_{\mu}(300 \text{ K})$; but since a reference sample was not measured, $\Delta\omega_{\mu}$ is not equivalent to the muonic Knight shift.

For LiCoO_2 , as T decreases from 300 K, A_{TF} is constant at its maximum value (~ 0.24) down to 50 K, indicating that the sample volume is 100% paramagnetic. Then, A_{TF} drops at 50 K with further decreasing T , and A_{TF} seems to level off to ~ 0.19 below 20 K. On the other hand, A_{fast} increases monotonically with decreasing T below 50 K up to ~ 0.05 at 1.8 K. This indicates the existence of a magnetic transition with an onset temperature $T_c^{\text{on}} \sim 50$ K and a transition width $\Delta T \sim 30$ K in LiCoO_2 with volume fraction of the magnetic phase (V_F) roughly estimated as $\sim 20\%$ even at 1.8 K. Interestingly, the transition around 50 K is not detected by χ and NMR experiments.¹³ Here, it should be noted that all components of the muon spin signal are observed even at 1.8 K,

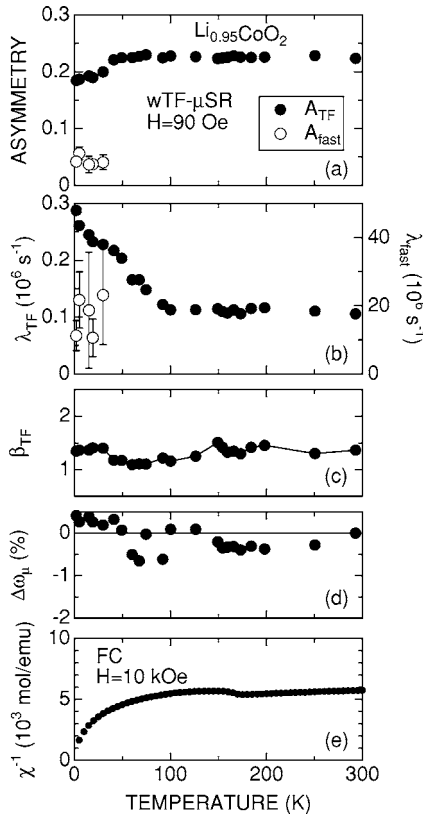


FIG. 4. Temperature dependences of (a) A_{TF} and A_{fast} , (b) λ_{TF} and λ_{fast} , and (c) the power of the exponential relaxation β_{TF} , (d) the shift of the muon precession frequency $\Delta\omega_{\mu}$, and (e) the inverse susceptibility χ^{-1} in a polycrystalline $\text{Li}_{0.95}\text{CoO}_2$ sample. The data were obtained by fitting the wTF- μ^+ SR spectra with Eq. (2).

because $A_{TF}(1.8\text{ K}) + A_{fast}(1.8\text{ K}) \sim A_{TF}(300\text{ K})$.

As T decreases from 300 K, λ_{TF} is almost constant (~ 0.15 MHz) down to 80 K, then increases with further decreasing T . At temperatures below 300 K, β_{TF} decreases monotonically with decreasing T down to 50 K, and then increases and levels off to a constant value below 20 K. The magnitude of λ_{fast} increases with decreasing T below 50 K (where it is first detected), and reaches ~ 41 MHz at 1.8 K, which is ~ 150 times larger than $\lambda_{TF}(1.8\text{ K})$.

For the Li deficient sample $\text{Li}_{0.7}\text{CoO}_2$, the $\lambda_{TF}(T)$, $\beta_{TF}(T)$, and $\Delta\omega_{\mu}(T)$ curves exhibit a clear change in their slope at 170 K, where the magnetic transition was found by the $\chi(T)$ measurement, while A_{TF} remains at 0.24 down to 25 K (see Fig. 5). This indicates that $\text{Li}_{0.7}\text{CoO}_2$ is still paramagnetic below 170 K. The transition is therefore attributed to the spin state transition of the Co^{4+} ions from the low-temperature low-spin (or mixture of low- and intermediate-spin) state to the high-temperature high-spin state, as in the case of the related cobaltites $[\text{Ca}_2\text{CoO}_3]_{0.62}^{\text{RS}}[\text{CoO}_2]$.^{21,22} This is consistent with the result of the present χ measurement above described.

Furthermore, the decrease in A_{TF} below 25 K (and the accompanying increase in λ_{TF}) indicate the existence of a magnetic transition with $T_c^{\text{on}} \sim 25\text{ K}$ in $\text{Li}_{0.7}\text{CoO}_2$. This also suggests that the magnetic transition at low- T is a common behavior in the layered cobaltites and T_c^{on} is strongly dependent on the valence of Co ions.

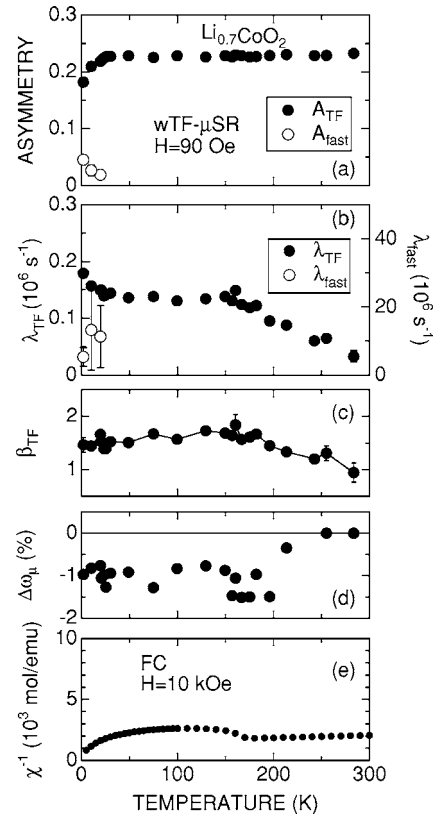


FIG. 5. Temperature dependences of (a) A_{TF} and A_{fast} , (b) λ_{TF} and λ_{fast} , (c) the power of the exponential relaxation β_{TF} , (d) the shift of the muon precession frequency $\Delta\omega_{\mu}$, and (e) the inverse susceptibility χ^{-1} in a polycrystalline $\text{Li}_{0.7}\text{CoO}_2$ sample. The data were obtained by fitting the wTF- μ^+ SR spectra with Eq. (2).

In order to understand the effect of x on the wTF- μ SR results, Fig. 6 shows the normalized $A_{TF}(N_{A_{TF}})$ and λ_{TF} as a function of T below 150 K for the three samples. Here, $N_{A_{TF}}$ is defined as $A_{TF}(T)/A_{TF}(300\text{ K})$ and roughly measures the volume fraction of paramagnetic phases in the sample. As x

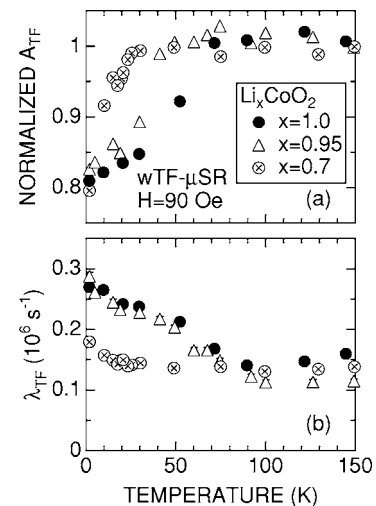


FIG. 6. Comparison of (a) normalized $A_{TF}[=A_{TF}(T)/A_{TF}(300\text{ K})]$ and (b) λ_{TF} as a function of T for the three Li_xCoO_2 samples with $x=1.0, 0.95,$ and 0.7 .

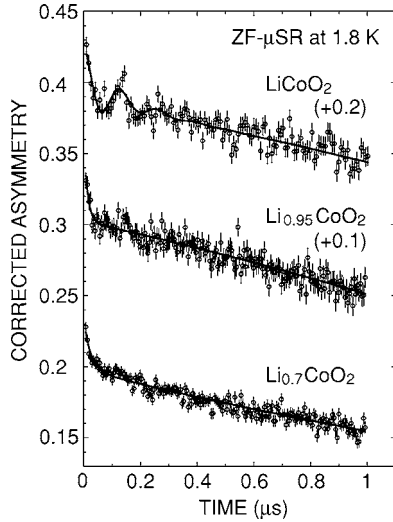


FIG. 7. ZF- μ^+ SR time spectra at 1.8 K for the three Li_xCoO_2 samples with $x=1, 0.95,$ and 0.7 in the time domain below $1 \mu\text{s}$. Only in the top spectrum for LiCoO_2 , a first minimum around 70 ns and a first maximum around 130 ns are clearly seen. The top two spectra are each shifted upwards by 0.1 for clarity of the display.

decreases from 1.0 to 0.7, the onset transition temperature T_c^{on} decreases $\sim 65, 50,$ and 25 K with decreasing x , while the values of N_{AF} are all around 0.8 at 1.8 K, i.e., the volume fraction of the magnetic phase is independent of x .

C. ZF- μ^+ SR

Figures 7 and 8 show ZF- μ^+ SR time spectrum at 1.8 K for the three samples of Li_xCoO_2 ($x=1, 0.95,$ and 0.7). The three spectra exhibit a clear fast relaxation in the time domain below ~ 50 ns (Fig. 7) caused by Co $3d$ spins, although the main signal shows a slow relaxation with a minimum at around $4\text{--}6 \mu\text{s}$ (Fig. 8) due to nuclear moments. In other

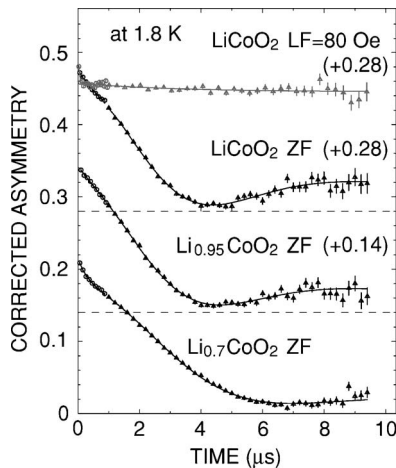


FIG. 8. ZF- and LF- μ^+ SR time spectra at 1.8 K for the three Li_xCoO_2 samples with $x=1, 0.95,$ and 0.7 at 1.8 K in the time domain below $10 \mu\text{s}$. The top LF spectrum for LiCoO_2 indicates the static nature of field distribution in the sample. The spectra are each shifted upwards by 0.14 for clarity of the display.

words, the ZF spectra indicate that the three samples are almost paramagnetic even at 1.8 K, while a small fraction of them enters into a magnetic phase, as well as the wTF- μ^+ SR measurement [see Fig. 6(a)].

In the top spectrum of Fig. 7, a first minimum around 70 ns and a first maximum around 130 ns are clearly seen as a strongly damped cosine oscillation, indicating a formation of quasistatic antiferromagnetic (AF) internal fields in LiCoO_2 . However, the oscillation is also well reproduced by 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.^{24,26,27} We therefore cannot refuse the possibility of an IC-SDW order in the sample.

The full spectrum was fitted using a combination of the following three signals: an exponential relaxing cosine oscillation, a dynamic Gaussian Kubo-Toyabe function $G^{\text{DGKT}}(t, \Delta, \nu)$ (for the signal from other muon sites experiencing fluctuating disordered magnetic fields due to nuclear moments), and an exponential relaxation from fluctuations of the longitudinal components

$$A_0 P(t) = A_{\text{AF}} \cos(\omega_{\text{AF}} t + \phi) e^{-\lambda_{\text{AF}} t} + A_{\text{KT}} G^{\text{DGKT}}(t, \Delta, \nu) + A_x e^{-\lambda_x t}, \quad (3)$$

where A_0 is the empirical maximum muon decay asymmetry, $A_{\text{AF}}, A_{\text{KT}},$ and A_x are the asymmetries associated with the three signals, λ_{AF} and λ_x are their relaxation rate, Δ is the static width of the local frequencies at the disordered sites, and ν is the field fluctuation rate. When $\nu=0$, $G^{\text{DGKT}}(t, \Delta, \nu)$ is the static Gaussian Kubo-Toyabe function $G_{zz}^{\text{KT}}(t, \Delta)$ given by

$$G_{zz}^{\text{KT}}(t, \Delta) = \frac{1}{3} + \frac{2}{3} (1 - \Delta^2 t^2) e^{-\Delta^2 t^2 / 2}. \quad (4)$$

The longitudinal field (LF) spectrum with $H=80$ Oe shows that such relaxation is mainly caused by a quasistatic but disordered weak field distribution in the sample (see the top spectrum in Fig. 8), implying that $\nu \sim 0$. This is because the applied LF competes with the internal random field distribution and aligns the muon spins in its original direction. As a result, if we ignore the fast relaxed component due to the AF field, the LF spectrum seems to be almost independent of time. This also suggests that the A_x signal is likely to be induced by a static random field caused by Co spins. In order to further elucidate the nature of the A_x signal, more precise work is needed, in particular, using a single crystal sample to eliminate the effect of randomly oriented grains.

Figures 9(a)–9(e) show the temperature dependences of (a) f_{AF} , (b) λ_{AF} , (c) λ_x , (d) $A_{\text{AF}}, A_{\text{KT}},$ and A_x , and (e) Δ and ν for the ($x=1.0$) LiCoO_2 sample. The muon precession frequency (f_{AF}) in the local magnetic field H_{int} due to the AF is given by

$$\omega_\mu \equiv 2\pi f_{\text{AF}} = \gamma_\mu H_{\text{int}}, \quad (5)$$

where γ_μ is muon gyromagnetic ratio. As T increases from 1.8 K, f_{AF} is almost independent of T up to ~ 25 K, and then, abruptly decreases towards 0 with further increasing T . The change around 25 K is too steep for the prediction in order parameter of the two-dimensional Ising model for the AF

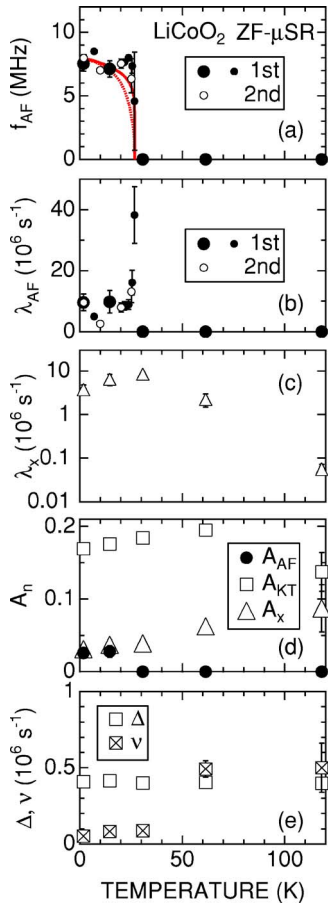


FIG. 9. (Color online) Temperature dependences of (a) f_{AF} , (b) λ_{AF} (c) λ_x , (d) A_{AF} , A_{KT} , and A_x , and (e) Δ and ν for the LiCoO_2 sample. The data were obtained by fitting the ZF- μ^+ SR spectra with Eq. (3). The solid line in (a) represents the temperature dependence of order parameter of the two-dimensional Ising model and broken line the BCS gap energy. Small solid circles in (a) and (b) were obtained from the ZF spectra measured in the time domain below 3 μs , to know the change in f_{AF} in detail. Small open circles in (a) and (b) are the data obtained for the samples from the other source.

state²⁸ or the BCS gap energy for the SDW state,²⁹ in contrast to the $f_{SDW}(T)$ curve for Na_xCoO_2 , which is well explained by BCS.^{17,18} Such abrupt change in the order parameter indicates a transition at ~ 30 K ($=T_N$). Considering a

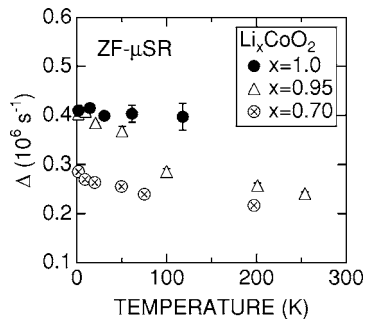


FIG. 10. Temperature dependences of Δ for the three Li_xCoO_2 samples. The data were obtained by fitting the ZF- μ^+ SR spectra with Eq. (3).

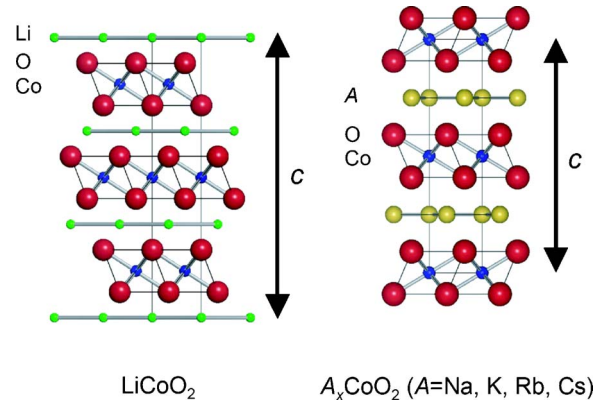


FIG. 11. (Color online) Crystal structures of LiCoO_2 and $A_x\text{CoO}_2$ ($A=\text{Na, K, Rb, Cs}$) in hexagonal unit cell.

small volume fraction of the magnetic phase, it is not surprising that the past measurements failed to detect the AF transition.

In order to confirm the existence of the ordered state in LiCoO_2 , a powder sample from the other source (Kusaka Rare Metal Labs.) was also checked by ZF- μ^+ SR. The result, shown by small open circles in Figs. 9(a) and 9(b), clarifies that the AF ordered state is an intrinsic behavior for LiCoO_2 .

The $\lambda_{AF}(T)$ curve exhibits a sharp maximum at T_N and decreases with decreasing T showing a critical behavior at the transition. Although the AF signal appears below T_N , a slow exponential relaxation signal is observed even at 120 K; that is, λ_x is $\sim 0.1 \times 10^6 \text{ s}^{-1}$, which is consistent with the wTF measurement. The value of λ_x increases with decreasing T down to 30 K, and then decreases with further lowering T . In other words, the $\lambda_x(T)$ curve is similar to the $\lambda_{AF}(T)$ curve below T_N .

The volume fraction (V_F) of the AF phase is estimated as 9% at 1.8 K [$=A_{AF}/(A_{AF}+A_{KT}+A_x)$], and V_F for the phase showing the exponential relaxation signal (A_x) as 8%. The total V_F for the magnetic phases is thus 17% and is in good agreement with the rough estimation from the wTF measurement [see Fig. 6(a)].

For the dynamic Kubo-Toyabe signal, Δ is almost independent of T below 120 K, while the $\nu(T)$ curve shows a critical change between 30 and 60 K. That is, ν is very small (below $0.1 \times 10^6 \text{ s}^{-1}$) below 30 K, as expected from the LF- μSR spectrum, while $\nu \sim 0.5 \times 10^6 \text{ s}^{-1}$ above 60 K, indicating that the internal random field is fluctuating above 60 K. This is consistent with the past μSR work on LiCoO_2 measured in the T range between 460 and 100 K by Dalmás *et al.*,³⁰ i.e., the ZF spectrum was well fitted by a dynamic Kubo-Toyabe function and Δ was almost constant ($0.4 \text{ mT} = 0.36 \times 10^6 \text{ s}^{-1}$) between 100 and 260 K. Above 260 K, Δ decreased linearly with increasing T up to 460 K ($\Delta = 0.28 \text{ mT} = 0.25 \times 10^6 \text{ s}^{-1}$ at 460 K). Finally, Fig. 10 shows the $\Delta(T)$ curve for the Li_xCoO_2 samples with $x=1.0$, 0.95, and 0.70. It is found that Li deficiency reduces Δ in the whole T range measured, suggesting that Li nuclear magnetic moments play a significant role for determining Δ .

IV. DISCUSSION

A. Origin of magnetism in LiCoO₂

The past χ measurements, XPS analysis and band-structural calculations indicate that Co³⁺ ions are in a low spin state (t_{2g}^6) with $S=0$ at ambient temperature.^{11–13} We therefore propose the following two hypothesis, in order to explain the experimental results, in particular, the appearance of magnetism below 60 K in LiCoO₂.

(1) *Charge disproportionation.* Although Co ions are surrounded by six O²⁻ ions to form CoO₆ octahedra, the valence state of Co ions would still be strongly affected by the nearest neighboring Li ions. The Co valence is therefore considered to be partially fluctuating as $2\text{Co}^{3+} \rightarrow \text{Co}^{2+} + \text{Co}^{4+}$ according to thermal vibration and/or self diffusion of Li ions. Past works on rocksalt-type CoO (Refs. 31 and 32) suggest that Co²⁺ ions are in a high spin state with $S=3/2(t_{2g}^5 e_g^2)$, whereas Co⁴⁺ in a low spin state with $S=1/2(t_{2g}^5)$ at low T . Both the different spin state and orbital symmetry (t_{2g} and e_g) and coexisting Co³⁺ ions with $S=0$ naturally induces wide distribution of the magnetic field at the μ^+ sites, which would be a reason for strong damping of the cosine oscillation (see Fig. 7).

For Li-deficient samples, such deficiency itself stabilize both Co³⁺ and Co⁴⁺ states in order to maintain charge neutrality. Since the Li deficiency also increases the average valence of Co ions, Co²⁺ ions are unlikely to exist in the sample.

(2) *Spin state transition.* Czyżyk *et al.* reported that the gap energy, which corresponds to the splitting between t_{2g} and e_g Co d states ($10D_q$), was calculated to be 1.2 eV by LDA,¹³ whereas it was measured as 2.7 ± 0.3 eV by XPS at ambient T .¹² In spite of the relatively large gap energy reported, the present work suggests that the spin state of Co⁴⁺ ions changes around 170 K. The existence of spin state transitions were also reported for the other thermoelectric layered cobaltites; such as, Na_{*x*}CoO₂,³³ (Na,Ca)_{*x*}CoO₂,³⁴ and [Ca₂CoO₃]_{0.62}[CoO₂].^{6,21,22}

On the contrary, the small $10D_q$, which induces the spin state transition at finite T , is considered to be an essential factor for explaining large thermopowers (II) in layered cobaltites.³⁵ Actually, the threefold degenerate t_{2g} Co d states are further split in the rhombohedral crystal field (due to a rhombohedral distortion of CoO₆ octahedra in the CoO₂ plane) into a nondegenerate a_{1g} and doubly degenerate e'_g states. As a result, the spin state transition is thought to be favored in the layered cobaltites. Since the split between a_{1g} and e'_g depends on the rhombohedral distortion of CoO₆,³⁶ a spin state of Co³⁺ in LiCoO₂ would vary from a low-spin state (t_{2g}^6) to an intermediate-spin state ($t_{2g}^5 e_g^1 = e'_g{}^4 a_{1g}^1 e'_g$) at low T without a structural phase transition.

(3) *Surface magnetism.* Since we used polycrystalline samples, μ^+ SR provides information concerning not only inside but also surface of particles. There is therefore the possibility that only the surface layer would be magnetic, while the rest (inside) nonmagnetic. This is because the change (decrease) in oxygen-coordination number at surface Co³⁺ ions could stabilize higher spin states ($S=1$ or $S=2$), as recently proposed for LaCoO₃.³⁷ Also, charge disproportion-

ation mentioned above would be favored at surface, to minimize surface energy.

In order to elucidate the effect of surface on magnetism, μ^+ SR experiments on single crystals are desirable, although large single crystals are currently unavailable; i.e., the maximum size of crystals grown by a flux technique is about $0.15 \times 0.15 \times 0.01$ mm³.³⁸ It is thus not impossible but very difficult to measure μ^+ SR spectra for LiCoO₂ crystals, at present.

First two hypotheses generate t_{2g} holes which play a significant role in the magnetic and transport properties of the layered cobaltites. Here we wish to comment on a dome-shaped magnetic phase diagram in the layered cobaltites, proposed by us.^{17,18} In order to determine the diagram of Na_{*x*}CoO₂, we used the past result that LiCoO₂ is a paramagnet down to the lowest T measured. A magnetic transition is however observed in LiCoO₂ below 65 K. This suggests that similar behavior would be detected in NaCoO₂. Therefore the dome-shaped phase diagram of Na_{*x*}CoO₂ should be further investigated for $0.9 \leq x \leq 1.0$.

B. Magnitude of internal magnetic field

Since the AF states are induced by the competition between AF correlation and geometrical frustration in the CoO₂ 2DTL,^{39–41} the nature of the ordered state in LiCoO₂ is considered to be essentially the same as in Na_{*x*}CoO₂, whose internal magnetic field in the ordered state, corresponded to a frequency $f_\mu(0 \text{ K}) \sim 3$ MHz. Assuming that the μ^+ s in A_{*x*}CoO₂ ($A=\text{Li}$ and Na) locate in the vacant sites in the A plane, $f_\mu(0 \text{ K})$ should depend on the distance $d_{A-\text{Co}}$ between the Li/Na layers and CoO₂ planes. The ratio of $d_{\text{Li-Co}}/d_{\text{Na-Co}}$ is about 0.86, although the c -axis length of the hexagonal unit cell for LiCoO₂ (=14.05 Å) (Ref. 1) is longer than that for Na_{0.74}CoO₂ (=10.92 Å) (Ref. 42) due to a different crystal symmetry (see Fig. 11). Thus $f_\mu(0 \text{ K})$ at the Li site would be roughly $\geq \sim 5$ MHz, because the dipolar field is proportional to d^{-3} . This is roughly comparable to the experimental result [$f_\mu(0 \text{ K}) \sim 8$ MHz].

This also leads to estimates the internal fields expected in the other A_{*x*}CoO₂ with $A=\text{K}$, Rb and Cs . The c -axis length of A_{*x*}CoO₂ is reported as 12.35, 13.04, and 13.98 Å for $A=\text{K}$, Rb , and Cs ,^{43,44} resulting in lower $f_\mu(0 \text{ K}) \sim 2.0$, 1.8, and 1.4 MHz, respectively. Actually, a preliminary μ SR experiment on K_{*x*}CoO₂ supports this prediction, because $f_\mu(0 \text{ K}) \sim 1.6$ MHz for K_{0.4}CoO₂.⁴⁵

V. SUMMARY

In order to elucidate the magnetism in layered cobaltites, μ^+ SR spectroscopy and bulk susceptibility (χ) measurements were performed on polycrystalline samples of Li_{*x*}CoO₂ with $x=1.0$, 0.95, and 0.70 in the temperature range between 300 and 1.8 K. Although all past bulk probes experiments suggested the absence of magnetic transitions at low T , weak transverse field (wTF-) μ SR measurements clearly show the appearance of magnetism below ~ 65 K ($=T_c^{\text{on}}$) even for the sample with $x=1.0$. The volume fraction of the magnetic

phase at 1.8 K is estimated as 20% for LiCoO₂. This means that the observed magnetism is not induced by impurities but is an intrinsic behavior. The magnetism at low T is probably induced by either a charge disproportionation ($2\text{Co}^{3+} \rightarrow \text{Co}^{2+} + \text{Co}^{4+}$), a spin state transition ($t_{2g}^6 \rightarrow t_{2g}^5 e_g^1$) of Co³⁺, or an appearance of magnetic Co³⁺ at surface. The ZF spectra of LiCoO₂ consists of mainly a Kubo-Toyabe signal (for fluctuating random field) plus a small amount of rapidly relaxing signal (for fluctuating field) and an oscillating component due to an antiferromagnetic or an incommensurate spin density wave order.

For Li-deficient Li_xCoO₂ samples, T_c^{on} decreases with decreasing x ; i.e., 50 K for $x=0.95$ and 25 K for $x=0.7$. The volume fraction of the magnetic phase is however almost independent of x and is estimated as 80% at 1.8 K, but no clear oscillations were seen in the zero field spectrum. Fur-

thermore, Li-deficient samples are found to exhibit a spin state transition at ~ 170 K.

ACKNOWLEDGMENTS

We thank Dr. B. Hitti, Dr. S. R. Kreitzman, and Dr. D. J. Arseneau of TRIUMF for help with the μ^+ SR experiments. We also acknowledge Mr. T. Takami of Nagoya University and Mr. P. L. Russo of Columbia University for their help in the measurements and Mr. Y. Kawai of Toyota CRDL for his ICP analysis. This work was partially supported at UBC by the Canadian Institute for Advanced Research, the Natural Sciences and Engineering Research Council of Canada, and at TRIUMF by the National Research Council of Canada.

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