Magnetic Phase Diagram of Layered Cobalt Dioxide Li_xCoO_2

K. Mukai,¹ Y. Ikeda,¹ H. Nozaki,¹ J. Sugiyama,^{1,*} K. Nishiyama,² D. Andreica,³ A. Amato,³ P. L. Russo,⁴ E. J. Ansaldo,⁴ J. H. Brewer,^{4,5} K. H. Chow,⁶ K. Ariyoshi,⁷ and T. Ohzuku⁷

¹*Toyota Central Research and Development Labs, Inc., Nagakute, Aichi 480-1192, Japan*

²*Institute of Materials Structure Science, High Energy Accelerator Research Organization, Tsukuba, Ibaraki 305-0801, Japan*

³*Laboratory for Muon-Spin Spectroscopy, Paul Scherrer Institut, Villigen PSI, Switzerland*

⁴*TRIUMF, 4004 Wesbrook Mall, Vancouver, BC, V6T 2A3 Canada*

⁵*Department of Physics and Astronomy, University of British Columbia, Vancouver, BC, V6T 1Z1 Canada*

⁶*Department of Physics, University of Alberta, Edmonton, AB, T6G 2G7 Canada*

⁷*Department of Applied Chemistry, Graduate School of Engineering, Osaka City University, Osaka 558-8585, Japan*

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The magnetism of Li_xCoO_2 (LCO), which has a similar structure to Na_xCoO_2 (NCO), has been investigated by muon-spin spectroscopy and susceptibility measurements using samples with $x = 0.1$ –1 prepared by an electrochemical reaction. In the x range below 0.75, LCO was found to be Pauli paramagnetic down to 1.8 K, suggesting an intermediate- or weak-coupling regime, although disordered local moments, with volume fractions below $\sim 20\%$, appear at low T for LCO with $x \geq 0.5$. The phase diagram and interactions of LCO are thus strikingly different from NCO, while the differences cannot be explained simply by structural differences between the two systems.

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The Na_xCoO_2 (NCO) system, in which Co ions form a two-dimensional triangular lattice, exhibits a variety of fascinating physical phenomena: unconventional transport properties for NCO with $x \sim 0.7$ [1], long-range antiferromagnetic (AF) order with $T_N \sim 22$ K for $x \geq 0.75$ [2], two successive transitions ($T_N = 87$ K and $T_{\text{CO}} = 53$ K, where T_{CO} symbolizes the charge-order transition) in $x = 0.5$ [3], and superconductivity with $T_c = 5$ K for $x = 0.35$ and absorbed water [4]. The essential physics in this system can be described within the Hubbard model [5] together with the additional effect of interplane coupling. Hence, two major parameters for determining the dynamics on the CoO_2 plane are the on-site repulsion U and the nearest neighboring hopping t .

In order to better understand the nature of NCO, the phase diagram should be experimentally clarified as a function of x since a subsequent comparison with theoretical considerations enables one to determine the ratio between U and t . The two doping extremes, that is, NCO with $x = 0$ and 1, are expected to provide crucial information on the U/t . However, both compounds are currently unavailable. The lowest x achievable is only ~ 0.3 due to limitations in the soft chemistry technique used to synthesize such materials [6]. Furthermore, NCO with $x \geq 0.95$ is very unstable in air because of the reaction between excess Na and water. As a result of the unavailability of suitable materials, the overall picture of the magnetism on the CoO_2 plane is still confusing.

By contrast, the related material Li_xCoO_2 (LCO) with $x = 1$, which belongs to the rhombohedral system (space group $R\bar{3}m$) with the layered $\alpha\text{-NaFeO}_2$ structure, i.e., similar to $\gamma\text{-NCO}$, is stable in air. Furthermore, Li ions are easily deintercalated by electrochemical reaction down

to $x \sim 0.1$; in fact, this is the principle behind the operation of Li-ion batteries [7]. The majority of previous research into LCO have focused primarily on their structural and electrochemical properties, with the aim of understanding their influence on the charge or discharge characteristics of Li-ion batteries [8,9]. Indeed, the structure of $\text{Li}_{1-x}\text{CoO}_2$ was already analyzed using a synchrotron x-ray source [10], but its magnetic and transport properties are still not fully understood [11,12]. Moreover, no systematic studies of the magnetic nature of LCO over a wide range of x have been reported.

Recently, we carried out a positive muon-spin spectroscopy ($\mu^+\text{SR}$) experiment on LCO with $1 \geq x \geq 0.7$ [13]. Following up on this work, we have performed both $\mu^+\text{SR}$ and susceptibility (χ) measurements on the LCO samples with $1 \geq x \geq 0.1$ prepared by electrochemical reaction. Here, we demonstrate the nearly full phase diagram of LCO and clarify the absence of magnetism in the x range below 0.5. In particular, a slow relaxation due to nuclear magnetic moments of ^{59}Co and ^7Li observed in the zero-field (ZF) $\mu^+\text{SR}$ spectrum together with the almost T -independent $\chi(T)$ curve predict metallic behavior of LCO with $x \leq 0.1$, in contrast to the theoretical prediction that the Na_0CoO_2 phase is a Mott insulator [14].

A powder sample of LiCoO_2 was prepared at Osaka City University by a solid-state reaction technique using reagent grade $\text{LiOH} \cdot \text{H}_2\text{O}$ and CoCO_3 powders as starting materials. A mixture of the two powders was heated at 900°C for 12 h in air. A powder x-ray diffraction analysis showed that the LiCoO_2 sample was single phase with a rhombohedral system of space group $R\bar{3}m$ ($a_H = 0.2814$ and $c_H = 1.4049$ nm in hexagonal setting). The Li-deficient samples were prepared by an electrochemical reaction

using Li | LiPF₆-ethylene carbonate-diethyl carbonate | LiCoO₂ cells. The LiCoO₂ powder was pressed into a disk with 15 mm diameter and 0.4 mm thickness, and the disk was used as a positive electrode. Figure 1 shows the cell voltage (E) as a function of x in LCO; the curve is usually called the charge (Li⁺-deintercalation) curve. Arrows show the samples prepared for the present experiments. Their compositions were checked by an induction coupled plasma (ICP) analysis. Note that the relationship between the crystal structure and E , and therefore x , has been well established by both *in situ* and *ex situ* x-ray diffraction studies [8,9,15,16]. Hence, it is widely accepted that E (and/or x) is a unique indicator of the quality of the structural phase of the sample.

The LCO disk was removed from the cell in a glovebox just before the μ^+ SR measurement, and then it was packed into a sealed powder cell. In order to know the possible change in the Li-deficient samples during the μ^+ SR measurement, the sample was returned to the cell after the measurement to check its E (versus Li electrode). The μ^+ SR spectra were measured at KEK, PSI, and TRIUMF. The experimental techniques were described elsewhere [17]. χ was measured using a SQUID magnetometer (MPMS, Quantum Design) in the T range between 300 and 5 K under magnetic field $H = 10$ kOe.

Figure 2(a) shows the T dependence of χ for the samples with $x \geq 0.1$. For LiCoO₂, the $\chi(T)$ curve increases very slowly with decreasing T down to ~ 50 K and then increases more rapidly with increasing slope ($d\chi/dT$), in-

FIG. 1 (color online). The Li_xCoO₂-vs-Li cell voltage (E) as a function of x . The positive electrode usually consists of LiCoO₂, binder, and graphite to increase density and conductivity. However, in order to avoid μ^+ SR signals from the binder and graphite, the electrode for this experiment was made of only LiCoO₂ powder. The current density for charging is thus relatively low (0.11 mA/cm²) compared to a typical case (1 mA/cm²). The slow charging also provides one-to-one correspondence between changes in structure and E . Arrows show the composition of the samples prepared for the μ^+ SR experiment. The inset table shows the nominal composition and analyzed result. R_i symbolizes the rhombohedral phase, M the monoclinic phase, and H the hexagonal phase.

dicating the appearance of localized moments. For LCO with $x = 0.75$, χ increases linearly but slowly down to ~ 175 K ($= T_m$) then suddenly decreases and reaches a broad minimum at ~ 100 K, and finally χ increases with increasing slope with further decreasing T . For LCO with $0.52 \geq x \geq 0.49$, the T dependence of χ is very similar to that for Li_{0.75}CoO₂, although the $\chi(T)$ curve is almost T independent above T_m , and T_m slightly lowers with decreasing x . For LCO with $x \leq 0.44$, T_m disappears from the $\chi(T)$ curve, and it also exhibits a Pauli-paramagnetic (PM) behavior down to ~ 100 K for $x = 0.44$ and down to ~ 50 K for $x = 0.1$. Below these T_s , the $\chi(T)$ curve shows a small increase due to localized moments.

The T -independent part of χ (χ_0) is found to increase monotonically with decreasing x , as in the case for NCO [18] [see Fig. 2(b)]. Considering the fact that LiCoO₂ is an insulator but LCO with $0.96 \geq x \geq 0.55$ are metallic [8], we assume that $\chi_0(x = 1) = \chi^{\text{dia}} + \chi^{\text{orb}}$, where χ^{dia} and

FIG. 2 (color online). (a) T dependence of χ for LCO with $x = 1, 3/4, 0.52, 1/2, 0.49, 0.44, 0.33$, and 0.1 . Each $\chi(T)$ curve is offset by 0.0005 for clarity of the display. χ was measured in field-cooling (FC) mode with $H = 10$ kOe. The composition of the samples determined by an induction coupled plasma analysis was (from bottom to top) 1.02, 0.76, 0.52, 0.51, 0.50, 0.46, 0.29, and 0.11, respectively. (b) The relationship between x and χ_0 , where χ_0 was estimated by fitting the data below T_m using $\chi = \chi_0 + C/(T - \Theta)$ [see solid lines in (a)].

χ^{orb} are the diamagnetic and the orbital contribution, respectively, and the two contributions are independent of x . The increase in χ_0 with x is thus attributed to a Pauli-PM component (χ^{Pauli}). The density of states at the Fermi level [$D(E_F)$] is estimated as 4.6, 4.8, and 7.7 states/eV for $x = 0.7, 0.5$, and 0.1 , respectively, using $\chi^{\text{Pauli}} = 2\mu_B^2 D(E_F)$. Comparing with the result of the LSDA + U calculation on NCO [19], we obtain the Stoner enhancement factor (S) as 9.2, 9.6, and 6.4 for $x = 0.7, 0.5$, and 0.1 . These values are comparable to $S(=5)$ evaluated for NCO with $x = 0$ by the LDA + U calculation [20].

Next, we carried out ZF- μ^+ SR measurements in order to know the microscopic magnetism of LCO, because

FIG. 3 (color online). (a) ZF- μ^+ SR spectrum for Li_xCoO_2 with $x = 1, 0.95, 3/4, 1/2, 1/3$, and 0.1 at 1.8 K, and (b) magnification of (a) for $x = 1, 1/2$, and 0.1 in the time domain up to $1 \mu\text{s}$. In (a), each spectrum is offset by 0.5 for clarity of the display, whereas 0.1 in (b). The solid lines represent the fit result using Eq. (1).

ZF- μ^+ SR is sensitive to weak local magnetic [dis]order in samples exhibiting quasistatic PM moments. Figure 3 shows the ZF- μ^+ SR spectra for LCO with $x \geq 0.1$ at the lowest T measured. For LiCoO_2 , the ZF spectrum exhibits mainly a slow relaxation with a broad minimum at $\sim 4 \mu\text{s}$, which is a typical behavior of a Kubo-Toyabe (KT) signal due to randomly oriented nuclear magnetic moments, in this case ^7Li and ^{59}Co . A fast relaxing component, however, appears in the early time domain [see Fig. 3(b)] due to the formation of the static AF ordered phase below 30 K, while its volume fraction (V_F) = $14 \pm 8\%$, as in the past experiment ($9 \pm 3\%$) [13]. The origin of the magnetism and/or the AF phase is thought to be one of the following three scenarios described in Ref. [13], that is, a spontaneous partial charge disproportionation, a partial spin-state transition, or surface magnetism.

For LCO with $x < 1$, all the spectra show a similar slow relaxing behavior except for the $x = 1/2$ sample which also exhibits a fast relaxing component with $V_F = 23\%$. Such component, however, disappears above 20 K. The time at which the spectrum exhibits the minimum increases with decreasing x , being consistent with the decrease in ^7Li , which mainly contributes to the slow relaxation. In addition, the origin of the transition at $T_m \sim 175$ K is found to be not magnetic ordering but either charge ordering or a change in spin state.

The spectrum was hence fitted by a combination of a dynamic KT signal (G^{DGKT}) [17] and a fast relaxing non-oscillatory signal and only for LiCoO_2 , an additional exponentially relaxing oscillatory signal below 30 K.

FIG. 4 (color online). (a) Field distribution width (Δ) and field fluctuation rate (ν) and (b) exponential relaxation rate (λ_{fast}) and normalized two asymmetries (A_{fast} and A_{AF}) as a function of x in Li_xCoO_2 . In (a), circles represent the data obtained at PSI at 1.8 K, triangles at KEK at 6 K, and diamonds at TRIUMF at 1.8 K. The solid line shows the calculated relationship between Δ and x , taking into account only ^7Li and ^{59}Co moments. In (b), solid symbols show the present result, while open symbols the past one in Ref. [13].

FIG. 5 (color online). Magnetic phases in Li_xCoO_2 . T_{CO} indicates a charge-ordering transition temperature, T_{SS} a spin-state transition temperature, and T_N^{on} the temperature below which a short-range AF order (SRO) appears.

$$A_0 P_{\text{ZF}}(t) = A_{\text{KT}} G^{\text{DGKT}}(t, \Delta, \nu) + A_{\text{fast}} \exp(-\lambda_{\text{fast}} t) + A_{\text{AF}} \cos(\omega t + \phi) \exp(-\lambda_{\text{AF}} t), \quad (1)$$

where A_0 is the maximum muon decay asymmetry, A_{KT} , A_{fast} and A_{AF} are the asymmetries associated with the three signals, λ_{fast} and λ_{AF} are their relaxation rates, Δ is the static width of the local fields at the disordered sites, and ν is the field fluctuation rate.

Figure 4 shows the x dependence of Δ , ν , λ_{fast} , and normalized A_{fast} and A_{AF} . As x decreases from 1, Δ decreases rapidly down at $x = 0.95$, then decreases slowly and almost linearly with further lowering x and reaches about half of $\Delta(x = 1)$ at $x = 0.1$. According to electrostatic potential calculations, μ^+ s locate in the vicinity of O^{2-} ions in LiCoO_2 , whereas they are situated in the vacant Li site in Li_0CoO_2 . Calculations assuming that Δ is due to the sum of dipole fields of randomly oriented ^7Li and ^{59}Co at the relevant muon site are shown in Fig. 4; there is reasonable agreement with the experimental $\Delta(x)$. The field fluctuation rate (ν) is almost 1/3 of Δ in the whole x range. Note that the magnitudes of Δ and ν are roughly comparable to those for NCO [18]. Since the present result is very consistent with the past one using the samples from the different source [see Fig. 4(b)], the appearance of the AF phase and localized moments is confirmed to be an intrinsic behavior of LCO.

Finally, we draw the schematic phase diagram of LCO with $1 \geq x \geq 0.1$ using the results of the present χ and $\mu^+\text{SR}$ measurements together with past ones [13] (see Fig. 5). Static AF order is observed only for LiCoO_2 below 30 K, but V_F of the AF phase is $\sim 10\%$. The phase diagram is thus very different from that for NCO, in which static AF order appears for $x \sim 0.5$ and ≥ 0.75 . Although the ar-

range of the Co ions along the c axis in LCO is different from that in NCO, the stacking sequence along the c axis was reported to be unimportant for determining the formation of the AF order in $\text{Na}_{0.5}\text{CoO}_2$ [21] and $\text{K}_{0.5}\text{CoO}_2$ [22]. The absence of magnetic order in LCO with $x < 1$ is thus currently not explained simply by the change in structural parameters. The lack of magnetism for LCO with $x < 0.5$ together with the Pauli-PM-like $\chi(T)$ curve also suggests metallic behavior for LCO with $x = 0$, being consistent with the ir measurement on CoO_2 [11]. This therefore indicates that the LCO system is not a strongly coupled electron system ($U/t > \sim 10$) but rather an intermediate or a weakly coupled one [23].

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*e0589@mosk.tytlabs.co.jp

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