Spin fluctuations above 100 K in stoichiometric LiCoO₂

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Abstract. Although stoichiometric lithium cobalt dioxide LiCoO₂ (ST-LCO) is the most common positive electrode material for Li-ion batteries, the magnetic nature of ST-LCO is still not fully understood. Therefore, we measured susceptibility (χ), electron paramagnetic resonance (EPR), and µSR for ST-LCO, particularly above 100 K. The temperature dependence of χ shows a Pauli paramagnetic behavior, supporting the previous conclusion that Co³⁺ ions are in a low-spin state with $S = 0$ ($t_{2g}^6$). However, the EPR and µSR measurements reveal a "dynamical" magnetic phase in ST-LCO above 100 K. Because the volume fraction of this magnetic phase reaches about 50% at 300 K, the appearance of the magnetic phase is not caused by impurities and/or muonium formation but is an intrinsic characteristic of ST-LCO. By considering the time windows of the three measurement techniques used in this study, we conclude that the origin of the dynamical magnetism is most likely spin fluctuations of the Co ions.

1. Introduction

Since the discovery that Li⁺ ions are reversibly extracted and inserted by an electrochemical reaction [1], lithium cobalt oxide LiCoO₂ (LCO) has been widely used as a positive electrode material for lithium-ion batteries (LIBs). Stoichiometric LCO (ST-LCO) has a layered structure with the $R\bar{3}m$ space group. The Li⁺ and Co³⁺ ions occupy the octahedral 3b and 3a sites, respectively, in the cubic close-packed array of O²⁻ ions (Fig. 1). In addition to LIB applications, ST-LCO has received much attention in the field of condensed matter physics because the Co ions form a two-dimensional triangular lattice, on which geometrical frustration often induces interesting magnetic behavior.

ST-LCO exhibits complicated magnetic properties as described by Chernova et al [2]. For instance, although susceptibility (χ) measurements indicate that the Co³⁺ ions are in a nonmagnetic low-spin (LS) state with $S = 0$ ($t_{2g}^6$) [3], µSR measurements clarify the complex magnetic nature below 60 K. That is, as temperature (T) decreases from 100 K, localized
magnetic moments appear below $\sim$60 K, and then, an antiferromagnetic (AF) ordered phase appears below 30 K. But, the volume fraction of such AF phase is $\sim$10% [4, 5]. Since ST-LCO is very stable in air, such magnetic properties are most unlikely to be caused by the degradation of a sample, but are an intrinsic behavior of ST-LCO. Furthermore, it was reported that, even for a large single crystal sample, $\chi$ rapidly increases with decreasing $T$ particularly below 50 K [6]. This also supports that the appearance of localized moments at low $T$ is an intrinsic feature for LiCoO$_2$. This is quite different from NaCoO$_2$ [7], which is an isostructural compound of ST-LCO. In this paper, we report another unique magnetic feature of ST-LCO, i.e., “dynamical magnetism” at $100 \, \text{K} \leq T \leq 500 \, \text{K}$ clarified by electron paramagnetic resonance (EPR) and $\mu$SR measurements up to 500 K.

Figure 1. Crystal structure of stoichiometric LiCoO$_2$.

Figure 2. (a) Rietveld analysis and (b) $T$ dependence of $\chi$ for stoichiometric LiCoO$_2$ sample.

2. Synthesis and Characterization

A polycrystalline sample of ST-LCO was prepared by the solid-state reaction technique, as reported previously [8, 9]. The reaction mixture of LiOH·H$_2$O and Co$_3$O$_4$ was heated at 1173 K for 12 h in air. A Rietveld analysis of the powder x-ray diffraction (XRD) pattern of the sample indicated a single-phase of the $R\bar{3}m$ space group with the lattice parameters of $a_h = 2.8135(4) \, \text{Å}$ and $c_h = 14.042(1) \, \text{Å}$ [Fig. 2(a)]. Impurities, such as CoO and Co$_3$O$_4$, were not detected in the XRD pattern.

Susceptibility ($\chi$) was measured in the $T$ range between 5 and 400 K using a field-cooling (FC) mode with $H = 10 \, \text{kOe}$ [Fig. 2(b)]. As $T$ decreases from 400 K, $\chi$ is almost $T$-independent down to $\sim$100 K, and then rapidly increases with further decreasing $T$. By fitting the $\chi(T)$ curve below 100 K with a Curie-Weiss formula [Fig. 2(b)], we obtain that $\chi_0 = 112(2) \times 10^{-6} \, \text{emu}\cdot\text{mol}^{-1}$, where $\chi_0$ is the $T$-independent $\chi$ and consists of a diamagnetic ($\chi_{\text{dia}}$) and an orbital ($\chi_{\text{orb}}$) contribution. Since $\chi_0$ for the ST-LCO sample is comparable to that for NaCoO$_2$ ($\chi_{\text{orb}}$
$= 150 \times 10^{-6}$ emu·mol$^{-1}$) [7], Co$^{3+}$ ions in ST-LCO are assigned in a nonmagnetic LS state with $S = 0$ ($t^6_6$), as reported previously [3].

EPR measurements were made in the $T$ range from 100 to 400 K by using an ESP300E spectrometer (Bruker BioSpin K. K.). The $\mu$SR spectra was measured in the $T$ range from 2 to 500 K at both $S\mu S$ of the Paul Scherrer Institut and ISIS of the Rutherford Appleton Laboratory. Details of the experimental setup for the EPR and $\mu$SR measurements are described elsewhere [8].

3. Results and discussion

Figure 3 shows the EPR spectra for the ST-LCO sample at 100 and 300 K. According to the $\chi$ measurements, the ST-LCO sample was predicted to be EPR-inactive because of the lack of unpaired electrons. However, an EPR signal is clearly observed at 100 K. The $g$ value and the EPR line width between the peaks ($\Delta H_{pp}$) is 2.12(1) and 42(1) Oe, respectively. The EPR signal is more notable at 300 K, although the values of $g$ and $\Delta H_{pp}$ are $T$ independent. Note that Co$_3$O$_4$ typically shows a broad EPR signal with $g \sim 5$ at room $T$ [10], whereas CoO has no EPR signal at 300 K [8]. Thus, the EPR signal observed at 100 and 300 K is not caused by the CoO or Co$_3$O$_4$ phases.

To further investigate the magnetism of ST-LCO, $\mu$SR was measured. Figure 4(a) shows the $T$ dependence of the normalized weak-transverse-field asymmetry ($N_{ATF}$) for the ST-LCO sample. The slight decrease in $N_{ATF}$ below $\sim 60$ K is attributed to the appearance of the localized moments before the formation of AF order, which is characteristic of ST-LCO [4, 5]. As $T$ increases from $\sim 100$ K, $N_{ATF}$ decreases almost linearly up to 300 K, then rapidly increases with changing slope ($dN_{ATF}/dT$), and finally reaches $\sim 1$ at 500 K. Because $N_{ATF} = 0.55$ at 300 K, 45 vol% of the sample is found to be in a magnetic phase. Such a large volume fraction is unlikely to be due to impurities such as CoO and Co$_3$O$_4$, because the Rietveld analysis clarified that the ST-LCO sample is single-phase with $R\bar{3}m$ [Fig. 2(a)]. In addition, the $T$ dependence of $N_{ATF}$ clearly excludes the possibility of muonium formation.

To clarify whether the sample contains a static magnetic ordered phase, Figure 4(b) shows the zero-field (ZF) $\mu$SR spectrum at 300 K. Although the asymmetry rapidly decreases in the time domain below $\sim 1 \mu s$, there is no oscillatory signal, which indicates a lack of static magnetic order in the magnetic phase. Thus, we suggest that this phase is a ”dynamical” magnetic phase. The ZF-$\mu$SR spectrum is fit by a combination of a fast-relaxing signal from the dynamical magnetic
phase, a dynamic Gaussian Kubo-Toyabe [11] (DGKT) signal from the nuclear moments of Li and Co in a nonmagnetic phase, and a background (BG) signal mainly from an Ag or Ti in the sample holder:

\[ A_0 P_{ZF}(t) = A_{fast} \exp(-\lambda_{fast}t) + A_{KT}G_{DGKT}(t, \Delta, \nu) + A_{BG}, \]  

(1)

where \( A_{fast}, A_{KT}, \) and \( A_{BG} \) are the asymmetries associated with the three signals, \( \lambda_{fast} \) is the relaxation rate of the dynamical magnetic phase, and \( \Delta \) and \( \nu \) are the field distribution width and the field fluctuation rate, respectively. The values of \( \Delta \) and \( \nu \) were determined by a global fit with ZF and longitudinal field (LF) \( \mu \)SR spectra [Fig. 4(b)]. The \( A_{fast}(T) \) curve shows a maximum (~0.5) at 300 K, and if it is flipped upwards down, such curve is almost equivalent to the \( N_{ATF}(T) \) curve [Fig. 4(a)]. Furthermore, the \( \nu(T) \) curve exhibits a maximum at around 300 K (not shown), which is probably due to a slight displacement of the Li ions, as for LiMn\(_2\)O\(_4\) [12].

As described briefly, not only the AF phase below 30 K, but also the dynamical magnetism at 100 K ≤ \( T \) ≤ 500 K is found to be an intrinsic character of ST-LCO. It should be emphasized again that both phenomena are neither due to impurities, degradation of the sample, nor muonium formation. The discrepancy of magnetic properties obtained with \( \chi \), EPR, and \( \mu \)SR are most likely caused by different time windows among the three techniques. That is, \( \chi \) reflects the static internal magnetic fields (\( H_{int} \)), whereas both EPR and \( \mu \)SR reflect the static and dynamic characteristics of \( H_{int} \) from ~10\(^{10}\) Hz and 10\(^{4}\)–10\(^{12}\) Hz, respectively. Therefore, the hypothesis that the dynamical magnetism in ST-LCO is caused by the spin fluctuation of Co ions is very reasonable.

There are two possible origins for such spin fluctuations. One is a spin-state transition of the Co ions, as for LaCoO\(_3\) [13]. As \( T \) increases from low \( T \), the spin state of the Co ions in

![Figure 4.](image-url) (a) Temperature dependence of normalized weak-transverse-field asymmetry (\( N_{ATF} \)) for ST-LCO sample. (b) Zero-field \( \mu \)SR spectrum for the ST-LCO sample at 300 K. The longitudinal-field \( \mu \)SR spectrum with a magnetic field of 20 G is also shown for comparison.
LaCoO$_3$ changes from an LS state with $S = 0(t_{2g}^6e_g^2)$ to a high-spin (HS) state with $S = 2(t_{2g}^4e_g^2)$ via an intermediate-spin (IS) state with $S = 1(t_{2g}^5e_g^1)$. Thus, a thermally induced spin-state transition from LS $\rightarrow$ IS $\rightarrow$ HS is a possible origin of the spin fluctuation. The other possibility is charge disproportionation of the Co$^{3+}$ ions:

$$2\text{Co}^{3+}(\text{LS}, S = 0) \leftrightarrow \text{Co}^{2+}(\text{LS}, S = 1/2) + \text{Co}^{4+}(\text{LS}, S = 1/2),$$

or

$$2\text{Co}^{3+} \leftrightarrow \text{Co}^{3+\delta} + \text{Co}^{3-\delta}.$$  

Because of thermal activation, both equilibrium reactions progress to the right in the $T$ range from 100 to 300 K, resulting in the formation of magnetic Co ions. However, the $N_{\text{ATF}}(T)$ curve above 300 K suggests the presence of the opposite contribution that shifts the equilibrium to the left side. On the basis of the $\nu(T)$ curve for ST-LCO and delithiated Li$_x$CoO$_2$ [14], Li diffusion could be the origin of this opposite contribution. In other words, in the $T$ range from 100 to 300 K, the CoO$_6$ octahedron would be most likely distorted because of the unusual spin states or charge states. However, at $T > 300$ K, the Li ions start to diffuse between the regular $3b$ site and the interstitial site, which tends to suppress the local distortions of the CoO$_6$ octahedron. As a result, as $T$ increases from 300 K, the nonmagnetic Co$^{3+}$ ions stabilize with $T$, and the volume fraction of the dynamical magnetic phase decreases with $T$.

It would be interesting to compare the LCO result with those for NaCoO$_2$ (NCO). Note that stoichiometric-NCO is very unstable in air, and a Na-deficient phase (Na$_{0.7}$CoO$_2$) is usually obtained by a conventional solid state reaction technique [7]. Since the exact 1:1 ratio between Li and Co is essential for the appearance of the dynamical magnetism in LCO [8], it is not surprising that the Na-deficient NCO does not exhibit a similar magnetic behavior.

In conclusion, we find a thermally induced dynamical magnetic phase in ST-LCO above 100 K, which we attribute to the spin fluctuations of Co ions. To better understand the nature of such spin fluctuations, neutron-scattering experiments with ST-LCO are planned.

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