Physica B 404 (2009) 769–772

Contents lists available at ScienceDirect

Physica B

journal homepage: www.elsevier.com/locate/physb

Annihilation of antiferromagnetic order in $LiCoO_2$ by excess Li

Jun Sugiyama [a,*], Yutaka Ikedo [a], Hiroshi Nozaki [a], Kazuhiko Mukai [a], Daniel Andreica [b], Alex Amato [c], Michel Ménétrier [d], Dany Carlier [d], Claude Delmas [d]

[a] Toyota Central Research and Development Laboratories Inc., Nagakute, Aichi 480-1192, Japan
[b] Faculty of Physics, Babes-Bolyai University, 3400 Cluj-Napoca, Romania
[c] Laboratory for Muon-Spin Spectroscopy, Paul Scherrer Institut, 5232 Villigen PSI, Switzerland
[d] ICMCB, CNRS, Université Bordeaux I, 87 Av. Schweitzer, F 33608 Pessac Cedex, France

ARTICLE INFO

Keywords:
Antiferromagnetic order
$LiCoO_2$
Triangular lattice
Oxygen vacancies

ABSTRACT

In order to elucidate the origin of antiferromagnetic (AF) order below 30 K in $LiCoO_2$, in which all the Co^{3+} ions are in a low-spin state with $S = 0$, the magnetic nature of the Li-excess sample $Li_{1.04}Co_{0.96}O_{1.96}$ was studied by muon-spin spectroscopy in the temperature range between 1.8 and 100 K. Although disordered localized moments appeared below 25 K, static AF order was not detected even at 1.8 K. Moreover, a small amount of excess Li ions (4%) and oxygen vacancies (2%) was found to change ~50% of the sample into a magnetically disordered phase at 1.8 K. The stoichiometric $LiCoO_2$, which was prepared from the same starting materials to those for the Li-excess sample, showed an AF transition at 30 K, while the volume fraction of the AF phase was 10% even at 1.8 K. This therefore excludes the possible role of the excess Li^+ on the formation of static AF order.

1. Introduction

Among several layered cobalt dioxides with the CoO_2 plane, in which Co ions form a two-dimensional triangular lattice, $LiCoO_2$ has attracted much attention, because of its reversible Li^+ deintercalation/intercalation [1]. Indeed, this is the basic principle behind the operation of the Li-ion batteries [2]. Therefore, a huge number of work was performed for investigating its structural and electrochemical properties, although its magnetic nature has been little studied. This is because $LiCoO_2$ was believed to lack magnetic transitions in the whole T range; that is, magnetic susceptibility measurements [3,4], X-ray photoelectron spectroscopic analysis [5] and band-structural calculations [6] confirmed that the Co^{3+} ions are in a low-spin state (t_{2g}^6) with $S = 0$ at ambient T, implying that the low-spin state is the most stable at low T. Nevertheless, our recent μ^+SR experiments on $LiCoO_2$ [7,8] have clearly demonstrated the formation of static antiferromagnetic (AF) order below 30 K ($= T_N$), although the volume fraction of the AF ordered phase is estimated as ~10%. Since the results using the samples from two different sources are in good agreement with that of the first sample, the AF order is thought to be an intrinsic behavior of $LiCoO_2$.

A Li-excess phase (i.e., $Li_{1+x}Co_{1-x}O_{2-x}$) has been recently prepared by a conventional technique [9]. Because of the oxygen vacancies, Co^{3+} ions in an intermediate-spin state with $S = 1(t_{2g}^5 e_g^1)$ are present in square-based pyramids of the Li-excess phase [3]. The AF order at low T would be, thus, explained by the excess Li ions and/or the presence of the CoO_5 pyramids. In order to elucidate the effect of the excess Li^+ ions on the microscopic magnetic nature of $LiCoO_2$, we have measured μ^+SR spectra on both stoichiometric and Li-excess samples down to 1.8 K. As a result, we have found the existence of the AF phase in the stoichiometric samples as reported in the past work and the absence of it in the Li-excess sample. This clearly confirms the origin of the AF order as a spin/charge fluctuation on the triangular lattice of stoichiometric $LiCoO_2$.

2. Experimental

Powder samples of $LiCoO_2$ and $Li_{1.04}Co_{0.96}O_{1.96}$ were prepared at ICMCB-CNRS by a solid-state reaction technique using reagent grade Li_2CO_3 and Co_3O_4 powders as starting materials. In particular, in order to reduce magnetic impurities (such as Ni and/or Fe) in Co_3O_4, a very pure Co_3O_4 powder synthesized from nitrates was used for the preparation. A mixture of Li_2CO_3 and Co_3O_4 was heated at 600 °C for 12 h in a dry-oxygen flow, and then fired at 900 °C for 15 days in a dry-oxygen flow for $LiCoO_2$. For the preparation of the Li excess sample, the 1 h fired sample with nominal Li/Co ratio of 1.2 was washed by water to remove unreacted Li_2CO_3. The washed powder was then mixed with a Li_2CO_3 powder with 1:1 mass ratio, and then the mixed powder was fired again at 900 °C for 48 h in a dry-oxygen flow. The fired powder was finally washed by water again. The composition of

---

[*] Corresponding author. Tel.: +81 561 71 8029; fax: +81 561 63 6137.
E-mail address: e0589@mosk.tytlabs.co.jp (J. Sugiyama).

0921-4526/$ - see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.physb.2008.11.177

the samples was determined by an induction coupled plasma (ICP) analysis. Powder X-ray diffraction analyses showed that the three samples are single phase with a rhombohedral crystal system ($R\overline{3}m$). The results of ICP and XRD analyses are summarized in Table 1.

The μ^+SR spectra were measured at the πE1-Dolly surface muon beam line at PSI in Switzerland. 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 $H \leqslant 10$ kOe.

3. Results

Fig. 1 shows the T dependence of χ for the LiCoO$_2$ and Li$_{1.04}$Co$_{1.96}$O$_{1.96}$ samples. The $\chi(T)$ curve for LiCoO$_2$ is almost T-independent in the whole T range, as for the $\chi(T)$ curve previously reported. This is consistent with the fact that the Co^{3+} ions are in the low-spin state with $S = 0$. A small increase in χ at low T is, however, an indication of the appearance of localized moments and AF order, according to our μ^+SR result. On the other hand, the $\chi(T)$ curve for Li$_{1.04}$Co$_{1.96}$O$_{1.96}$ exhibits a typical Curie–Weiss behavior due to localized moments.

Table 1
The composition and other parameters of the Li$_{1+x}$Co$_{1-x}$O$_{2-x}$ samples for the present μ^+SR experiment.

Assumed composition	Measured Li/Co	Measured d (g/cm^3)	Theoretical d (g/cm^3)
LiCoO$_2$	0.98	5.028	5.055
Li$_{1.04}$Co$_{0.96}$O$_{1.96}$	1.08	4.868	4.913

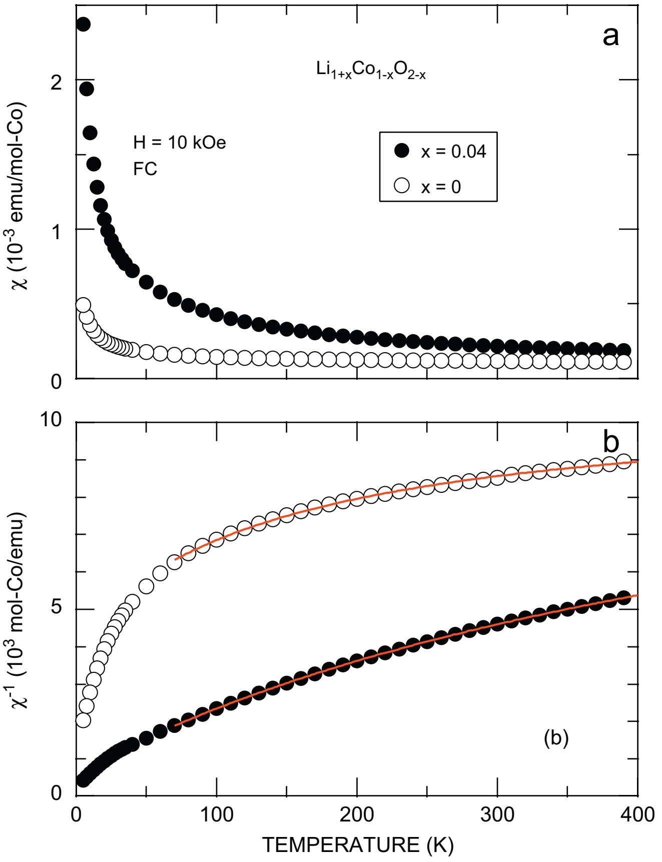

Fig. 1. T dependences of (a) χ and (b) χ^{-1} for the LiCoO$_2$ and Li$_{1.04}$Co$_{1.96}$O$_{1.96}$ samples. Solid lines in (b) represents the fit result using Eq. (1).

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

$$\chi = \frac{N\mu_{\rm eff}^2}{3k_{\rm B}(T - \Theta_{\rm p})} + \chi_0, \tag{1}$$

where N is the number density of Co ions, $\mu_{\rm eff}$ is the effective magnetic moment of Co ions, $k_{\rm B}$ is the Boltzmann's constant, T is the absolute temperature, $\Theta_{\rm p}$ is the paramagnetic Curie temperature and χ_0 is the T-independent susceptibility. Using Eq. (1) over the T range above 70 K, we obtain the values of $\mu_{\rm eff}$ and $\Theta_{\rm p}$ for LiCoO$_2$ as 0.255(6)$\mu_{\rm B}$ and $-57(6)$ K and for Li$_{1.04}$Co$_{1.96}$O$_{1.96}$ as 0.596(2)$\mu_{\rm B}$ and $-28.8(6)$ K, respectively.

Fig. 2 shows the ZF-μ^+SR spectrum for the LiCoO$_2$ and Li$_{1.04}$Co$_{1.96}$O$_{1.96}$ samples at the lowest T measured, in order to demonstrate the existence/absence of static magnetic order. The ZF-spectrum of the stoichiometric sample exhibits a slow relaxation with a broad minimum around 4.5 μs, which is a typical behavior for randomly oriented nuclear moments and is described by a Kubo–Toyabe (KT) formula. A rapidly relaxing component, however, exists in the fast time domain due to a muon-spin precession caused by the AF order, as reported previously. The ZF-spectrum of the sample ♯2 (from a different lot using "regular" Co nitrate as precursor with possible Fe and Ni impurities below 0.1%) is essentially the same to that of the first sample. On the other hand, the ZF-spectrum for the $x = 0.04$ sample shows a rapid relaxation without oscillation in the early time domain, suggesting the existence of localized disordered moments. Also, the spectrum exhibits a slow relaxation with a broad minimum around 4 μs. Considering the fact that the ZF-spectrum for the Li-deficient sample Li$_{0.95}$CoO$_2$ lacks the oscillation [8], this clearly demonstrates that the AF order appears only for the stoichiometric LiCoO$_2$.

The ZF-spectrum for Li$_{1+x}$Co$_{1-x}$O$_{2-x}$ is hence fitted by a combination of three signals; that is, an exponentially relaxing cosine oscillation signal due to static magnetic order, an exponentially relaxing non-oscillatory signal due to localized disordered moments, and a KT signal due to randomly oriented nuclear moments:

$$\begin{aligned} A_0P_{\rm ZF}(t) = {} & A_{\rm AF}\cos(\omega_{\rm AF}t + \phi)\exp(-\lambda_{\rm AF}t) + A_{\rm fast}\exp(-\lambda_{\rm fast}t) \\ & + A_{\rm KT}G^{\rm DGKT}(t, \varDelta, \nu), \end{aligned} \tag{2}$$

where A_0 is the maximum muon decay asymmetry, $A_{\rm AF}$, $A_{\rm KT}$, and $A_{\rm fast}$ are the asymmetries of the three signals, $\omega_{\rm AF}$ is the muon Larmor frequency, ϕ is the initial phase of the precession, $\lambda_{\rm AF}$ and $\lambda_{\rm fast}$ are exponential relaxation rates, $G^{\rm DGKT}$ is the dynamic Gaussian-KT function, $\varDelta$ is the static width of the local frequencies at the disordered sites, and ν is the field fluctuation rate.

Fig. 3 shows the T dependences of μ^+SR parameters for LiCoO$_2$ and Li$_{1.04}$Co$_{0.96}$O$_{1.96}$. The muon precession frequency ($f_{\rm AF}$) and its relaxation rate ($\lambda_{\rm AF}$) for the present LiCoO$_2$ sample are very consistent with the past results [7,8]. The $\lambda_{\rm AF}(T)$ curve exhibits a sharp maximum at $T_{\rm N}$ and decreases with decreasing T. Since this is thought to be a critical behavior at the AF transition, the appearance of the oscillatory signal below 30 K is most unlikely to be caused by the other possibilities, such as, the wide field distribution of internal fields or the variation of the characteristic energy.