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LE-μ^+SR Study of Superconductivity in the Thin Film Battery Material $LiTi_2O_4$

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$LiTi_2O_4$ and related spinel compounds have attracted considerable attention both as a superconductor as well as an electrode material for Li-ion batteries. In this brief report we have studied thin (220 nm) films of $LiTi_2O_4$ using the low-energy muon spin rotation/relaxation (LEM) technique. By performing temperature dependent measurement using the vortex state protocol in moderate magnetic fields it is possible to follow the entrance into the superconducting state below $T_c = 12$ K. Further, the London penetration depth at $T = 5$ K and 100 G applied field is extracted as $\lambda_{ab} \approx 226$ nm.

KEYWORDS: superconductivity, vortex state, battery materials, low-energy muon spin rotation

1. Introduction

Modern functional materials currently being used in our everyday high-tech applications are becoming more and more advanced. What was considered *fundamental* physics not so many years ago is at present day quickly being labelled *applied* physics. Such developments is a direct consequence from the fact that our everyday devices (*e.g.* smart phones) have become technically very advanced. However, it is also related to the rapid development of modern condensed matter and quantum physics. The latter stems from a drastic technological development of both experimental techniques as well as theoretical/modeling tools and sample synthesis equipment. With such developments applied and fundamental physicists have increased their interactions and now common interests and joint efforts are favourably being formed. This also means that some materials that were previously studied and published separately (in completely different scientific journals) are now instead being investigated with several parallel viewpoints in mind already from the start.

One good example of such a material is Na_xCoO_2 that has rendered considerable interest among fundamental condensed matter physicists for decades due to its very rich low-temperature phase-diagram [1] containing exotic magnetic phases, superconductivity [2] and density waves. At the same time this compound is also the sodium analogue [3] of the most archetypical Li-ion battery cathode material, namely Li_xCoO_2 [4]. Finally, Na_xCoO_2 also have shown to display thermoelectric properties [5] making it even more interesting for energy applications. Only recently has a few key publications [6–10] started to make the link between these different fields, allowing for further advances in the understanding and potential applications of this complex material.

Another group of "similar" materials are the spinel lithium titanates, which have recently received considerable attention for the usage as electrode material in rechargeable Li-ion batteries. However, also beyond the more applied interests, the group of spinel oxides display many intriguing fundamental physical properties *e.g.* catalytically active [11], charge density wave ordering [12], exotic magnetism and quantum spin liquids [13], multiferroicity [14] as well as superconductivity [15]. The title compound, $LiTi_2O_4$ (from hereon abbreviated LTO) is no exception since this compound, besides being considered as a battery anode material [16], also display superconductivity.

For LTO the spinel crystal structure is face-centered cubic (space group $Fd3m$). As a superconductor LTO [17–19] display a transition temperature $T_C \approx 12$ K and is being considered as a pure d-electron superconductor. The reason is that calculations of the electronic band structure reveal that the Ti-3d bands, located approximately 2.5 eV above the O-2p bands, will contribute most strongly to the conduction band states. Such large separation between d and p orbitals is completely opposite from other transition-metal spinels, which display strongly pd hybridized bands crossing the Fermi level. Unfortunately, stoichiometric LTO is very hard to synthesize, which has made studies of its superconducting properties very unreliable. It has been understood that it is mainly the ratio between Li and Ti that strongly affects the superconducting transition temperature [15]. In the current investigation high-quality thin LTO films have been carefully grown in order to obtain a good control of the chemical composition and hereby the superconducting properties.

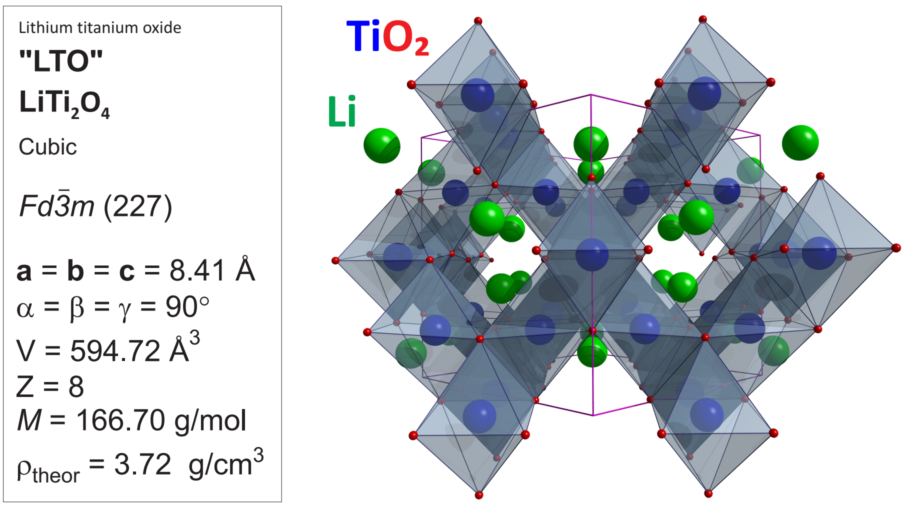

Fig. 1. Crystallographic data and atomic structure of $LiTi_2O_4$.

2. Experimental Details

For the present study high-quality stoichiometric LTO epitaxial films were deposited by a pulsed laser deposition (PLD) technique ontop of $MgAl_2O_4$(111) substrates [20]. Here the substrate was chosen since it has a 4% smaller in-plane lattice constant than LTO, which results in a compressive strain that has been proposed to increase the superconducting transition temperature [21]. For the current low-energy μ^+ (LEM) investigations the thickness of the $LiTi_2O_4$ films were chosen to be 220 nm and from bulk magnetization measurements it is clear that the films display a very sharp superconducting transition of $T_C \approx 12$ K. [20].

The current μ^+SR study was performed using the low-energy μ^+ (LEM) beamline at SμS of PSI in Switzerland. Four nominally identical film samples, covering a 2.2×2.2 cm^2 area, were glued using Ag-paste onto a Ni-coated aluminium plate, which was then mounted onto a cryostat. The implanted beam energy was chosen as $E_\mu^{\rm im} = 24.25$ keV in order to stop the muons in the center of the film.

The temperature range for LEM-μ^+SR measurements was between 5 and 20 K using a ^{4}He(l)-cooled cryostat. The investigations of the superconducting properties were performed using transverse-field (TF) setup in a vortex state protocol with the TF applied parallel to the film surface normal. More details concerning the LEM setup can be found elsewhere [22–25].

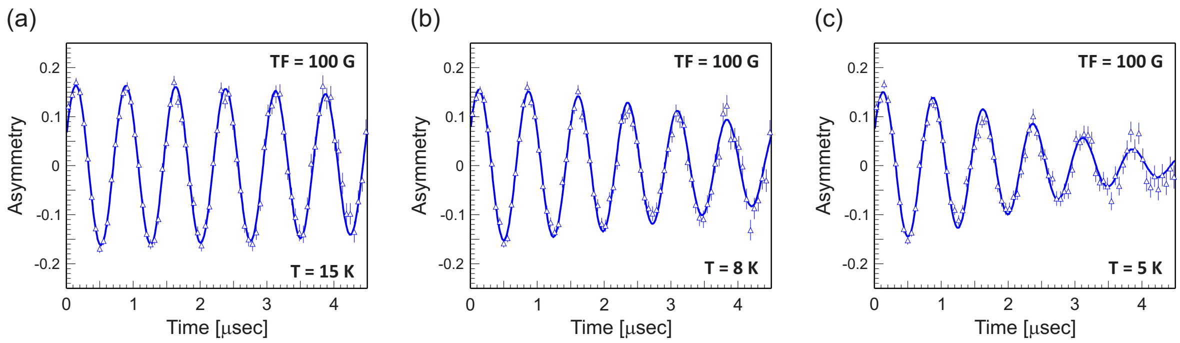

Fig. 2. Temperature dependence of the LEM time spectra with an applied transverse field TF = 100 G where it is evident that an additional relaxation appears below T_c = 12 K. Please note that data for only one channel is shown, while the actual fits (and results presented in Fig. 3) were conducted for the complete data-set.

3. Results & Discussion

For this initial LEM study the $LiTi_2O_4$ films were investigated using the vortex state protocol i.e. the samples were field-cooled (FC) down to T = 5 K in a transverse-field (TF) applied parallel to the film surface normal. For the first set of measurements a lower field TF = 100 G was chosen along with the implantation depth of z = 110 nm (i.e. middle of the film) and measurements were then performed on heating. The TF LEM time spectra for selected temperatures are shown in Fig. 2 where the data was fitted to a simple Gaussian relaxing TF oscillation:

$$A_0\,P_{\mathrm{TF}}(t) = A\cdot\cos(2\pi\cdot f\cdot t+\phi)\exp(-\frac{\sigma^2\cdot t^2}{2}) \tag{1}$$

Here A is the asymmetry, f and ϕ the frequency and phase, respectively, of the oscillation, and σ the relaxation rate. The latter comes from nuclear moments as well as the additional relaxation appearing when entering into the mixed superconducting state. Here, the presence of a vortex lattice creates a highly inhomogeneous field distribution leading to an increase of the relaxation rate (σ) below T_c. The fitting results using Eq. 1 clearly reveal that the temperature dependence $\sigma(T)$ display a strong increase below T_c, as shown in Fig. 3.

The relaxation rate measured (σ) is composed of the relaxation from the vortex lattice (σ_{VL}) and the relaxation due to nuclear dipole fields (σ_n) through the following expression:

$$\sigma^2 = \sigma_n^2 + \sigma_{\mathrm{VL}}^2 \tag{2}$$

Here, the nuclear relaxation can be estimated from the data point acquired at T = 15 K as $\sigma_n \approx 0.125\ \mu s^{-1}$. By calculating σ_{VL} we are then able to extract the effective London penetration depth (λ_{eff}) through the following expression [26,27]:

$$\sigma_{\mathrm{VL}}[\mu s^{-1}] = a\cdot(1-H_{\mathrm{TF}}/H_{c2})\cdot[1+1.21\cdot(1-\sqrt{H_{\mathrm{TF}}/H_{c2}})^3]\cdot\lambda_{\mathrm{eff}}^{-2}[\mathrm{nm}] \tag{3}$$

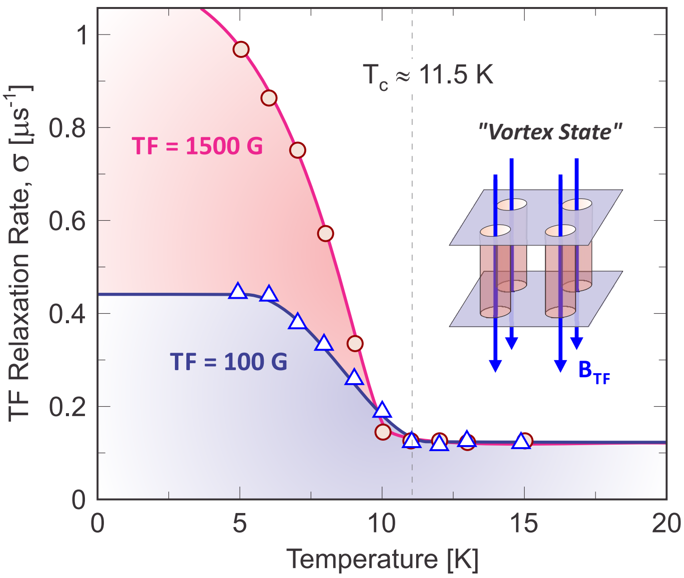

Fig. 3. Temperature dependence of the transverse field (TF) relaxation rate, $\sigma(T)$ for two different TF = 100 and 1500 G, respectively. Solid lines are only guides to the eye.

Here the constant a is related to the geometry of the vortex lattice (VL) where $a = 4.83 \cdot 10^4$ for a triangular VL while $a = 5.07 \cdot 10^4$ for a rectangular one. To the best of our knowledge there are no direct measurements (by *e.g.* small-angle neutron scattering, SANS) of the VL in LTO. Considering its cubic crystallographic structure we here assume the VL to be rectangular. Further the critical upper field of our current LTO films has not been measured, however, from literature [28] we are able to estimate $H_{c2} = 11.6$ T. Using the σ_{VL} at lowest measured temperature ($T = 5$ K) it is possible to extract $\lambda_{\mathrm{eff}} = 464$ nm. It is important to realize that λ_{eff} will be an overestimation for the actual λ_{ab} since we are here measuring a thin film where the VL is known to *'spread out'* close to the surface/interface. To a first order approximation this can be corrected by:

$$\lambda_{\mathrm{eff}} = \frac{2 \cdot \lambda_{\mathrm{ab}}^2}{d} \tag{4}$$

where d is simply the thickness of the film i.e. $d = 220$ nm. This finally yield that $\lambda_{\mathrm{ab}} = 226$ nm for the current $\mathrm{LiTi_2O_4}$ at $T = 5$ K using an applied field TF = 100 G. Finally, we have also performed a similar measurement using a higher applied field TF = 1500 G (see also Fig. 3) from which it is possible to extract $\lambda_{\mathrm{ab}} = 165$ nm. The next step in order to obtain a more accurate estimate for λ_{ab} will clearly be to conduct further LEM studies of the films using the Meissner state protocol with the TF applied perpendicular to the film surface normal (i.e parallel to the film surface).

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