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The magnetic phase of Lithium transition metal phosphates LiMPO$_4$ (M=Mn, Co, Ni) detected by μ^+SR

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Abstract

The magnetic properties of the olivine-type compounds LiMPO$_4$ (M = Mn, Co, Ni) are probed using muon spin rotation/relaxation (μSR). These materials pose an appealing magnetic structure and a high - potential technological interest as cathode materials for future rechargeable Li-ion batteries. The LiMPO$_4$ family of compounds consists of a corner-sharing MO_6 octahedra of high-spin M^{2+} ions manifesting an antiferromagnetic ground state below $T_N \approx$ 30 K. Additionally, these compounds belong to a class of materials exhibiting properties between two- and three-dimensional systems. A comparative study between the family members is presented.

Keywords: Li-ion batteries, magnetism, Phospho-olivines

1. Introduction

The lithium metal phospho-olivines, LiMPO$_4$ (M=Mn,Co,Ni) have become a current topic in recent studies due to their high potential as a positive electrode material for rechargeable Li-ion batteries. Unlike the currently used layered LiCoO$_2$, where highly oxidized redox couples (Co$^{3+/4+}$) cause chemical instability and safety issues, the LiMPO$_4$ show high stability in lithium extraction and insertion cycles[1]. One promising compound in this group is the LiFePO$_4$ with a stable Fe$^{2+/3+}$, which offers a theoretical capacity of $\approx$ 170 mAh/g and an operating voltage of 3.45 V, compatible with the current electrolytes used. However, by replacing the Fe with Mn, Co or Ni, the successful solid-state reaction in these compounds show higher operating voltages (4.1 V, 4.8 V and 5.1 V, respectively) suggesting a higher power density. Moreover, these phosphates possess high-spin M^{2+} metal ions which have been the focus of electronic[2] and magnetic[3, 4, 5] calculations and measurements[6, 7, 8, 9] in order to elucidate the exchange paths between the M ions.

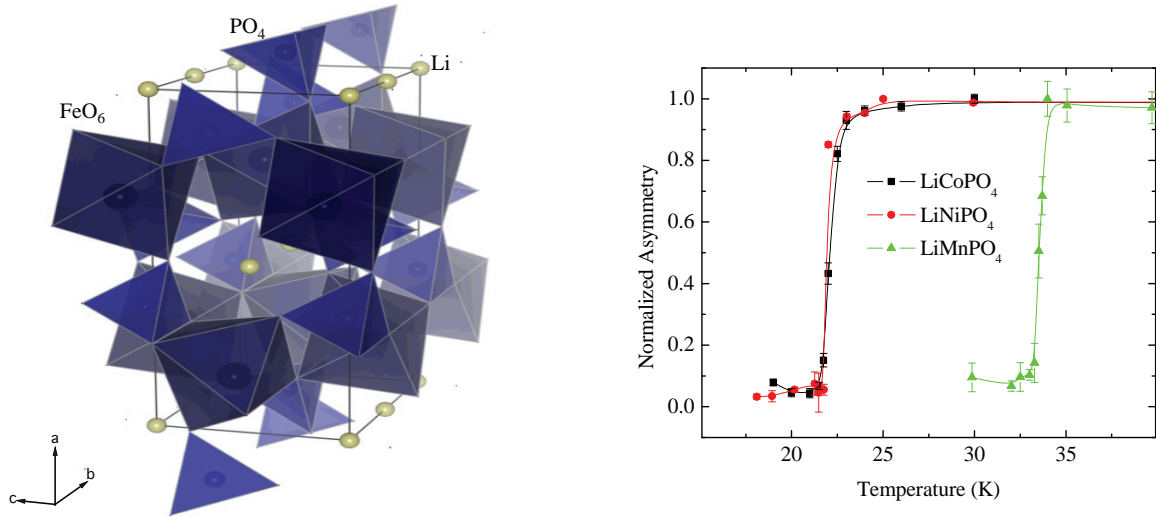*Corresponding author.
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Figure 1: The orthorhombic crystal structure of LiMPO$_4$. (b) The temperature dependence of the normalized wTF asymmetry, lines are guide to the eye.

Neutron diffraction on LiNiPO$_4$ reveals that below $T_N = 20.8$ K, the system adopts a collinear antiferromagnetic phase, with an intermediate incommensurate phase at $T_N \leq T \leq 2T_N \approx 40$ K[9]. Similar behavior was observed in LiMnPO$_4$[7]. However, this was not observed in the isostructural LiCoPO$_4$ which, at $T < T_N$, the spin structure of the Co is slightly rotated from the principal crystallographic b axis[6]. Moreover, LiCoPO$_4$ was found to have isotropic domains, unlike LiNiPO$_4$[10]. Despite these extensive measurements, the microscopic magnetic nature of the Néel phase has, to our knowledge, have not been investigated by μSR. Dipolar field calculations indicate that there are several possible muon sites in LiMPO$_4$ and therefore we would naturally expect multiple muon-spin precession frequencies below T_N. Here, following the μSR study on LiFePO$_4$[11], we aim to characterize the magnetic phase of LiMPO$_4$ using the local probe μSR and bulk susceptibility. Our major finding is a second Néel phase in LiMnPO$_4$ and LiCoPO$_4$ observed by ZF-μSR and bulk susceptibility. In LiNiPO$_4$ a single static phase is observed below T_N.

2. Experimental

Powder samples of LiMPO$_4$ were prepared by the flux technique using Li$_3$PO$_4$ and MCl$_2$ as starting agents. X-ray diffraction show the successful synthesis of a single phase orthorhombic olivine structure (space group *Pnma* no. 62) of LiMPO$_4$ revealing the crystallographic parameters which agree with previously published data. The μSR spectra were measured on the **M20** surface muon beam line using the **LAMPF** spectrometer at TRIUMF, Canada. Approximately 500 mg powder sample were placed in a very thin 1×1cm^2 Al-coated Mylar envelope, placed onto a low-background sample holder in a liquid-He flow cryostat. Subsequently, weak-Transverse field (wTF) and Zero-Field (ZF) measurements were taken at $1.7 \leq T \leq 50$ K. Complementary bulk dc-susceptibility measurements were performed using a Quantum Design Magnetic Properties Measurements System superconducting quantum interference device (SQUID) at temperatures between $1.7 \leq T \leq 400$ K under zero-field cooled and field-cooled conditions.

3. Results and Discussion

The magnetic phase transitions are probed using the wTF technique. In this technique, a small applied field of $H_{\mathrm{TF}} = 30$ Oe is applied perpendicular to the initial muon polarization and the initial asymmetry is proportional to the volume fraction of the paramagnetic phase. The wTF asymmetry was well described by

$$A_{\mathrm{TF}}(t) = A_0 \exp(-\lambda_{\mathrm{TF}}t)\cos(\gamma_\mu H_{\mathrm{TF}}t + \varphi) + A_{\mathrm{Fast}}\exp(-\lambda_{\mathrm{Fast}}t) \tag{1}$$
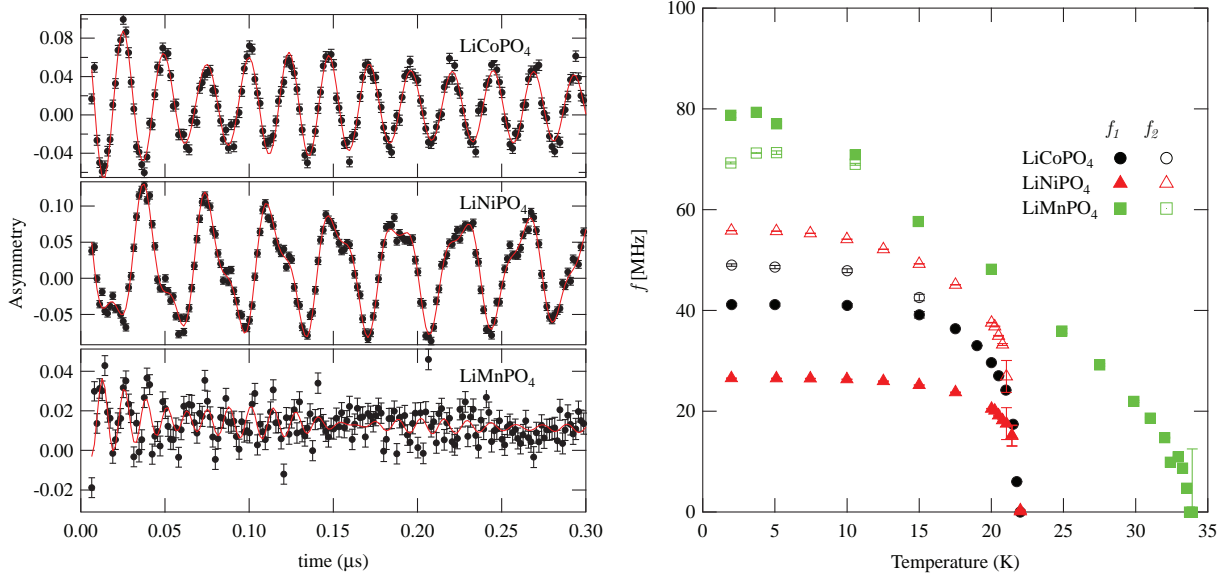
Figure 2: (a) The ZF-μSR spectra for LiMPO$_4$ taken at base temperature (T = 1.8 K), the solid lines are the fits to Eq. (2). (b) The temperature dependence of the muon precession frequencies (f_1 and f_2) identified in the ZF-spectra.

where the gyromagnetic ratio γ_μ = 135.54 MHz/T, A_0 (A_{Fast}) and λ_{TF} (λ_{Fast}) are the initial precessing (fast relaxing) asymmetry and relaxation, respectively. In Figure 1 we depict the normalized asymmetry ($A_0(0)$) versus the tempera-ture. The transition to the ordered state is clearly seen by the abrupt decrease in the asymmetry as the temperature is lowered, and corresponds to 22.09 K (LiCoPO$_4$), 21.95 K (LiNiPO$_4$) and 33.504 K (LiMnPO$_4$) when the normalized asymmetry is 0.5 . These temperatures also correlate with the transition temperature measured by the SQUID (see Fig. 3).

ZF-μSR measurements were taken as described in Sec. 2. Figure 2a displays the time dependence of the raw ZF-μSR data for LiMPO$_4$ taken at T = 1.8 K. A beat is clearly observed in the spectra, indicating more than a single frequency. Moreover, the initial asymmetry of the LiMnPO$_4$ is much smaller than LiCoPO$_4$ and LiNiPO$_4$. The origin of this mismatch is not understood at the moment. Nonetheless, the ZF asymmetry was well fitted, for each compound at $T \leq T_M^*$ (M =Mn, Co and Ni), by a sum of two relaxing frequencies and a slowly relaxing tail,

$$A_0 P_{\text{ZF}}(t) = A_1 \exp(-\lambda_1 t)\cos(\omega_1 t + \varphi_1) + A_2 \exp(-\lambda_2 t)\cos(\omega_2 t + \varphi_2) + A_{\text{tail}} \exp(-(\lambda_{\text{tail}} t)^\beta) \tag{2}$$

where $\omega_i = \gamma_\mu B_i$ is the muon frequency at its interstitial site ($i = 1, 2$) experiencing an internal field B_i. λ_i and λ_{tail} are the relaxation rates of each of the sites i or tail. The solid lines in Fig. 2a demonstrate the fit. For temperatures $T > T_M^*$, a single frequency is observed and hence the asymmetry of the second frequency is a priori set to nil, $A_2 = 0$ in Eq. (2). The temperature dependence of the frequencies $f_i \equiv \omega_i/2\pi$ for the three compounds are depicted in Fig. 2. Several points can be considered. First, as expected, the frequencies decrease monotonically with increasing temperatures, this is more pronounced in LiMnPO$_4$ where the frequencies at T = 1.7 K are $\approx$ 80 MHz. Secondly, unlike LiMnPO$_4$ and LiCoPO$_4$ with T_{Mn}^* = 12.7 $\pm$ 2.2 K, and T_{Co}^* = 16.2 $\pm$ 1.25 K, LiNiPO$_4$ experiences two frequencies for all $T \leq T_N$, thus $T_{\text{Ni}}^* = T_N$. Therefore, we suggest that the muon experiences a single static antiferromagnetic phase in LiNiPO$_4$ and an additional transition to a second antiferromagnetic phase below T_M^* for M =Co and Mn. We now try to observe whether these additional ordered phases can also be seen with bulk susceptibility.

Bulk susceptibility (χ) data for the three compounds are shown in Fig. 3. Due to the appearance of the second frequency in the μSR spectra of LiCoPO$_4$ and LiMnPO$_4$ at T_M^*, we performed detailed measurements and analysis of the bulk data. At first glance, for all three compounds, χ increases towards T_N and then decreases sharply indicating the antiferromagnetic transition temperature as expected, which also correlates with the wTF-μSR measurements with no obvious field-cooled or zero-field-cooled dependence. However, by computing $\partial\chi/\partial T$ for $T \leq T_N$, changes are
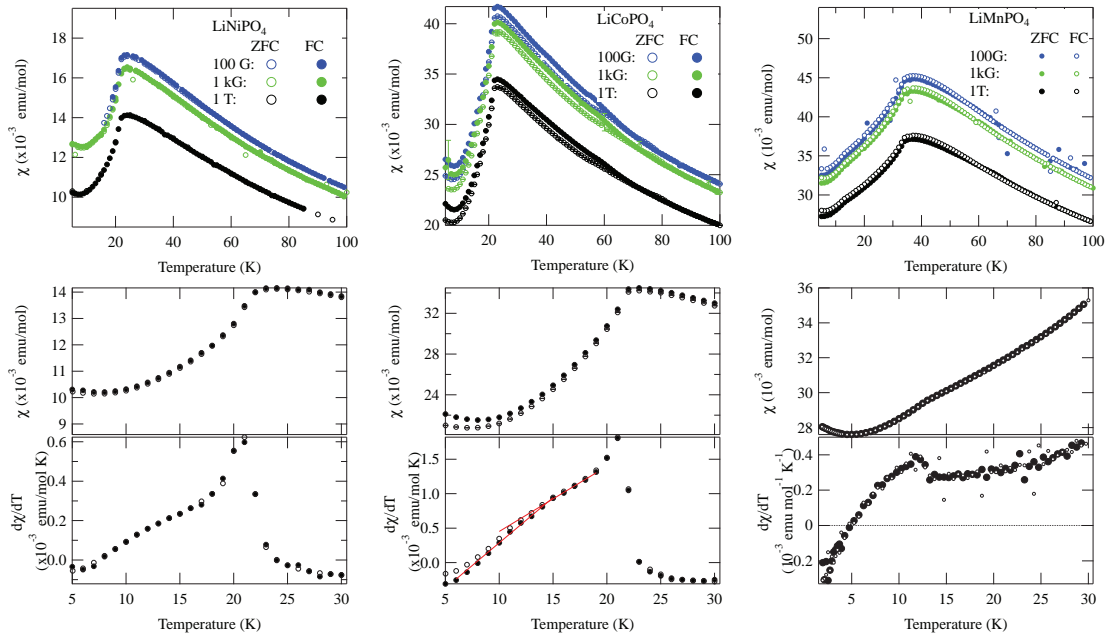
Figure 3: The bulk susceptibility of LiMPO$_4$.

revealed. In LiNiPO$_4$ and LiCoPO$_4$, apart from the transition, $\partial\chi/\partial T$ is smooth and no additional transitions are observed. In fact, the two compounds are very similar in their χ and $\partial\chi/\partial T$ behavior, and a small change in the slopes of $\partial\chi/\partial T$ is observed at $\approx$ 15 K. In LiCoPO$_4$ this is accompanied by an increasing deviations between the ZF and FC measurements as T decreases below T_{Co}^*, which is not seen elsewhere. Moreover, such deviations are not observed in LiNiPO$_4$ consistent with a $T_{\text{Ni}}^* = T_N$. In LiMnPO$_4$, χ shows a small kink at 13 K, which is clear in $\partial\chi/\partial T$, corresponding to T_{Mn}^*.

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5. References

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