TRIUMF

Canada's national laboratory for particle and nuclear physics
Laboratoire national canadien pour la recherche en physique nucléaire
et en physique des particules

The Magnetic Phase of Lithium transition-metal phosphates Li*M*PO$_4$

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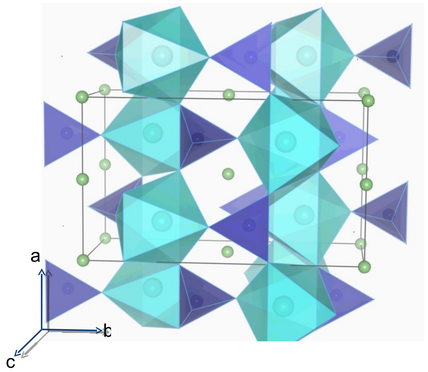
Introduction

The magnetic properties of the olivine-type compounds Li*M*PO$_4$ (*M*=Mn, Co, Ni) are probed using μSR. These materials pose appealing magnetic sturcutres and a high potential technological interest as cathode materials for future rechargeable Li-ion batteries. The Li*M*PO4 family of compounds structures a corner-sharing *M*O6 octahedra of high spin M^{2+} ions manifesting an antiferromagnetic ground state below T_N~30K. It has been suggested that LiNiPO$_4$ and LiMnPO$_4$ have more than one ordered state. Additionally, these compounds belong to a class of materials exhibiting properties between two- and three-dimensional systems.

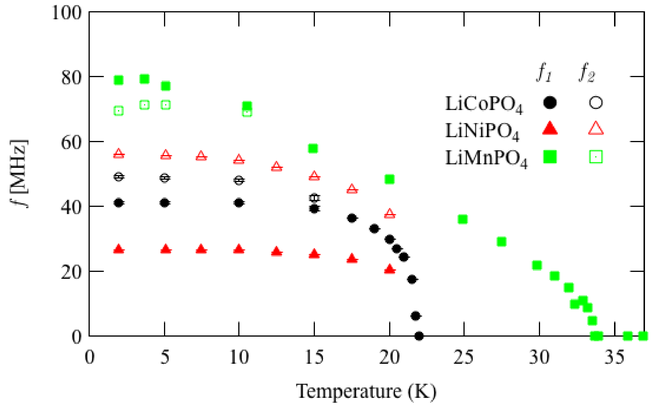
Structure

Li*M*PO$_4$ were prepared by solid state reaction, adopting an orthorhombic olivine structure (space group *Pnma* no. 62). This structure is composed of corner shared and MO_6 octahedra and cross-linked with PO_4 tetrahedra forming a 3-dimensional network with tunnels which are occupied by the Li ions along the [100] and [001] directions.

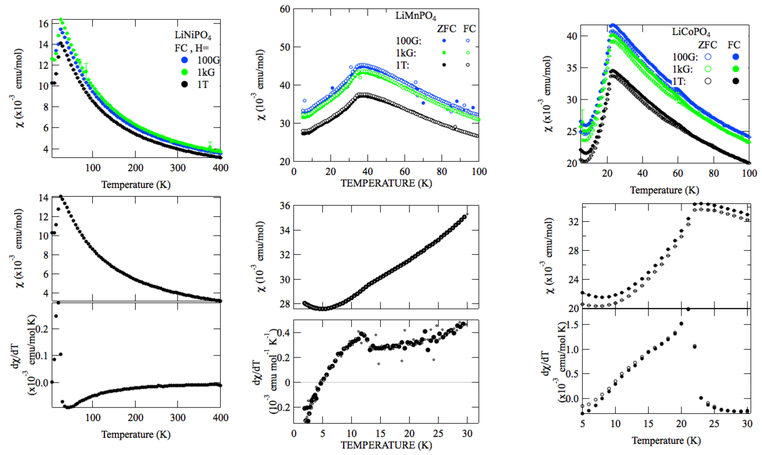


Ordered Neél State

The observed frequencies in the ordered state by means of ZF-μSR are shown. As the temperature decreases, LiCoPO4 and LiMnPO4 show splitting of single frequency into 2 frequencies, below the ordered state suggesting a second phase transition, i.e., a second Neel phase, at ~15 and 10K respectively. In contrast, LiNiPO4 experiences only one phase, with no splitting of the frequencies. Careful bulk SQUID measurements, below TN, show a pronounced change in the bulk susceptibility, χ, which is also evident in $\partial\chi/\partial T$ at 13K (LiMnPO4) and 15K (LiCoPO4) whereas LiNiPO4



The muon frequencies observed at ZF, versus the temperature.

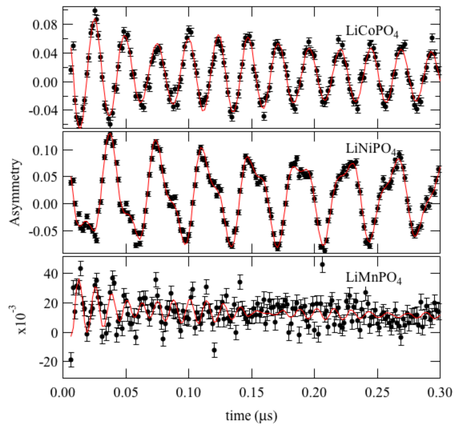


The bulk susceptibility data. Anomalies below T_N are seen in M=Co and Mn, LiNiPO4 does not show any anomalies.

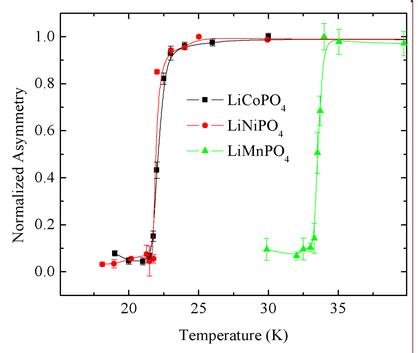
μSR data

Zero field (ZF) and weak Transverse Field (wTF) were measured to characterize the ordered state and transition temperature, respectively.

The wTF probes the transition temperature by observing the decrease in the asymmetry amplitude, where in the normal (paramagnetic) the muon precess about the weak external field.



Muon-spin Asymmetry versus time, for LiMPO4 with M=Co (top), Ni and Mn (bottom).. Precession and beating frequencies are visible. Lines demonstrate the fit.



The Normalized wTF Asymmetry, A_0, vesus the temperature for LiMPO$_4$.

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References

J. Sugiyama, submitted to PRB.