

Hyperfine Fields at the Li Site in LiFePO₄-Type Olivine Materials for Lithium Rechargeable Batteries: A ⁷Li MAS NMR and SQUID Study

Michael C. Tucker^a, Marca M. Doeff^b, Thomas J. Richardson^a, Rita Fiñones^b, Elton J. Cairns^a,
and Jeffrey A. Reimer^a

a) Environmental Energy Technologies Division, b) Materials Sciences Division, Ernest Orlando Lawrence Berkeley National Laboratory and Department of Chemical Engineering, University of California at Berkeley, Berkeley, CA 94720

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Olivines in the solid solution Li(Fe,Mn)PO₄ have received much recent attention as promising positive electrode active materials for lithium rechargeable batteries.¹⁻³ Appropriate spectroscopic studies will undoubtedly lead to improved understanding of these materials' electrochemical properties and performance. ⁷Li nuclear magnetic resonance (NMR) spectroscopy allows observation of Li in the bulk of the material, complementing Mössbauer spectroscopy, which has been used to observe Fe in LiFePO₄.² In this work, we discuss the nature of the NMR shift of ⁷Li in LiMPO₄ (M = Mn, Fe, Co, Ni). All compositions were prepared at high temperature, except LiFePO₄ which was prepared hydrothermally.⁴ The compositions LiFePO₄ and LiMnPO₄ are of interest as end-members of the industrially-relevant Li(Fe,Mn)PO₄ series, whereas LiCoPO₄ and LiNiPO₄ provide isostructural samples with alternative metal cation electronic structures to aid interpretation of the results. All compositions studied here contain paramagnetic metal ions, leading to bulk magnetism and NMR-observable electron-nuclear coupling. The NMR shift is attributed to through-bond transfer of unpaired d-electron density to Li s-orbitals on the basis of the temperature-dependencies of the magnetic susceptibility and NMR shift. This work elucidates the ⁷Li NMR shift mechanism in an industrially-significant class of materials; we anticipate the successful application of NMR to the study of important aspects of these materials' electrochemical performance.

Olivine LiMPO₄ crystallizes in the *Pnma* space-group, and consists of distorted LiO₆, MO₆ and PO₄ units.¹ The local environment of Li in LiFePO₄ is shown in Figure 1. Each Li is connected by oxygen atoms to 6 FeO₆ units. The FeO₆ units are

distorted, reducing the symmetry from O_h to C_s.² In C_s symmetry, the metal d-orbitals split into 3 A' orbitals at higher energy than the two remaining A'' orbitals, unlike O_h symmetry where 2 orbitals at higher energy are expected.

The temperature dependence of the inverse susceptibility measured with a Superconducting Quantum Interference Device (SQUID) magnetometer (Quantum Designs) is shown in Figure 2. All compositions show a Curie-Weiss type dependence on temperature. The data are consistent with a previous report of the magnetism in olivines, where antiferromagnetic ordering at low temperatures was the primary subject of interest.⁵ Linear fits to the data provided the Weiss constants and the effective magnetic moments that are compared to the theoretical spin-only values in Table 1. The magnitude and direction of the discrepancies between the theoretical and experimental values are similar to those reported previously for first transition series salts.⁶ The reduced MO₆ symmetry has a noticeable effect on the magnetic susceptibility of LiCoPO₄: Co²⁺ is expected to have 3 unpaired electrons (A') in C_s symmetry, consistent with the experimental value (Table 1) but only a single unpaired electron (e_g) in O_h symmetry. The negative values of the Weiss constants are consistent with the antiferromagnetic couplings known for these materials.⁵

The ⁷Li magic angle spinning (MAS) NMR spectra for LiMPO₄ are shown in Figure 3. Details of the experimental setup are provided elsewhere.⁴ The spectra are characterized by single isotropic peaks and broad spinning sideband manifolds, as expected for paramagnetic materials containing a single type of Li site. The asymmetry in the sideband manifold arises

Figure 1. The local environment of Li in LiFePO₄. Bonds responsible for the STH interaction are highlighted in gray. P atoms are omitted for clarity.

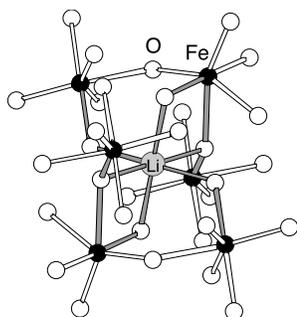


Figure 2. Temperature-dependence of the inverse magnetic susceptibility for all compositions. The lines are linear fits to the data.

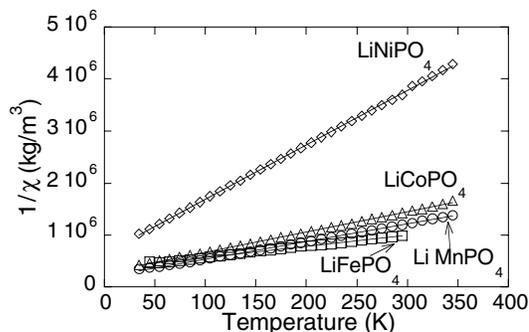
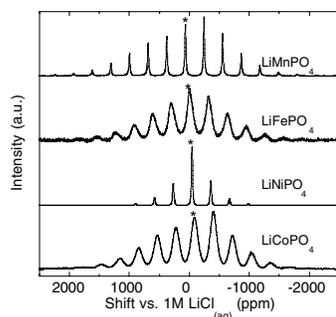


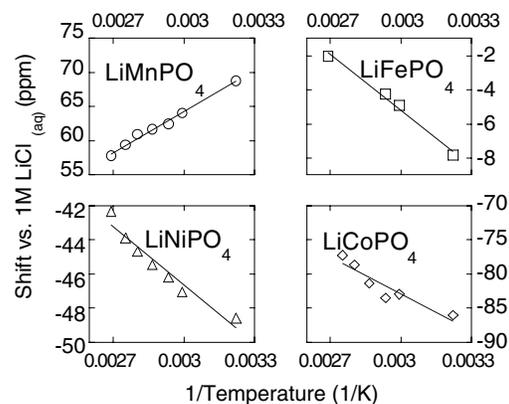
Table 1. Summary of SQUID and ^7Li NMR parameters for LiMPO_4 .

Composition	Unpaired A" electrons	Unpaired A' electrons	μ_{eff} (μ_B) Theoretical	μ_{eff} (μ_B) Experimental	Weiss Constant (K)	Isotropic Shift @ 37°C (ppm)	A/η (10^6 rad/s)
LiMnPO_4	2	3	5.91	5.4	-58	68	0.86
LiFePO_4	1	3	4.89	6.8	-161	-8	0.48
LiNiPO_4	0	2	2.82	3.1	-60	-49	1.53
LiCoPO_4	0	3	3.87	5.1	-70	-86	0.94

**Figure 3.** ^7Li MAS NMR spectra of all samples studied. Isotropic peaks are marked with an asterisk. Spectra were obtained at a ^7Li frequency of 38.9MHz, 10 kHz spinning speed.

from the paramagnetic interaction between the lithium nucleus and transition metal unpaired electrons.⁴ The isotropic shifts observed here (Table 1) fall outside the known chemical shift range for Li in diamagnetic compounds (+20 to -30 ppm),⁷ suggesting that paramagnetic electron effects are important. Variable-temperature NMR can be used to decompose the isotropic shift into a temperature-dependent part and a temperature-independent part which may contain contributions from the Knight shift, and diamagnetic and van Vleck susceptibilities.⁷ The possibility of a Knight shift, common in metals, can be ignored for the present materials, which are electronically insulating. Hyperfine coupling of the ^7Li nucleus to unpaired metal d-electrons can result from through-bond transfer of unpaired electron density via the oxygen p-orbitals to the Li s-orbitals. Such coupling is expected to give rise to a temperature-dependent shift that follows the paramagnetic susceptibility of the electrons.⁷ The temperature dependence of the isotropic shift observed here is shown in Figure 4. The data indeed follow the Curie-Weiss law trend observed for the bulk susceptibility, supporting the earlier assignment of the ^7Li shift in LiMnPO_4 to hyperfine coupling on the basis of single-crystal wide-line NMR,⁸ and extending that assignment to the other compositions studied here.

The variation in the value of the isotropic shift with the identity of the transition metal, M, in LiMPO_4 can be rationalized on the basis of the electronic structures of the M^{2+} ions. The number of unpaired electrons for each metal is shown in Table 1. High spin configurations are assumed on the basis of a previous Mössbauer study.² The value of the isotropic shift (Table 1) is seen to follow a linear superposition of the interactions between the ^7Li nucleus and individual metal electrons; we find that each of the unpaired A' electrons contributes roughly -24 to -28 ppm to the isotropic shift at 37°C while each unpaired A" electron contributes roughly +70 to +79 to the shift. The Li-O-M pathways for through-bond hyperfine coupling are highlighted in Figure 1. There are 4 "right-angle" bonds with a Li-O-Fe angle of 95-97° and 4 "bent" bonds with a Li-O-Fe angle of 110-122°. We surmise that the difference in sign for the A' and A" contributions arises from geometric and magnetic superexchange constraints on the

**Figure 4.** Temperature-dependence of the ^7Li NMR isotropic resonance for all samples studied. Temperature was calibrated using an external lead nitrate standard.

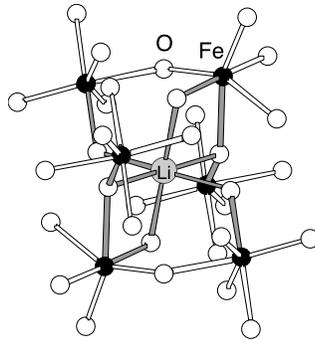
Li-O-M bond as was discussed previously for the LiMn_2O_4 system, where Mn t_{2g} electrons contribute +60 to +150 ppm to the ^7Li NMR shift depending on the bond angle and e_g electrons contribute -327 ppm per 1/2 electron.⁹

The hyperfine coupling constant, a measure of Li-O-M bond covalence, was calculated for each composition according to Ref 7. The value of the coupling constant, A/η , is seen to vary considerably with the identity of the transition metal (Table 1). The values obtained here for LiMPO_4 are an order of magnitude lower than those reported for LiMn_2O_4 .⁷ This is consistent with the longer bond lengths in LiMPO_4 ¹ and the polarization of oxygen electrons into the PO_4^{3-} unit that reduces the covalence of the Fe-O bond.³

In conclusion, we have elucidated the nature of the hyperfine fields at the ^7Li nucleus that give rise to temperature-dependent NMR shifts for LiMPO_4 olivines. This work will provide the basis for future NMR studies of the factors affecting the electrochemical performance of these promising materials.

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The ${}^7\text{Li}$ NMR isotropic shift for olivine LiMPO_4 ($M = \text{Fe, Mn, Co, Ni}$) is assigned to hyperfine coupling between the ${}^7\text{Li}$ nucleus and the transition metal unpaired electrons on the basis of the Curie-Weiss temperature dependence of the shift. The hyperfine shift arises from a linear combination of Li-O-M through-bond interactions wherein the unpaired A' electrons contribute a negative shift and the unpaired A'' electrons contribute a positive shift. The hyperfine coupling constant is determined for each composition.
