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

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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. [7]Li 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 [7]Li 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 ^{7}Li 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 LiO_6, MO_6, and PO_4 units.[1] The local environment of Li in LiFePO4 is shown in Figure 1. Each Li is connected by oxygen atoms to 6 FeO_6 units. The FeO_6 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 MO_6
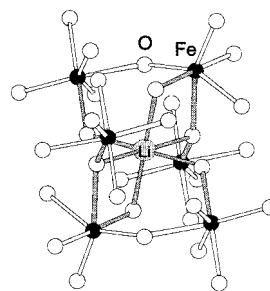

Figure 1. The local environment of Li in LiFePO4. Bonds responsible for the STH interaction are highlited in gray. P atoms are omitted for clarity.
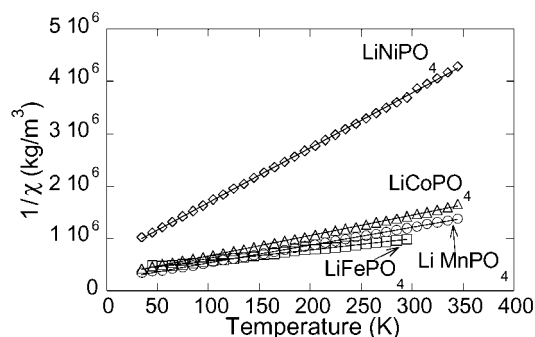

Figure 2. Temperature dependence of the inverse magnetic susceptibility for all compositions. The lines are linear fits to the data.

symmetry has a noticeable effect on the magnetic susceptibility of LiCoPO4: Co^{2+} 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 [7]Li 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 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

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Table 1. Summary of SQUID and ^{7}Li NMR Parameters for LiMPO$_4$

composition	unpaired A″ electrons	unpaired A′ electrons	μ_{eff} (μ_B) theoretical	μ_{eff} (μ_B) exptl	Weiss constant (K)	isotropic shift at 37 °C (ppm)	A/$\hbar$ (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
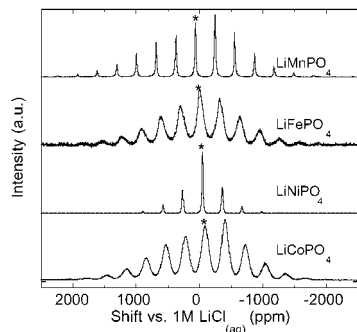
Figure 3. ^{7}Li MAS NMR spectra of all samples studied. Isotropic peaks are marked with an asterisk. Spectra were obtained at a ^{7}Li frequency of 38.9 MHz, 10 kHz spinning speed.
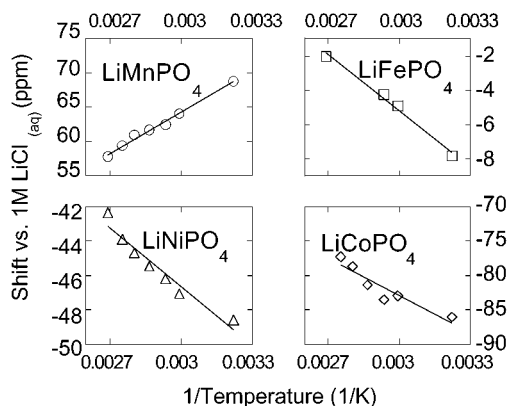
Figure 4. Temperature dependence of the ^{7}Li NMR isotropic resonance for all samples studied. Temperature was calibrated with use of an external lead nitrate standard.

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 ^{7}Li 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 ^{7}Li 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 ^{7}Li 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 Li−O−M bond as was discussed previously for the LiMn$_2$O$_4$ system, where Mn t$_{2g}$ electrons contribute +60 to +150 ppm to the ^{7}Li 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/$\hbar$, is seen to vary considerably with the identity if the transition metal (Table 1). The values obtained here for LiMPO$_4$ are an order of magnitude lower than those reported for LiMn$_2$O$_4$.[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 ^{7}Li 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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