

⁶Li MAS NMR spectroscopy and first-principles calculations as a combined tool for the investigation of Li₂MnSiO₄ polymorphs†

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Polymorphism of Li₂MnSiO₄ was inspected by ⁶Li MAS NMR spectroscopy. The detected isotropic shifts and spinning-sideband patterns were successfully reproduced by first-principles calculations and offered an insight into structural differences among the polymorphs. The approach for predicting isotropic shifts was also tested on several other Li-containing paramagnetic structures.

The search for storage materials for Li-ion batteries with high energy density has recently lead to intensive studies of Li₂MSiO₄ (M = Mn, Co, Fe) materials.^{1–3} Beside theoretically expected high energy densities, low-price preparation and safety, this family of cathode materials also exhibits rich polymorphism.^{3–5} Most often the as-prepared Li₂MSiO₄ samples are mixtures of different polymorphs, because the differences in formation energies of the latter are very small. In the case of Li₂MnSiO₄ at least three different polymorphs have been isolated so far. Two low-temperature β-Li₂MnSiO₄ polymorphs (*i.e.* polymorphs crystallized in *Pmn*2₁ and *Pmnb* space groups) were reported in our earlier study.² We showed that the *Pmn*2₁ polymorph can be isolated by applying high pressure at high temperature, while the *Pmnb* polymorph can be isolated by slowly cooling the as-prepared sample from 900 °C to room temperature.⁵ The high-temperature polymorph, γ-Li₂MnSiO₄, was reported by Politaev⁶; it could be isolated by quenching the as-prepared sample from 900 °C. Structures of all three polymorphs were determined by combined X-ray powder- and electron diffraction studies.

In this communication we use carefully prepared Li₂MnSiO₄ samples and show that ⁶Li MAS NMR spectroscopy is perfectly suited to investigate the purity of these samples and to easily distinguish among different Li₂MnSiO₄ polymorphs. With the aid of first-principles calculations we relate isotropic shifts and spinning-sideband patterns observed by NMR spectroscopy to structural motifs in Li₂MnSiO₄ polymorphs. In this way we verify the proposed structural models and demonstrate that first-principles calculations can faithfully reproduce NMR observations for periodic systems containing abundant paramagnetic centers.

Three Li₂MnSiO₄ samples were prepared by hydrothermal synthesis and were subjected to different temperature

treatments afterwards. Detailed descriptions of sample preparation are presented in the ESI.† X-Ray powder diffraction patterns of the three samples are presented in Fig. 1. Analyses with Rietveld refinement confirmed that the diffraction patterns belong to three different structures (ESI†), which we shall denote simply by *Pmn*2₁, *Pmnb*, and *P*2₁/*n* polymorphs. Small differences in the structures are also reflected in different isotropic shifts and spinning-sideband patterns in ⁶Li MAS NMR spectra of these samples (Fig. 2). For *Pmn*2₁ and *Pmnb* polymorphs the spectra are characterized by single contributions with isotropic shifts of –125 ppm and –103 ppm, respectively. The spectrum of the *P*2₁/*n* polymorph comprises two equally strong contributions that can be assigned to Li nuclei occupying two crystallographically inequivalent Li sites within this polymorph. Isotropic shifts of the two contributions are –66 ppm and –94 ppm.

In Li₂MnSiO₄ materials the isotropic shifts and the spinning-sideband powder patterns are determined by hyperfine (contact) and dipolar (through-space) interactions between ⁶Li nuclei and unpaired electronic spins, respectively. The spinning-sideband powder pattern stemming from electron-nucleus dipolar interaction can be calculated relatively easily when locations of electronic spins are known.⁷ Using the proposed structural models for the three polymorphs we calculated the dipolar-interaction tensors. We considered electronic spins as being localized on Mn sites and took into account all sites within the sphere of radius of 0.8 nm around a Li nucleus. The corresponding results are presented in Fig. 3. The calculated anisotropy parameters correlate very well with the measured values. In *Pmn*2₁ and

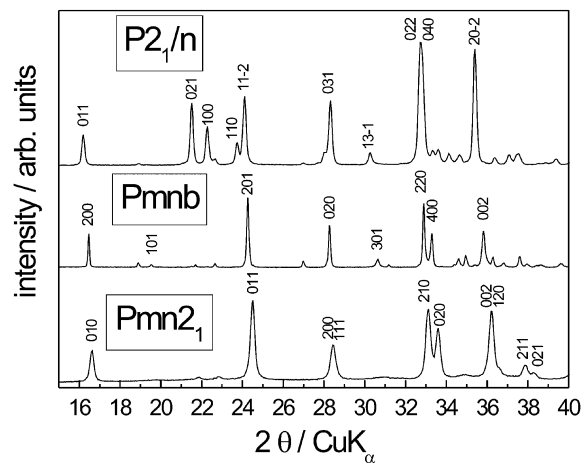


Fig. 1 X-Ray powder diffraction patterns of three Li₂MnSiO₄ polymorphs. Indexing of major diffraction peaks is based on the structural models, proposed by Rietveld analyses.

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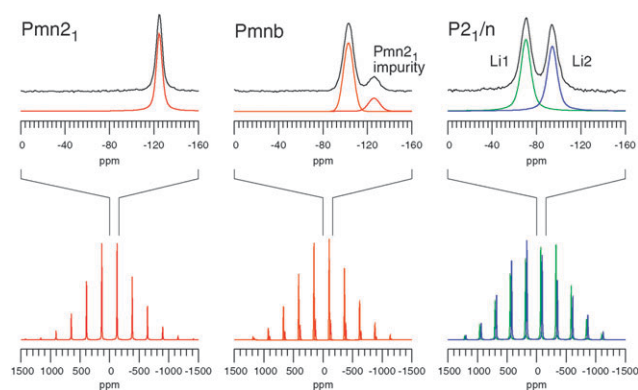


Fig. 2 ^6Li MAS NMR spectra of three $\text{Li}_2\text{MnSiO}_4$ polymorphs. The upper part shows isotropic bands, and the lower part presents the entire manifolds of spinning sidebands.

Pmnb polymorphs Li nuclei are surrounded by four Mn^{2+} ions that are sitting at the corners of slightly distorted tetrahedra. Such relatively symmetric environments lead to quite small electron–nucleus anisotropy parameters. In the *P2₁/n* polymorph, the Li nucleus occupying the Li1 crystallographic site is also surrounded by four Mn^{2+} ions, but it is displaced from the interior of the tetrahedron to one of the Mn–Mn edges. The resulting anisotropy parameter is therefore substantially larger. The Li nucleus on Li2 site is surrounded by only three Mn^{2+} ions and occupies an even less symmetric position on a Mn–Mn edge of the triangle. Li on this site experiences the largest electron–nucleus anisotropy parameter. Obviously, the anisotropy parameters reflect the short-range structural motifs very well and enable assignment of individual contributions of ^6Li MAS NMR spectra to individual Li crystallographic sites. In particular, NMR signals with anisotropy parameters of 1000 ppm and –1200 ppm in the spectrum of the *P2₁/n* polymorph can unequivocally be assigned to crystallographically inequivalent Li1 and Li2 sites, respectively.

Isotropic shifts in ^6Li MAS NMR spectra of $\text{Li}_2\text{MnSiO}_4$ polymorphs depend on the spin-density at the position of Li nuclei. Knowing the structure of the polymorphs, one could conduct first-principles calculations to determine spin-density⁸ within them and, using the latter, one could derive hyperfine coupling constants and isotropic shifts. This would open up an additional possibility for relating structural details to characteristics of NMR spectra.

In $\text{Li}_2\text{MnSiO}_4$ polymorphs isotropic shifts are small and differences among them are tiny. In order to improve accuracy of first-principles predictions and to establish a better relationship between the proposed structure and the detected isotropic shifts we employed a DFT projector-augmented-wave (PAW) approach as implemented in the GIPAW module of the Quantum Espresso code.⁹ In the first step the code performs a spin-polarized ground state calculation using norm-conserving pseudopotentials. In the second step the all-electron information is reconstructed using PAW, and hyperfine coupling constants are calculated. The above mentioned reconstruction yields correct spin-densities at positions of Li nuclei and thus provides hyperfine coupling constants without the need for integration of spin-density over a sphere

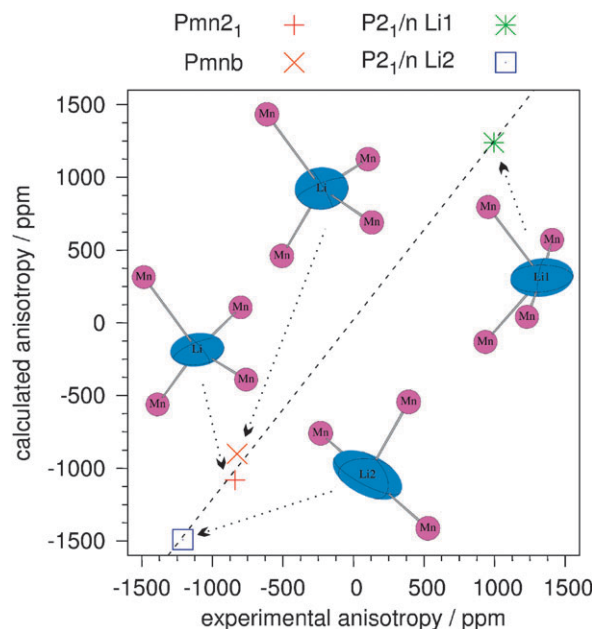


Fig. 3 Calculation of tensors, describing through-space electron–nucleus dipolar interaction. The graph shows the correlation between the measured and the calculated dipolar-interaction anisotropy parameters. The figure also shows arrangements of Mn ions around Li nuclei for each Li site within the three $\text{Li}_2\text{MnSiO}_4$ polymorphs. Ellipsoids on Li sites represent dipolar tensors, *i.e.* directions of principal axes and magnitudes of the corresponding eigenvalues. Oxygen atoms are omitted for clarity.

around a nucleus. Finally, isotropic shifts are obtained using the relation:

$$\delta^{\text{iso}} = \frac{1}{\gamma_n} \frac{g\mu_B S(S+1)}{3k_B T} A_{\text{en}}^{\text{iso}} \quad (1)$$

Here γ_n is the nuclear gyromagnetic ratio, μ_B is the Bohr magneton, S is the spin quantum number of the paramagnetic ion, and $A_{\text{en}}^{\text{iso}}$ is the hyperfine coupling constant. In our calculations we assumed $g = 2$, $T = 300$ K, and S is equal to the theoretical value for a particular ion (Mn^{2+} , Mn^{4+} , Co^{2+}).

In addition to $\text{Li}_2\text{MnSiO}_4$ polymorphs, the approach was also applied to three other potential cathode materials, Li_2MnO_3 ,¹⁰ LiMnPO_4 ,¹¹ and Li_6CoO_4 . In this way the DFT/PAW method was further tested. Prior to calculation of hyperfine coupling constants, geometry optimization of all structures was performed with Quantum Espresso's pwscf program. During the optimization only atomic coordinates were allowed to vary. The finally obtained isotropic shifts are presented in Fig. 4. In spite of the assumption that in NMR measurements all sample temperatures were equal, agreement between the calculated and the measured values is very good. The sign of the isotropic shift is proper and the magnitudes of the calculated shifts for ten different Li environments are very close to the measured ones. These results indicate that, as spinning-sideband patterns, isotropic shifts stemming from hyperfine coupling between paramagnetic transition-metal ions and ^6Li nuclei can also be related to short-range structural motifs.

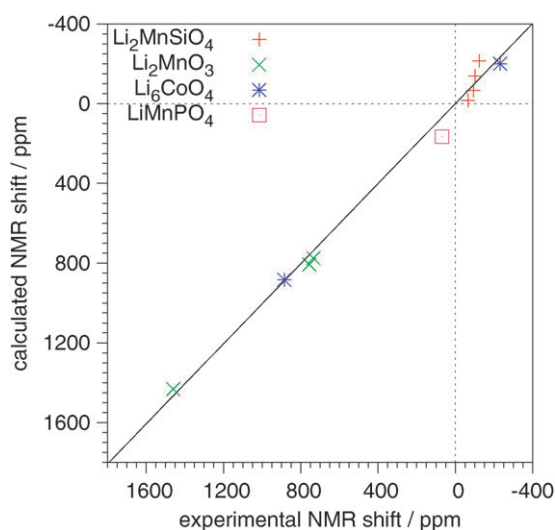


Fig. 4 The correlation between the measured and the calculated (using DFT with PAW reconstruction) isotropic shifts due to contact electron–nucleus hyperfine interactions in $\text{Li}_2\text{MnSiO}_4$ polymorphs and in several other potential Li cathode materials.

In conclusion, we have shown that NMR spectra not only clearly distinguish between polymorphs of $\text{Li}_2\text{MnSiO}_4$, but also correlate very well with the proposed structural models. The first-principles calculations of hyperfine coupling constants lead to remarkably accurate predictions of isotropic shifts in crystalline systems with abundant paramagnetic centers. So far successful calculations of NMR shifts have mostly been limited to paramagnetic materials with diluted paramagnetic centres and with isotropic shifts stemming from pseudo-contact interaction.¹² In our study we have, however,

demonstrated that isotropic shifts can also be accurately predicted for crystalline systems with abundant paramagnetic centres, where the shifts are governed by contact hyperfine interaction.

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