Experimental report

24/04/2019

Proposal: 5-31-2539 **Council:** 4/2017

Title: Crystal and magnetic structure of Pmnb-Li2FeSiO4

Research area: Physics

This proposal is a new proposal

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Samples: Li2FeSiO4

Instrument	Requested days	Allocated days	From	To
D2B	0	1	23/05/2018	24/05/2018
D20	2	1	22/05/2018	23/05/2018

Abstract:

The orthosilicates Li$_2FeSiO$_4$ are discussed as new high-capacity battery materials. We have recently grown the first small (ca. 10 mg) γ-Li$_2FeSiO$_4$ single crystals and the crystal structure was solved for the first time. Magnetic studies imply an antiferromagnetic ground state with a N\'eel-temperature of \tn\ = 17.0(5)\,K. The easy magnetic axis corresponds to the crystallographic a-axis. Despite a reasonably small anisotroy of 0.5 meV inferred from our high frequency ESR studies, magnetic fields of 15 T do not yield the spin-flop state. In addition, our high frequency ESR data imply short range AFM order up to around 150 K. We assume a non-trivial magnetic ground state in a frustrated magnetic system. We hence propose to study the magnetic structure of polycrystalline γ-Li$_2FeSiO$_4$ using neutron diffraction. In addition, we propose to investigate the crystal structure of γ-Li$_2FeSiO$_4$ by means of neutron diffraction because potential Li-site exchange is supposed to be relevant for the usage of this material for lithium-ion batteries.

Our experimental study in Li_2FeSiO_4 aimed at precise refinement of Li-positions in the crystal structure as well as on determination of the yet unknown magnetic ground state. Additionally, we intended to investigate the temperature evolution of the magnetic order parameter by performing a series of shorter scans. In preliminary studies, we had refined the crystal structure of Li_2FeSiO_4 laboratory single-crystal XRD data that are not very sensitive to weakly-scattering Li atoms. In the battery literature on Li_2FeSiO_4 significant site exchange between Li and Fe is discussed as a possible ingredient for the observed Li-ion mobility [1]. Therefore, a careful examination of the antisite defect formation is required.

We have carried out diffraction experiments on D2B and D20, one day each, in order to clarify the magnetic ground state and site exchange between Li and Fe ions. Additionally, we followed the temperature evolution of the magnetic order parameter by performing a series of shorter scans.

Magnetic Structure of Li_2FeSiO_4: The diffraction profiles obtained on the high intensity D20 powder diffractometer are displayed in Fig. 1 for selected temperatures in the two-theta range 10 – 50 °. A comparison of the PND patterns shows that superstructure reflections show up below 17 K due to magnetic scattering. As the temperature decreases, the intensity of the magnetic peaks increases, indicative of long-range magnetic ordering. The positions of the magnetic Bragg reflections do not change in the measured temperature range. The appearance of additional Bragg reflections (one exemplary peak is labeled by the asterisk in Fig. 1) at angles smaller than the angular position of the first nuclear reflection at 26.3 ° confirms the antiferromagnetic nature of spin ordering. By indexing the corresponding Bragg reflections, a magnetic propagation vector **k**=(½,0,½) is found. We conclude that the magnetic structure is commensurate with the nuclear lattice. The magnetic unit cell is double the crystallographic one in both the a and c-axis directions, while it is the same in the b-axis direction. Consequently, there are 16 Fe ions in the magnetic unit cell while the crystallographic unit cell features 4 Fe. For the space group $Pmnb$ and for **k**=(½,0,½) the magnetic reducible representation $\Gamma_{\rm mag}$ for the Fe^{2+} (4c) site is decomposed as direct sum of 2 non-zero irreducible representations (IRs):

$$\Gamma_{\rm mag} = 3\Gamma_1^2 \oplus 3\Gamma_2^2 \qquad (1)$$

From the two allowed antiferromagnetic spin configurations, only Γ_1 can reproduce the measured magnetic intensities. The resultant spin configuration is visualized in the inset of Fig. 2. The magnetic moments of Fe^{2+} are aligned antiferromagnetically along the a-axis

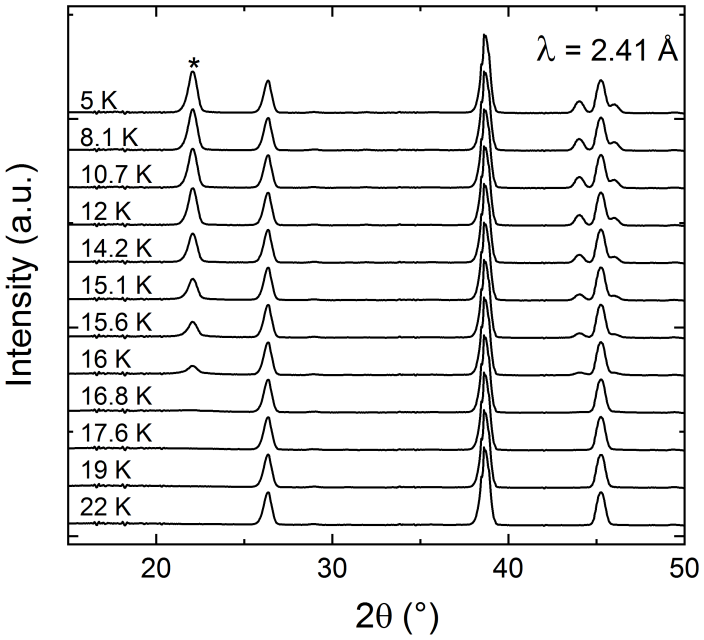

Figure 1: Neutron diffractograms at various temperatures between 5 and 22 K. The asterisk labels the (010) magnetic peak (and equivalents) used for determining the temperature dependence of sublattice magnetisation shown in Fig. 2.

with an ordered moment of 2.50(2) $\mu_{\rm B}$/Fe at $T = 1.5$ K. Its magnitude is significantly smaller than the theoretical value of 4.9 $\mu_{\rm B}$ for spin-only magnetic moment of Fe^{2+} in the high-spin $S = 2$-state.

Fig. 2 shows the integrated intensity ($I_B \propto |M_s|^2$, M_s is the order parameter) of the strongest magnetic peak (010) in the temperature range 2 – 19 K. The intensity vanishes at around $T_{\rm N} \approx 17.0$ K which agrees with the macroscopic measurements. In the conventional picture of a continuous phase transition the magnetic order parameter obeys a power-law equation. By fitting the integrated intensity to the power-law scaling function $I_B = I_0|t|^{2\beta}$, where $t = 1 - T/T_{\rm N}$ is the reduced temperature, an estimate for the critical exponent of $\beta = 0.32(3)$ is obtained.

Antisite defects in Li_2FeSiO_4: The powder neutron diffractogram on Li_2FeSiO_4 shown in Fig. 3 confirms the $Pmnb$-structure and in addition enables investigating possible antisite defect formation in this material. The data were collected on the D2B diffractometer using a wavelength of 1.051 Å corresponding to the (557) reflecting planes of a germanium monochromator. In general, the crystal structure of lithium transition metal orthosilicates Li_2MSiO_4 (M = Mn, Fe) exhibits comparable Li – O and M – O bond lengths which is known to give rise to Li – M antisite defects. Due to the large difference in the coherent neutron scattering lenghts of Li and Fe (-1.90 and 9.45 fm, respectively) high-resolution neutron diffraction (PND) studies open the possibility

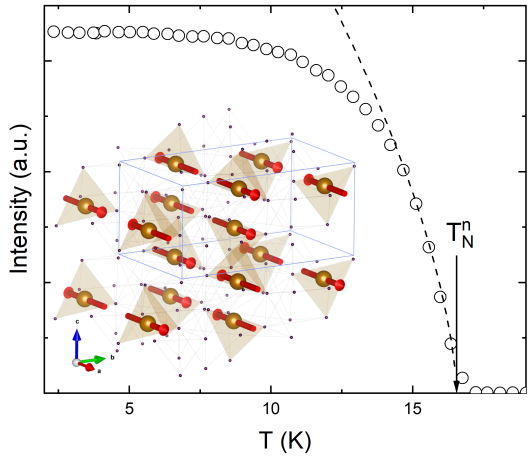

Figure 2: Magnetic order parameter as derived from integrating the peak intensity of the (010) magnetic superstructure reflection (see Fig. 1). The dashed line shows a fit to the data (see the text). Inset: sketch of the spin configuration. Lines show the crystallographic unit cell.

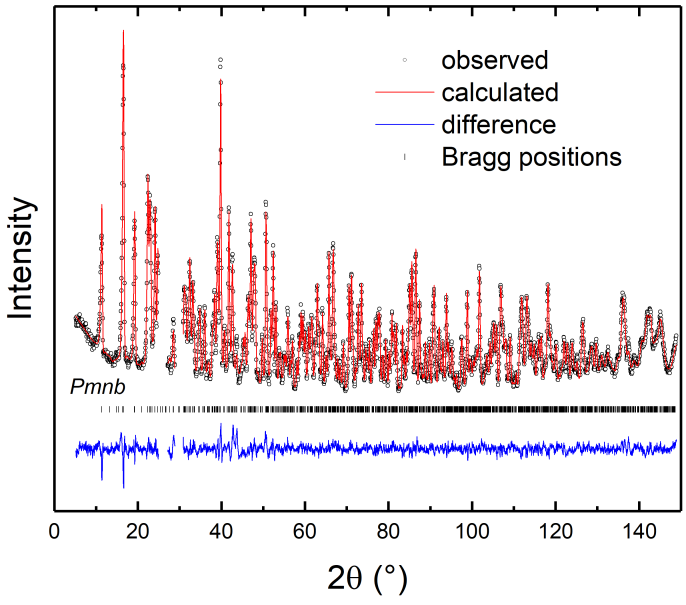

Figure 3: Observed (open circles), calculated (full line) and difference (bottom) intensities for the neutron Rietveld refinement of polycrystalline $Pmnb$-Li_2FeSiO_4 at 25 K. Vertical ticks refer to the nuclear Bragg positions. Some regions with extra diffraction peaks due to the sample mount in a cryostat were excluded from the refinement. Reliability factors: $\chi^2 = 2.57$, Rwp = 9.25, Rp = 7.98, Bragg R-factor = 3.13.

to study the antisite disorder. Generally, compounds with tetrahedrally coordinated ions are more prone to site exchange than compounds with octahedral coordination since the crystal field stabilization energies are usually lower. Note, that DFT calculations on the $Pmnb$-polymorph suggest that additional exchange of Li and Fe over their primary sites is favourable upon delithiation [2]. The high-resolution PND pattern in Fig. 3 indicates cation mixing between the two crystallographic sites 8d and 4c. The data were recorded with a wavelength λ = 1.051 Å in the paramagnetic regime at 25 K. Rietveld refinement in the $Pmnb$ space group was done with total occupancy of each site constrained to unity. The analysis yields that the fit quality significantly improves when considering Li – Fe site exchange. Structural refinement was stable and the reliability factors minimized when assuming a fraction of around 2 % antisite defects for the final model [3].

The results have been partly (i.e., analysis of antisite defects) published in [3] while publication of the spin configuration including numerical studies is in preparation [4].

References:

[1] A. Boulineau et al:, Dalton Trans. 39, 2010, 6310-6316.
[2] A. Liivat: Solid State Ionics, 228, 2012, 19-24.
[3] W. Hergett et al: J. Cryst. Growth 515, 2019, 37-43.
[4] W. Hergett, N. Bouldi et al., unpublished.