Structural, magnetic, and diffusive nature of olivine-type Na$_x$FePO$_4$

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Abstract. In order to investigate the microscopic magnetic nature of a sodium phospho-olivine, we have measured $\mu$+SR spectra for Na$_x$FePO$_4$ using a powder sample in the temperature range between 2 and 500 K. ZF-$\mu$+SR measurements below 200 K at TRIUMF showed the appearance of static magnetic order below $T_N \sim 61$ K, where the susceptibility-vs.-temperature curve exhibits a sharp maximum due to an antiferromagnetic (AF) transition. The wide distribution found for the internal magnetic field ($H_{int}$) was explained by the formation of AF order with the spread in $H_{int}$ due to random distribution of Na vacancies. At higher temperatures, the ZF-spectrum for Na$_{0.7}$FePO$_4$, obtained at J-PARC, is found to change from a low-$T$ static behavior to a high-$T$ dynamic behavior above $\sim 300$ K. This is consistent with the fact that Na$^+$ ions are reversibly extracted from and intercalated into the Na$_x$FePO$_4$ lattice, while there is no NMR study on Na-diffusion in Na$_x$FePO$_4$ due to large Fe moments.

1. Introduction

Recently, Na-ion battery materials attracted great attention [1, 2, 3], since sodium is more abundant than Li, resulting in lower material costs. For instance, Na$_x$CoO$_2$, which is an analogue to LiCoO$_2$, was originally studied as a positive electrode material for Na-ion batteries [4], before the huge amount of work on its thermoelectric [5], magnetic [6, 7], and superconducting properties [8]. In 2010, phospho-olivines with Na, i.e. NaFePO$_4$ and Na$_{0.7}$FePO$_4$ were reported to show reversible insertion and extraction of Na into olivine FePO$_4$ [9]. In the initial study, only the above two compositions were obtained as single phase. More detailed study, however, suggests that Na$_{2+x}$FePO$_4$ with $2/3 \leq x \leq 1$ is a single phase region below ambient temperature [10]. Since then, the electrochemical properties of Na$_x$FePO$_4$ have been naturally eagerly investigated [11, 12, 13, 14, 15, 16], while the physical properties are still not fully clarified, partially due to difficulty of sample preparation.
Very recent specific heat and neutron diffraction (ND) measurements showed that NaFePO$_4$ is also an antiferromagnet with $T_N \sim 50$ K and a collinear spin structure along the $b$-axis [17], as for LiFePO$_4$ with $T_N = 53$ K. But, since Li$_x$FePO$_4$ is known to be a mixture between $x$ LiFePO$_4$ and $(1-x)$ FePO$_4$ [18, 19], a single phase sample of Li$_x$FePO$_4$ with $0 < x < 1$ can not be obtained by usual chemical and electrochemical reactions. Fortunately, that is not the case for Na$_x$FePO$_4$, for which the change in physical properties can be investigated in single-phase samples with $x$ down to 2/3. Particularly, due to Na deficiency together with low-dimensionality, a complex magnetic behavior, such as short-range order or incommensurate order could be expected to appear at low temperatures, as for Li$_x$CoO$_2$ [20] and Li$_x$NiO$_2$ [21]. Here, we report initial $\mu^+$SR studies of the local magnetic environment and diffusion properties of Na$_{0.7}$FePO$_4$.

![Figure 1. Crystal structure of Na$_{0.7}$FePO$_4$.](image)

The Rietvelt refinement of a power XRD pattern obtained at 295 K indicates as follows; space group = $Pnma$, $a = 10.2841(2)$ Å, $b = 6.0800(2)$ Å, and $c = 4.9373(2)$ Å. The atomic positions are; Na: (0, 0, 0), Fe: [0.28392(6), 3/4, 0.9860(2)], P: [0.1065(2), 3/4, 0.4391(3)], O1: [-0.0391(4), 3/4, 0.3502(6)], O2: [0.6200(3), 3/4, -0.2460(6)], and O3: [0.1766(3), 0.5520(4), 0.3035(4)]. The occupancy of the Na site is 0.7, indicating random distribution of Na.

![Figure 2. $T$ dependences of (a) $\chi$, and (b) $1/\chi$ for Na$_{0.7}$FePO$_4$. In (b), solid lines represent a linear fit in the $T$ range between 100 and 400 K using a Curie-Weiss formula.](image)

2. Experimental

As starting material a powder sample of LiFePO$_4$ was prepared by a solid-state reaction technique using reagent grade Li$_2$CO$_3$, Fe(II)C$_2$O$_4$•2H$_2$O, and (NH$_4$)$_2$HPO$_4$. A stoichiometric mixture of the raw materials was thoroughly mixed by a conventional planetary milling apparatus, and then sintered at 700°C for 6 h in a purified argon gas flow. Then, in order to obtain FePO$_4$, the LiFePO$_4$ powder was immersed into an acetonitrile solution of NO$_2$BF$_4$ and was refluxed at room temperature for a day. Finally, in order to obtain Na$_x$FePO$_4$, the FePO$_4$ powder was immersed into an acetonitrile solution of NaI and was refluxed at room temperature for a day.

According to powder x-ray diffraction (XRD) analysis, the Na$_x$FePO$_4$ sample consists of a major Na$_{0.7}$FePO$_4$ phase (see Fig. 1) and a minor FePO$_4$ phase. The volume fraction of
the FePO₄ phase was estimated below 3%. The XRD result is very consistent with that of the composition analyses by an inductively coupled plasma atomic emission spectral (ICP-AES) technique. In order to know the macroscopic magnetic properties, susceptibility (χ) was measured below 400 K under a H ≤10 kOe field with a SQUID magnetometer (MPMS, Quantum Design). The χ(T) curve clearly indicates the presence of the AF transition at T_N = 66 K (Fig. 2).

The μ⁺SR spectra were measured at the surface muon beam lines using the LAMPF spectrometer of TRIUMF in Canada and the D-OMEGA1 spectrometer of MUSE/MLF/J-PARC in Japan. In TRIUMF, the approximately 500 mg powder sample was placed in an envelope with 1 cm×1 cm area, which is made of very thin Al-coated Mylar tape, and then the envelope was attached to a low-background sample holder in a liquid-He flow-type cryostat for the T range between 1.8 and 250 K. In J-PARC, a ~ 2 g powder sample was pressed into a disc with 23 mm diameter and 1 mm thickness, and packed into an Au O-ring sealed titanium cell. The window of the cell was made of a titanium film with 25 μm thickness. The cell was mounted onto the Cu plate of a liquid-He flow-type cryostat for measurements between 10 and 500 K.

3. Results and discussion

3.1. low temperature magnetism

We have measured the wTF-μ⁺SR spectrum with H_TF = 50 Oe to study the volume fraction of non-magnetic phases in the sample. Figure 3 shows the T dependences of the normalized A_{TF} (N_{ATF} ≡ A_{TF}/A_0) and λ_TF. The A_{TF}(T) curve shows a step-like change at T^T_N = 64.5 K, at which N_{ATF} = 0.5, indicating the sample is almost single phase.

Figure 4 shows the ZF-μ⁺SR time spectrum at the lowest T measured (2 K). One can clearly

![Figure 3](image-url)  
Figure 3. T dependences of (a) the normalized wTF asymmetry and (b) its exponential relaxation rate (λ_{TF}) for Na₀.₇FePO₄. The data were obtained by fitting the wTF-μ⁺SR spectra measured with H_{TF} = 50 Oe.

![Figure 4](image-url)  
Figure 4. The ZF-μ⁺SR time-spectrum for Na₀.₇FePO₄ at 2.0 K.
see a rapidly damping oscillation. Indeed, it is hard to find a third maximum even at 2 K. Such situation is easily understood from the Fourier Transform of the time spectrum. That is, the full width at half maximum (FWHM) of the peak is comparable to the oscillation frequency, reflecting the wide distribution of $H_{\text{int}}$. The ZF-spectrum was fitted by a combination of a Gaussian relaxing cosine oscillation due to the ordered field, and two exponentially relaxing non-oscillatory signals; one is for a fast relaxing signal apparent even in the ordered state, and the other, labeled slow signal, for the typical ZF "1/3 tail" due to the field component parallel to the initial muon-spin polarization.

\[ A_0 P_{\text{ZF}}(t) = A_{\text{AF}} \cos(2\pi f_{\text{AF}} t + \phi_{\text{AF}}) \exp(-\frac{\sigma_{\text{AF}}^2 t^2}{2}) + A_I \exp(-\lambda_I t) + A_s \exp(-\lambda_s t), \]  

where $P_{\text{ZF}}(t)$ is the muon spin polarization function under ZF, $A_{\text{AF}}, A_I$, and $A_s$ are the asymmetries associated with the three signals, and $\sigma_{\text{AF}}, \lambda_I$, and $\lambda_s$ ($\lambda_I \gg \lambda_s$) are their Gaussian and exponential relaxation rates. The fit using Eq. (1) at each $T$ showed that $A_{\text{AF}}, A_I, A_s$, and $\lambda_I$ are almost $T$ independent. At 2 K, $\phi_{\text{AF}} = -17$ degree and, as $T$ increases from 2 K to 45 K, $\phi_{\text{AF}}$ decreases slowly down to -30 degree, then decreases rapidly down to -70 deg with further increasing $T$. Therefore, we finally fitted all the ZF-spectra using common $A_{\text{AF}}, A_I, \lambda_I$, and $A_s$. Such a “global fit” provides that $A_{\text{AF}} = 0.090(2), A_I = 0.0250(9), \lambda_I = 1.1(1) \times 10^9 \text{ s}^{-1}$, and $A_s = 0.0577(12)$.

Figure 5 show the $T$ dependences of the four independent $\mu^+\text{SR}$ parameters, i.e. $f_{\text{AF}}, \phi_{\text{AF}}, \sigma_{\text{AF}}$ and $\lambda_s$. The $f_{\text{AF}}(T)$ curve exhibits an order-parameter-like $T$-dependence. Namely, as $T$ decreases from $T_N$, $f_{\text{AF}}$ increases monotonically down to the lowest $T$ measured with decreasing slope $(df_{\text{AF}}/dT)$. $\phi_{\text{AF}}$ shows a remarkable $T$-variation below the vicinity of $T_N$ probably due to the change in the field distribution, while it looks almost $T$-independent below 45 K. The relaxation rate $\sigma_{\text{AF}}$ exhibits a maximum at $T_N$, then decreases with decreasing $T$, and levels off to a constant value below $\sim 50$ K [Fig. 5(b)]. On the contrary, $\lambda_s$ approximately decreases with decreasing $T$, and finally approaches 0 with $T \to 0$. The fact that $\lambda_s \ll \sigma_{\text{AF}}$ is also very reasonable for a 1/3 tail signal.

Since there are four Na ions in the NaFePO$_4$ lattice, we attempted to calculate dipole fields in Na$_3^+\text{Fe}_3^{2+}\text{Fe}^{3+}(\text{PO}_4)_{4}^{3-}$ (= Na$_{3/4}$FePO$_4$) using the same structural data for NaFePO$_4$ and the assumption that the implanted muons locate at the vicinity of O$^{2-}$ ions 1 Å away. We further assumed that the valence of the Fe ion close to the vacant Na site (□) is not 2+ but 3+ in order to keep charge neutrality. Such a simple model drastically altered the electrostatic potential around each oxygen, resulting in 16 different muon sites in the lattice. In addition, if we assume a collinear AF spin structure along the b-axis with full Fe moments for Na$_{3/4}$FePO$_4$ as proposed for NaFePO$_4$ [17], dipole field calculations provided an internal field $[(\gamma_\mu/2\pi)H_{\text{int},i} = f_i, (i = 1-16)]$ for each muon site, where $\gamma_\mu/2\pi = 13.554 \text{ kHz/Oe}$ is the muon gyromagnetic ratio. The predicted distribution of $H_{\text{int}}$ reasonably reproduces the measured $H_{\text{int}}$ (see Fig. 6). Here, we define the number density ($D_i = 1$) for each $f_i$ and $A_{\text{real}}$ for the real amplitude of the Fourier transform of the ZF-$\mu^+\text{SR}$ time spectrum. Assuming that $f_{\text{calc}}$ at which $\frac{1}{\pi} \sum_{i=1}^{16} D_i = 0.5$ is equivalent to $f$ at which $\int_0^f A_{\text{real}} df = 0.5 \int_0^{100\text{MHz}} A_{\text{real}} df$, $\mu_{\text{org}}$ is estimated as 48% for the full Fe moments at 2 K; that is, 2.3 $\mu_B$ for Fe$^{3+}$ and 2.8 $\mu_B$ for Fe$^{2+}$. This is consistent with the presence of the fast relaxing signal in the ZF-spectrum even at 2 K. Note that the employed model naturally leads to the order of Na vacancies and Fe$^{3+}$. For the disordered state, which is more suitable for Na$_{0.7}$FePO$_4$, the field distribution is expected to be broader and, therefore, this model is the more reasonable approach for interpreting the data.

In the above discussion, we simply reduced both Fe$^{3+}$ and Fe$^{2+}$ moments with the same factor (48%) to the full moments. This is because $\chi$ measurements with $H = 10$ kOe (Fig. 2) show a typical AF nature and luck an indication for ferrimagnetism, which might change the sum
of the moments. In order to further clarify the magnetic structure, we definitely need neutron diffraction measurements for Na$_{0.7}$FePO$_4$.

Back to the fit results, the fact that $\phi_{AF} \sim -30 \text{ degree} \text{ below} \text{ 45 K}$ implies the wide distribution of an internal field at the muon site(s). Because of the mismatch of the period between the muon site(s) and magnetic order, incommensurate (IC) order always provides an oscillatory signal with wide field distribution in the ZF-$\mu^+$SR spectrum. Thus, the delay of $\phi_{AF}$ is thought to be a signature of IC magnetic order [22]. However, if there are multiple muon sites with different $H_{int}$s, the ZF-$\mu^+$SR spectrum also shows a damped oscillation due to wide field

Figure 5. $T$ dependences of (a) the muon-spin precession frequency ($f_{AF}$), (b) its initial phase ($\phi_{AF}$), (c) its Gaussian relaxation rate ($\sigma_{AM}$), and (d) the exponential relaxation rate ($\lambda_{tail}$) for the 1/3 tail signal. In (a), the red solid line on the $f_{AF}(T)$ curve corresponds to $f(T)/f(0 \text{ K}) = [(T_N - T)/T_N]^\beta$ with $f(0 \text{ K}) = 45(2) \text{ MHz}$, $T_N = 61.22(2) \text{ K}$, and $\beta = 0.18(3)$.

Figure 6. (a) Dipolar field distribution for Na$_{0.7}$FePO$_4$ and (b) the Fourier transformed frequency spectrum of the ZF-$\mu^+$SR time spectrum at 2 K. In (a) and (b), black solid lines represent the integral of the number density or amplitude.
distribution, as in the case for Ag\textsubscript{2}NiO\textsubscript{2} [23] and LiCrO\textsubscript{2} [24]. Based on the above discussion, the latter is most likely for Na\textsubscript{0.7}FePO\textsubscript{4}.

### 3.2. high temperature diffusion

In the paramagnetic state above \(T_N\), the ZF-\(\mu^+\)SR spectrum is well explained by an exponentially relaxing dynamic Gaussian Kubo-Toyabe function \(\exp(-\lambda t)G^\text{DGKT}(\Delta, \nu, t, H_{LF})\) caused by a fluctuating nuclear magnetic field due to \(^{23}\text{Na}\) and \(^{31}\text{P}\) and an offset background (BG) signal from the fraction of muons stopped mainly in the sample cell, which is made of high-purity titanium (Fig. 7). The multiplied exponential relaxation \(\exp(-\lambda t)\) is caused by paramagnetic Fe moments [25].

![Figure 7. ZF- and LF-\(\mu^+\)SR spectra for Na\textsubscript{0.7}FePO\textsubscript{4} obtained at 150 K. Applied LF were 5 and 10 Oe.](image)

Figure 8 shows the \(T\)-dependences of \(\mu^+\)SR parameters. Here, we assumed that the \(T\) dependence of \(\lambda\) is similar to that of \(\chi\). As \(T\) increases from 150 K, \(\Delta\) is almost \(T\)-independent until 400 K, and decreases slightly with \(T\). On the other hand, \(\nu\) starts to increase above around 200 K, reaches a maximum at 425 K, and then decreases with further increasing \(T\). Making comparison with the result of LiFePO\textsubscript{4} [26, 27], the reason for the increase in \(\nu\) is most likely due to Na-diffusion in the lattice.

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