Na diffusion in Na_xFeO_2

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In order to develop next-generation Na-ion batteries,[1] we have attempted to measure Na diffusion in several candidate materials with μ^+SR.[2] The present target compound, α-$NaFeO_2$, has a layered rocksalt structure with the trigonal space group $R\bar{3}m$ (Fig. 1). The isostructural compound, $NaCoO_2$, works as a positive electrode material owing to reversible Na^+ deintercalation from and intercalation into the lattice.[3] Furthermore, μ^+SR clearly detected Na diffusive behavior in Na_xCoO_2 at high T,[2] which is consistent with electron diffraction and neutron scattering results.[4] However, α-$NaFeO_2$ does not exhibit reversible Na deintercalation and intercalation behavior.[5]

The following two explanations were proposed for such behavior in α-$NaFeO_2$, 1) Na ions do not diffuse, or 2) Na ions diffuse, but electrons are not transferred for charge compensation. Since α-$NaFeO_2$ is an antiferromagnetic insulator,[6,7] the second explanation is more reasonable.

Figure 2 shows the T dependences of the field fluctuation rate (ν) and field distribution width (Δ) for α-$NaFeO_2$ and $Na_{0.7}CoO_2$ extracted from the μ^+SR spectra measured on ARGUS. Here, ν corresponds to the spin-lattice relaxation rate (T_1^{-1}) of NMR, and Δ corresponds to the spin-spin relaxation rate (T_2^{-1}). For $Na_{0.7}CoO_2$, ν increases with T particularly above 325 K, while Δ decreases with T. This is a typical motional narrowing behavior due to Na diffusion.

For α-$NaFeO_2$, both ν and Δ are scattered in the whole T range measured. In particular, there is no acceptable reason for the increase in Δ above 300 K. Note that even for stoichiometric $NaFeO_2$, there are interstitial sites between two adjacent Na^+ ions, to which Na^+ ions jump, as in the case for $LiNiO_2$.[8] Back to the data analysis, the ZF- and LF-spectra were fitted by a combination of an exponentially relaxing dynamic Kubo-Toyabe signal and a time-independent background signal from the muons stopped in the sample holder. This indicates the presence of two muon sites in the lattice, although the muon sites are unknown at present. However, owing to the large exponential relaxation of the two terms caused by the fluctuation of the Fe^{3+} moments, it is very difficult to extract ν and Δ from the present μ^+SR spectrum with the statistics of 18M events. Thus, we need additional data with higher statistics.

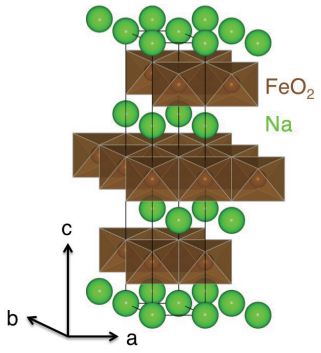

Fig. 1. Crystal structure of α-$NaFeO_2$ consisting of a two-dimensional triangular lattice of FeO_2 layers formed by edge sharing FeO_6 octahedra separated by the Na layer.

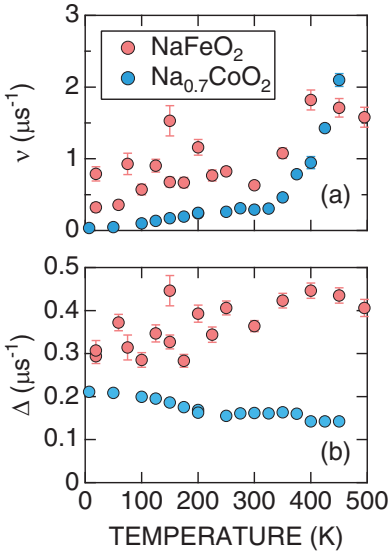

Fig. 2. T dependences of the field fluctuation rate (ν) and field distribution width (Δ) for α-$NaFeO_2$ and $Na_{0.7}CoO_2$.

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