Na dynamics in the quasi-one-dimensional ionic conductor NaM_2O_4 (M=Ti and V)

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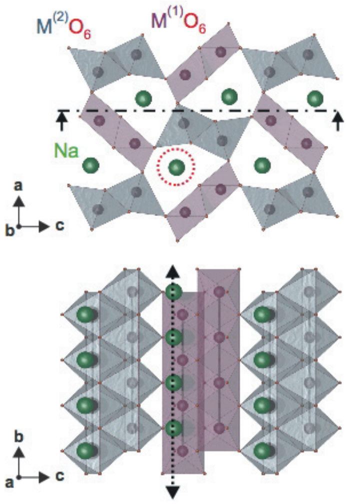

Fig. 1. Crystal structure of NaM_2O_4.

In the NaM_2O_4 lattice with a $CaFe_2O_4$-type orthorhombic structure, the Na^+ ions are located at the center of a one-dimensional (1D) tunnel along the b-axis, which is formed by 1D double chains consisting of edge-sharing MO_6 octahedra (M: transition metal) (see Fig. 1). The physical properties of NaM_2O_4 are reported to strongly depend on M. In particular, it is very important to clarify their Na^+-ion conductivity (σ_{Na}) and/or Na^+-ion diffusion coefficient (D_{Na}) when using NaM_2O_4 as a solid electrolyte in an all-solid-state Na-ion battery.

Following the preliminary report on NaV_2O_4[1], we explain here in the results of μ^+SR measurements on NaM_2O_4 (M=Ti and V). The former is a semiconductor with a small band gap[2], while the latter is a half metal with anisotropic electric conductivity[3]. Both ZF- and LF-μ^+SR spectra were measured in the temperature (T) range between 145 and 500 K. The obtained spectra were fitted by a combination of an exponentially relaxing dynamic Kubo-Toyabe signal from a sample and a non-relaxing background signal from a titanium sample holder.

Figure 2 shows the T dependences of field fluctuation rate (ν), field distribution width (Δ), and exponential relaxation rate (λ) for (a) $NaTi_2O_4$ and (b) NaV_2O_4. For $NaTi_2O_4$, as T increases from 150 K, Δ slowly decreases, while ν increases rapidly particularly above 350 K. This indicates that the local nuclear magnetic field experienced by μ^+ starts to fluctuate because of Na^+ diffusion. For NaV_2O_4, on the other hand, even at 150 K ν is comparable to that for $NaTi_2O_4$ at 450 K. This indicates that Na^+ ions diffuse even at 150 K in NaV_2O_4. The anomaly around 450 K in the $\nu(T)$ curve is probably caused by a structural phase transition.

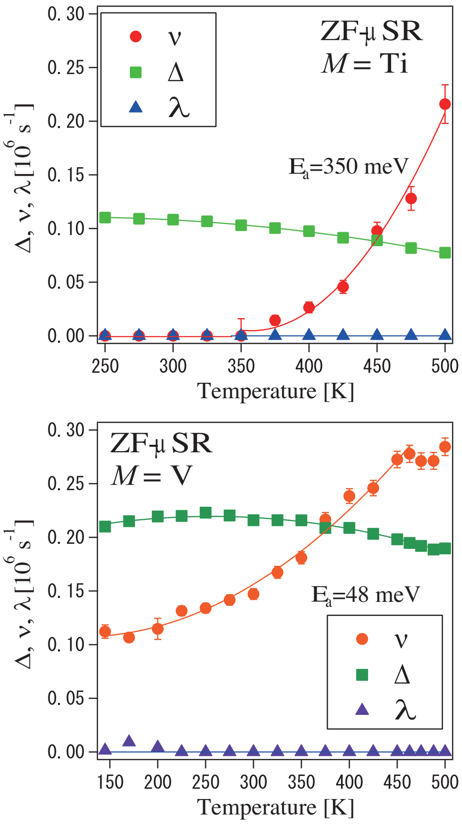

Fig. 2. T-dependences of field fluctuation rate (ν), field distribution width (Δ), and exponential relaxation rate (λ) for (a) $NaTi_2O_4$ and (b) NaV_2O_4.

If we assume a thermal activation process for the T dependence of ν, the activation energy (E_a) is estimated to be 350 meV for $NaTi_2O_4$ and 48 meV for NaV_2O_4. Since the simple Nernst-Einstein equation states that $\sigma_{Na} \propto D_{Na}$, where $D \propto \nu$, NaV_2O_4 is expected to be a good candidate for a Na^+-ionic conductor.

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References

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