Structural analysis of magnetically ordered NaV_6O_{11}

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Introduction

NaV_6O_{11} is interesting from viewpoints of S=1 *kagomé* lattice and magnetic metal character. Its magnetic susceptibility (χ) obeys Curie-Weiss law above T_t (=242.7 K), but shows a spin gap between 80.1 K (=T_C) and T_t. Below T_C, it shows uniaxial magnetic anisotropy with an easy axis of magnetization parallel to [001] direction [1].

NaV_6O_{11} shows two-step structural phase transitions on cooling: $P6_3/mmc$ – $P6_3mc$ – $Cmc2_1$, with transition temperatures at T_t and 80.1 K (=$T_{h\text{-}o}$), respectively [2-4]. Crystal structures of the former two have been determined, however, structural study of the $Cmc2_1$ form is limited to qualitative so far.

In this study, the $P6_3mc$ – $Cmc2_1$ transition was investigated by X-ray powder diffraction study at BL-1B coupled with Rietveld analysis.

Experimental

Diffraction data (λ=1.0028 Å) were obtained at BL-1B with exposure time of 4 min. and ω-oscillation of ±10 deg. The data were analyzed by RIETAN-2000 [5].

Results and discussion

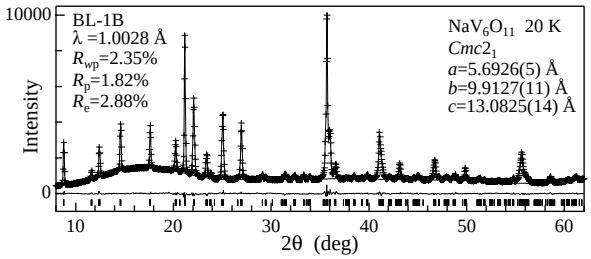

Fig. 1. Diffraction profile of NaV_6O_{11} at 20 K.

The Rietveld analyses (Fig. 1) were carried out for the data at 20 –60 K and 80–120 K with intervals of 10 K.

The $P6_3/mmc$ form consists of three types of V atoms. The $V(1)O_6$ octahedra form a regular *kagomé* lattice perpendicular to [001] by edge-sharing. The $V(2)O_6$ octahedra form a face-sharing dimer parallel to [001]. The $V(3)O_5$ is a coordination trigonal-bipyramid. Here we focus on the V(1) and V(2) atoms.

In the $P6_3mc$ form, the V(1) regular *kagomé* lattice distorts to form a $V(1)_3$ trimer. The V(2) atoms branch into two types, so the $V(2)_2$ dimer changes to a V(21)-V(22) pair. In the $Cmc2_1$ form, the V(1) atoms branch into two types, V(1a) and V(1b). The $V(1)_3$ trimer distorts from regular triangle to the $V(1a)V(1b)_2$ isosceles triangle. Remaining V atoms show no branching.

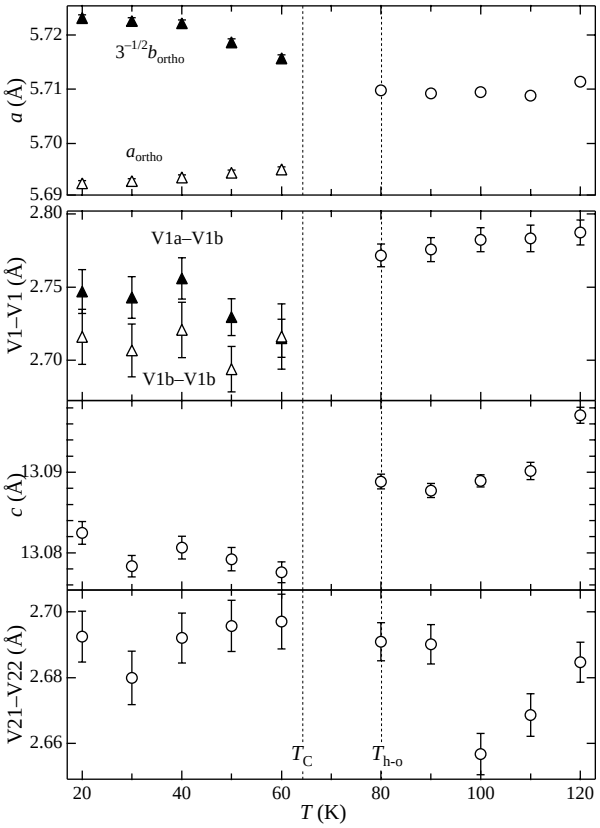

Fig. 2. Lattice parameters and V-V distances.

The V(1)-V(1) distance decreases gradually on cooling in the $P6_3mc$ form, but decreases abruptly on the $P6_3mc$ – $Cmc2_1$ transition (Fig. 2). The $V(1a)V(1b)_2$ triangle shows a pair of longer V(1a)–V(1b) and a shorter V(1b)–V(1b). The former increases gradually while the latter remains almost unchanged on cooling. The V(21)–V(22) does not show any detectable change on the $P6_3mc$ – $Cmc2_1$ transition.

References

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