

Crystal structure of the spin-1/2 frustrated square lattice magnet $2\text{VOSO}_4 \cdot \text{H}_2\text{SO}_4 \cdot n\text{H}_2\text{O}$

Kazuhiro Nawa^A, Miwako Takahashi^B, Yukio Noda^{A,C}, and Taku J Sato^A

^AIMRAM, Tohoku University, ^BDept. of Materials Science, Institute of Pure and Applied Sciences, University of Tsukuba, ^CISSP, The Univ. of Tokyo

A spin-1/2 J_1 - J_2 frustrated square lattice magnet with competing ferromagnetic nearest-neighbor (NN) interactions J_1 and next-nearest neighbor (NNN) antiferromagnetic interactions J_2 has attracted interests in terms of the expectation of a spin nematic state, where time-reversal symmetry is preserved but rotation symmetry is broken [1, 2]. Recently, we discovered that magnetic interactions of the spin-1/2 J_1 - J_2 frustrated square lattice magnet $2\text{VOSO}_4 \cdot \text{H}_2\text{SO}_4 \cdot n\text{H}_2\text{O}$ can be tuned by changing the cooling rate. This compound crystallizes in the space group $P4_2/mnm$ with the unit cell constants $a = 8.982$ and $c = 15.61$ Å [3]. The magnetic interactions J_1 and J_2 were estimated by the magnetization measurements under rapid (>200 K/min) and slow cooling (1 K/min) rates as (-2.5 K, 5.3 K) and (-2.1 K, 6.7 K) respectively.

The key to understand the cooling rate dependence is the structural transition near room temperature. We deduce that the structural transition is induced by switching of hydrogen bonding and influence the magnetism, as proposed for volborthite but not confirmed experimentally [4]. The position of water molecules in this compound is not known but should be present at a vacant space between Vanadium sulfate layers. To confirm our expectation, we have performed single crystalline neutron diffraction experiments using four circle diffractometer FONDER, using the wavelength of 1.2464 Å. A deuterated platelike sample with a mass of 16 mg was used for the experiments.

Although the tetragonal structure is expected at the room temperature, the crystal includes not only a domain of the high temperature tetragonal phase but also a few structural domains of the low-temperature phase. The crystal orientation was defined mainly based on the 00L reflections and some in-plane reflections that are found near the plane

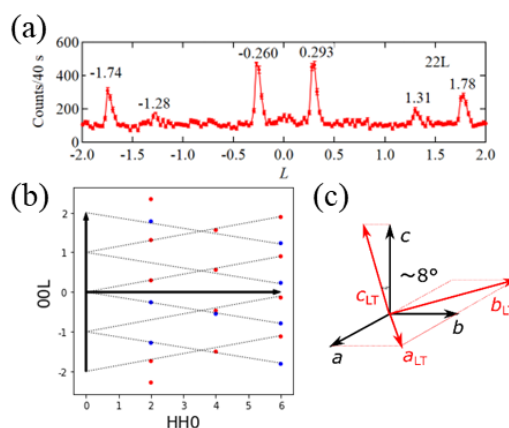


Figure (a) Representative 22L scan. (b) Distribution of nuclear reflections in the HHL plane. (c) Schematic view comparing the unit cell of the low temperature (red) and the room temperature phases (black).

perpendicular to the c^* -axis. Figure (a) shows the representative 22L scan. A lot of strong nuclear reflections are found at non-integer positions. Figure (b) illustrates the positions of the observed nuclear reflections in the HHL plane. Their positions were explained by a structural model with a different unit cell, where a^* and b^* axes are inclined away from the plane perpendicular to the c^* axis. The expected unit cell of the low-temperature and the high-temperature phases are compared in Figure (c). Structural domains should be created when the room temperature around the sample (stored in the globeox in the lab) becomes lower (<20 °C). Based on these results, we have prepared fresh and well-sized (nondeuterated) single crystals and completed further single neutron diffraction experiments using FONDER in 2024.

[1] B. Schmidt et al., Phys. Rev. B **76**, 125113 (2007). [2] N. Shannon et al., Phys. Rev. Lett. **96**, 027213 (2006). [3] P. M. Tachez and F. Theobald, Acta. Cryst. **B37**, 1978 (2008). [4] Z. Hiroi et al., Inorg. Chem. **58**, 11949 (2019).