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Crystal structure of geometrically frustrated spinel AlV_2O_4

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Introduction

Spinel compound AlV_2O_4 is known to show charge-ordering (CO) behavior below T_{CO} ~ 700K [1]. Upon the phase transition at T_{CO}, the electrical resistivity sharply increases and the magnetic susceptibility is suppressed. The CO state has a rhombohedrally distorted spinel structure. A structural model reported previously is that the V ions on the *Kagome* lattices and those on the triangular lattices with different valences stack alternately along the [111] direction. However, both x-ray powder diffraction and electron diffraction (ED) experiments show the presence of the superlattice structure with the wave vector q=1/2[111], which was not considered in the proposed model. In this study, we investigate the crystal structure by high resolution x-ray powder diffraction measurement to clarify the CO state in AlV_2O_4.

Experimental

The sample of AlV_2O_4 was prepared by the same way as the previous report [1]. The powder diffraction experiment at room temperature was carried out using multiple-detector system (MDS) installed at BL-4B$_2$ station. A flat Ge(111) analyzer was used to improve the angular resolution. The diffraction data of AlV_2O_4 were collected at a step interval of 0.004° in 2θ and a counting time of 5 sec at each step. The asymmetric 2θ scan mode was used at a fixed incident angle of α = 7°. The wavelength of incident beam was λ = 1.2060 Å.

Results and Discussion

Figure 1 shows the powder pattern of AlV_2O_4 at room temperature. First, the lattice constants are determined from the peak position of each reflection and estimated as a ~ 5.75 Å and c ~ 28.85 Å with a rhombohedral symmetry (hexagonal axis choice). Based on this information and various electron diffraction patterns, we have constructed several structural models and the structural refinement for each model was carried out by Rietveld method. The structural parameters for the best fitting model are shown in Table 1. The overall quality of the fitting is fairly good. Further, the refined structural model is consistent with the high resolution electron microscope images [2].

Here, we discuss the CO state of AlV_2O_4 based on the present structural model. There are three independent V sites, two V atoms (V_1 and V_2) on the triangular lattice and one V atom (V_3) on the *Kagome* lattice. On the other hand, there are four kinds of V-V bond length. Two of them are shorter (V_3-V_3: 2.610 Å, V_2-V_3: 2.809 Å) and the others are longer (V_3-V_3: 3.141 Å, V_2-V_3: 3.039 Å). The shorter V_3-V_3 bonds form "trimers" and all the V_2 atoms are sandwiched by two V_3 trimers. As a result, seven V atoms form a V cluster, i.e., "heptamer". The stabilization of the V heptamer is consistent with the physical properties and theoretical consideration [2].

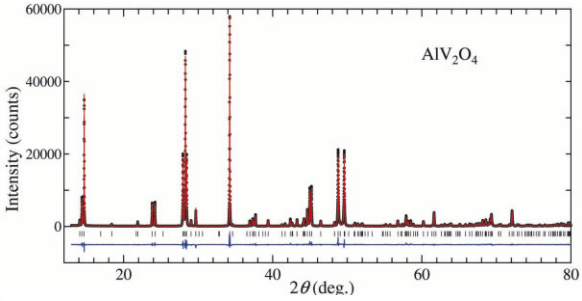

Fig. 1. Portion of the synchrotron x-ray powder diffraction pattern (black points) and the Rietveld fit (red line).

Table 1. Structural parameter of AlV_2O_4

Space group R-3m
a = 5.75148(3) Å, c = 28.85407(14) Å

atom	site	x	y	z	B(Å^2)
Al_1	6c	0	0	0.18298(3)	0.146(12)
Al_2	6c	0	0	0.30931(3)	0.103(11)
V_1	3a	0	0	0	-
V_2	3b	0	0	1/2	-
V_3	18h	0.84873(2)	=1-x	0.41786(1)	-
O_1	6c	0	0	0.12132(6)	0.259(7)
O_2	6c	0	0	0.37045(6)	=B(O_1)
O_3	18h	0.83153(8)	=1-x	0.53921(4)	=B(O_1)
O_4	18h	0.82972(8)	=1-x	0.29034(4)	=B(O_1)

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
V_1	0.0014(2)	=β_{11}	0.000086(8)	=β_{11}/2	0	0
V_2	0.0007(2)	=β_{11}	0.00176(2)	=β_{11}/2	0	0
V_3	0.00231(7)	=β_{11}	0.000059(2)	0.00047(8)	0.00002(1)	=-β_{13}

R_{WP} = 7.82 %, R_B = 2.10 %, S = 1.605

References

[1] K. Matsuno et al., J. Phys. Soc. Jpn 70, 1456 (2001).
[2] Y. Horibe et al., submitted.

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