Structural Analysis of Spinel Compound CuV$_2$S$_4$ with Incommensurate Charge-Density Wave

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Abstract. Spinel Compound CuV$_2$S$_4$ exhibits incommensurate charge-density wave (CDW) transition at $T_t \sim 90$ K accompanied by a structural phase transition. We have performed synchrotron powder diffraction experiments in order to determine the crystal structure for low temperature phase. The CDW phase has an orthorhombic symmetry with the superspace group $Imm\bar{2}(0\beta0)$. It was found that the crystal structure is characterized by the significant change of bond lengths between vanadium atoms along $a$–axis. We suggested that this change is related to the orbital ordering of $t_{2g}$ orbitals, which is the origin of the formation of the CDW.

1. Introduction

Spinel compounds with chemical formula AB$_2$X$_4$ (X is O, S, or Se) have been studied for decades, because of their unique physical properties. The spinel structure consists of face–centered cubic lattice of X anions within which A and B cations occupy the tetrahedral and octahedral interstitial sites, respectively. Moreover, the B site cations have a corner sharing tetrahedral network known as a pyrochlore lattice with three dimensional geometrical frustration. When the B cations are mixed in valence, exciting physics accompanied by orbital ordering often arises. For example, CuIr$_2$S$_4$ (Ir$^{3.5+}$) exhibits a metal–insulator transition at 230 K accompanied by charge and orbital ordering simultaneously [1]. AlV$_2$O$_4$ (V$^{2.5+}$) shows the orbital ordering of vanadium $t_{2g}$ orbitals with the formation of a molecular–like vanadium heptamer below 700 K [2]. Furthermore, CuV$_2$S$_4$ (V$^{3.5+}$) displays anomalies in magnetic susceptibility and electrical resistivity accompanied by a structural phase transition at $T_t \sim 90$ K [3]. It has been discussed that these anomalies are related to the formation of the incommensurate charge–density wave (CDW) with wave vector $q = (1/4,\delta[110])$ below $T_t$. The CDW state of CuV$_2$S$_4$ with three dimensional lattice has attracted significant interest over recent decades [3–6] since the CDW formation is well known as general phenomena of low–dimensional systems. However, the origin of CDW formation in CuV$_2$S$_4$ is not understood at present. Because only the crystal system for CDW phase is reported [4] and the detailed crystal structure below $T_t$ has not determined so far.
In this paper, we report the details of the crystal structure of CDW phase in CuV$_2$S$_4$, which were investigated by X–ray powder diffraction measurements using synchrotron radiation.

2. Experimental details
A polycrystalline sample was synthesized by a solid state reaction. The stoichiometric mixture of high purity Cu, V and S powders was heated in an evacuated quartz tube at 1123 K for a week. Subsequently, the sample was ground and pressed into pellets in a glove box filled with argon gas to avoid oxidation of the sample. The pellet was sintered in an evacuated silica tube at 1123 K for 5 days.

X–ray powder diffraction experiments using synchrotron radiation source were carried out on the large Debye–Scherrer camera installed at the beamline BL02B2 in SPring–8 by using an imaging plate as a detector [7]. The wavelength of an incident X–ray was 0.4999 Å. The diffraction data were collected in the range between 20 K and 150 K using a low temperature helium gas blower. The JANA 2006 program [8] was used for the structural refinements by the Rietveld method from the synchrotron powder diffraction data.

3. Results and Discussion
X–ray powder diffraction patterns at 70 K and 150 K are shown in figure 1 (a). At 150 K, CuV$_2$S$_4$ has a cubic normal spinel structure with a lattice parameter $a = 9.8203(1)$ Å, which is obtained by Rietveld refinement. Figure 1 (b) shows that the peak profile of 800 reflection, which splits into two peaks at 70 K. This peak splitting means the structural phase transition from cubic symmetry to tetragonal or orthorhombic one at $T_t$ as previous report [4]. The lattice constants calculated from the peak positions of some fundamental reflections corresponding to the pseudo–cubic axes, were $a_c = b_c \approx 9.82$ Å and $c_c \approx 9.80$ Å, where it was assumed that the crystal symmetry is tetragonal since it is difficult to distinguish between tetragonal and orthorhombic symmetry from the peak splitting.

In addition, we observed weak superlattice reflections whose intensities are less than about 0.2 % of maximum intensity of the fundamental reflections. These reflections can be indexed with four integer $h k l m$ with respect to the reciprocal basis vectors $a^*$, $b^*$ and $c^*$ of the fundamental structure and modulation vector $q$, according to $H = ha^* + kb^* + lc^* + mq$, where $H$ is a reciprocal lattice vector.

In order to determine the superspace group, the peak positions of both fundamental and superlattice reflections observed are checked carefully. We should note that the tetragonal symmetry should be excluded because one dimensional modulation perpendicular to $c$–axis cannot possess a

Figure 1. (a) Portion of the Rietveld fitting of the synchrotron powder diffraction patterns at 150 K and 70 K (arrows show superlattice reflections). The dots (black and red) and the solid line (green) exhibit observed pattern and calculated pattern, respectively. (b) X–ray scans in the vicinity of the 800 cubic Bragg peak at 150 K and 70 K.
four-fold rotation axis normal to \( c \)-axis. Hence, we examined the orthorhombic space groups among the group–subgroup relation of \( Fd\bar{3}m \rightarrow I4_{1}/amd \rightarrow Imma \rightarrow Ima2, I2_{1}2_{1}2_{1} \), or \( Imm2 \) because the phase transition at \( T_{t} \) is the second order one [4]. Here, the orthorhombic space groups \( Imma, Ima2 \) and \( I2_{1}2_{1}2_{1} \) cannot explain the peak positions of the superlattice reflections. As a result, we concluded that the structure for the low–temperature phase has a superspace group \( Imm2(00\beta) \) with a lattice parameter \( a = 6.94 \) Å, \( b = 6.94 \) Å, \( c = 9.80 \) Å and the modulation vector of \( q \sim 0.74 b^{*} \), where all superlattice reflections can be indexed by \( m = \pm 1 \).

As a next step, we have performed incommensurate structural analysis by Rietveld refinement on the basis of the initial structure model so as to determine the magnitude and the direction of the atomic displacements for each atom. In this analysis, the positional modulation was considered. The overall quality of the fitting was fairly good as shown in figure 1(a), and the details of structural parameters of the average structure and modulation vector are listed in Table 1.

The displacements of \( V \) atoms are much larger than those of \( Cu \) and \( S \) atoms; for instance, the amplitudes of \( u^{V1} \) and \( u^{V2} \), where \( u^{\mu} \) is the displacement from the atomic position of the \( \mu \)-th site for average structure [9, 10], are 0.47 Å, whereas those of \( u^{Cu1} \) and \( u^{Cu2} \) are less than 0.16 Å. These results mean that the displacements of \( V \) atoms play an important role in the phase transition at \( T_{t} \). Figure 2 shows the crystal structure including modulation along \( b \)-axis schematically, where the \( Cu \) and \( S \) atoms are not shown for clarity. There are two independent \( V \) sites. The blue and red atoms are \( V1 \) and \( V2 \) site, respectively. Note that the \( V-V \) bond lengths at 70 K range from 3.0 Å to 4.0 Å, though those at 150 K are 3.49 Å for all \( V-V \) bonds. Here, we define three kinds of the \( V-V \) bonds in terms of bond lengths at 70 K; Shorter Lengths (SL): 3.0 − 3.3 Å, Longer Lengths (LL): 3.7 − 4.0 Å, and

### Table 1. Structural parameters of average structure at 70 K from the Rietveld refinement of synchrotron powder diffraction data. The superspace group is \( Imm2(00\beta) \).

| Structural parameters | Atom | Wyck. | \( x \) | \( y \) | \( z \) | \( U_{iso} \)(Å\(^2\)) |
|----------------------|------|-------|--------|--------|--------|-----------------|
| \( a \) (Å)          | 6.9477(1) | Cu1   | 2a     | 0      | 0      | 7/8             | 0.0071(2) |
| \( b \) (Å)          | 6.9416(1) | Cu2   | 2b     | 0      | 1/2    | 0.127(1)       | 0.0071(2) |
| \( c \) (Å)          | 9.8011(1) | V1    | 4c     | 0.250(4)| 0      | 0.250(3)       | 0.0027(6) |
| \( q \)              | 0.7391(5)| V2    | 4d     | 0      | 0.252(3)| 0.500(3)       | 0.0027(6) |
| \( R_{wp} \) (%)     | 4.52   | S1    | 4c     | 0.267(3)| 0      | 0.003(3)       | 0.0007(8) |
| \( R_{B} \) (%)      | 1.82   | S2    | 4c     | 0.235(4)| 0      | 0.494(3)       | 0.0007(8) |
| \( R_{wp} \) (%)     | 2.71   | S3    | 4d     | 0      | 0.238(2)| 0.254(3)       | 0.0007(8) |
| \( R_{B} \) (%)      | 2.80   | S4    | 4d     | 0      | 0.742(3)| 0.742(3)       | 0.0007(8) |

**Figure 2.** (a) Crystal structure of \( CuV_{2}S_{4} \) at 70 K schematically. There are two inequivalent \( V \) atoms (\( V1, V2 \)). SL (green), IL (grey) and LL (red) bonds are three different types of the \( V-V \) bond lengths.
Intermediate Length (IL): 3.4 – 3.6 Å. Most of the V1–V1 bonds along $a$–axis have SL and LL bonds alternately. On the other hand, all the V2–V2 bonds along $b$–axis have IL bonds.

We suggest that the feature of V1–V1 bonds in CuV$_2$S$_4$ is similar to that in AlV$_2$O$_4$ on the kagomé net planes in which the electron transfer is dominated by the $d$–$d$ direct overlap of the $\sigma$ bond [2, 11]. In CuV$_2$S$_4$, the V1–V1 bonds alternating SL and LL bonds can be formed by orbital ordering of $d_{xy}$ orbitals in vanadium $t_{2g}$ orbitals. In addition, the temperature dependence of magnetic susceptibility and electrical resistivity show abrupt decrease and increase, respectively at $T_c$ [4–6]. These facts indicate that conduction electrons are likely to be localized. Thereby, the orbital ordering transition most likely occurs in V1–V1 bonds, and the V1–V1 bonds are formed by strong electronic bonding such as spin–Peierls transition in CuIr$_2$S$_4$[1]. It is conceivable that the orbital ordering of $d_{xy}$ orbitals is related to the formation of incommensurate CDW. However, to understand the origin of the CDW completely, it is necessary to consider not only V1–V1 bonds lengths but also V1–V2 bond lengths. The construction of the novel orbital ordering model is now in progress.

4. Conclusion
We have first determined the crystal structure for the low temperature phase of CuV$_2$S$_4$ by synchrotron powder diffraction experiments at 70 K. Considering the superlattice reflections, the crystal symmetry is orthorhombic with the wave vector $q = 0.7391(5)\ b^*$. The difference in bond lengths between V1–V1 and V2–V2 bonds occurs in the structural phase transition at $T_c$. We suggest that orbital ordering of $d_{xy}$ orbitals should occur in the V1 atoms and is expected to be related to the formation of incommensurate CDW.

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