

# Crystal structure of spinel type compound $\text{CuIr}_2\text{S}_4$ at low temperatures

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## Introduction

A spinel-type compound  $\text{CuIr}_2\text{S}_4$  is known to show a metal-insulator transition (MIT) at  $T = 226$  K, which is accompanied by a structural transition<sup>1)</sup>. This transition is considered to be due to charge ordering of  $\text{Ir}^{3+}$  and  $\text{Ir}^{4+}$  ions at low temperatures. Further, the local magnetic moment of  $\text{Ir}^{4+}$  ( $S = 1/2$ ) vanishes at low temperature simultaneously, which is suggested to make spin dimerization of the  $\text{Ir}^{4+}$  ions. However, the detailed structure such as the atomic position of Ir has not been determined except for the symmetry<sup>2)</sup>. It is important to clarify the crystal structure in order to make the mechanism of the MIT clear. In the present study, the structural analysis is performed for the low temperature phase of  $\text{CuIr}_2\text{S}_4$ .

## Experimental

The  $\text{CuIr}_2\text{S}_4$  sample was prepared by heating the mixture of high purity Cu, Ir and S powder in evacuated quartz tube. The powder diffraction experiment at 50 K was performed using high-resolution diffractometer installed at a beam line of BL-3A station. A wavelength of incident beam used was 1.5470 Å. A flat Si(111) crystal analyzer was used in order to obtain the data with high angular resolution. The powder pattern was collected in the angular range of  $15^\circ < 2\theta < 57^\circ$  in  $2\theta/\theta$  step scanning with a step width of  $0.004^\circ$  in  $2\theta$  and a counting time of 4 s at each step. The Rietveld refinements were carried out using the program GSAS.

## Results and Discussion

The low temperature phase of  $\text{CuIr}_2\text{S}_4$  has a triclinic symmetry as reported previously<sup>2)</sup>. The refined lattice constants are  $a = 11.92776(9)$  Å,  $b = 6.98016(8)$  Å,  $c = 11.92776(9)$  Å,  $\alpha = 91.0550(7)^\circ$ ,  $\beta = 108.4672(6)^\circ$  and  $\gamma = 91.0320(7)^\circ$ . There are eight independent Ir sites in the unit cell if the space group P-1 is assumed. Table 1 shows the atomic position of Ir atoms. For this structural model, all reflections including superlattice and forbidden peaks can be indexed. Table 2 shows the atomic distances between Ir and Ir atoms. From table 2, there are two pairs whose atomic distances are shorter than the others, i.e., Ir1-Ir4 and Ir2-Ir3. If we assume that Ir1, Ir2, Ir3 and Ir4 has a valence +4 and that the pairs of Ir1-Ir4 and Ir2-Ir3 are dimerized, we can explain the physical properties of  $\text{CuIr}_2\text{S}_4$  at low temperatures; The MIT is caused by the charge ordering of  $\text{Ir}^{3+}$  ( $S = 0$ ) and  $\text{Ir}^{4+}$  ( $S = 1/2$ ) and the vanishing the local magnetic moment of  $\text{Ir}^{4+}$  is due to spin dimerization of  $\text{Ir}^{4+}$ . The charge-ordering pattern for both

$\text{Ir}^{3+}$  and  $\text{Ir}^{4+}$  forms octamers with isomorphous  $\text{Ir}^{3+}_8\text{S}_{24}$  and  $\text{Ir}^{4+}_8\text{S}_{24}$ . The direction of the dimerization is along [110] or [-110] for pseudo-cubic notation. This result indicates that  $\text{CuIr}_2\text{S}_4$  shows a simultaneous charge-ordering and spin-dimerization. Not only this phenomena but the charge-ordering pattern is unique and this pattern provides a new way to look at the spinel structure. The detail of the above results is reported in elsewhere<sup>3)</sup>.

Table 1: Atomic position of Ir

|     | <i>x</i>  | <i>y</i>  | <i>z</i>  |
|-----|-----------|-----------|-----------|
| Ir1 | 0.2336(4) | 0.0106(6) | 0.7530(4) |
| Ir2 | 0.2483(4) | 0.0204(6) | 0.2330(4) |
| Ir3 | 0.2499(4) | 0.2296(6) | 0.0158(4) |
| Ir4 | 0.0111(4) | 0.2177(6) | 0.7557(4) |
| Ir5 | 0.2460(5) | 0.5021(6) | 0.7497(4) |
| Ir6 | 0.2498(4) | 0.5181(6) | 0.2483(5) |
| Ir7 | 0.5080(4) | 0.2403(6) | 0.2519(4) |
| Ir8 | 0.7551(5) | 0.2335(8) | 0.5022(4) |

Table 2: bond length of Ir-Ir

|         |          |         |          |
|---------|----------|---------|----------|
| Ir1-Ir3 | 3.464(7) | Ir5-Ir7 | 3.478(7) |
| Ir1-Ir4 | 3.012(5) | Ir5-Ir8 | 3.493(5) |
| Ir2-Ir3 | 2.956(5) | Ir6-Ir7 | 3.602(5) |
| Ir2-Ir4 | 3.582(7) | Ir6-Ir8 | 3.487(7) |
| Ir3-Ir4 | 3.490(8) | Ir7-Ir8 | 3.470(9) |
| Ir1-Ir5 | 3.551(7) | Ir2-Ir8 | 3.605(7) |
| Ir1-Ir5 | 3.437(7) | Ir3-Ir5 | 3.658(5) |
| Ir1-Ir7 | 3.540(7) | Ir3-Ir6 | 3.458(8) |
| Ir1-Ir8 | 3.554(7) | Ir3-Ir7 | 3.458(7) |
| Ir2-Ir6 | 3.507(6) | Ir4-Ir5 | 3.486(7) |
| Ir2-Ir6 | 3.483(6) | Ir4-Ir6 | 3.581(5) |
| Ir2-Ir7 | 3.432(7) | Ir4-Ir8 | 3.554(8) |

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## References

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