

Band Structure Analysis of the Insulating Phase of Sulphospinel Compound CuIr_2S_4 with the Density-Functional Theory

Taizo Sasaki, Takao Furubayashi¹ and Takehiko Matsumoto²

Computational Materials Science Center, National Institute for Materials Science
1-2-1, Sengen, Tsukuba, Ibaraki 305-0047, Japan

Fax: 81-29-859-2618, e-mail: SASAKI.Taizo@nims.go.jp

¹Nanomaterials Laboratory, National Institute for Materials Science

1-2-1, Sengen, Tsukuba, Ibaraki 305-0047, Japan

²Ecomaterials Research Center, National Institute for Materials Science

1-2-1, Sengen, Tsukuba, Ibaraki 305-0047, Japan

The band-structure calculations have been performed for the insulating triclinic phase of the sulphospinel compound, CuIr_2S_4 , which appears below the metal-insulator transition temperature, 230K. While the properties of transition-metal spinel compounds have been discussed with the electron correlation theory in many cases, we found that the electronic structure of CuIr_2S_4 can be analyzed within the band-structure theory. In the results we obtained the small energy gap at the Fermi energy with the magnitude comparable to the measured ones. It has been also shown that the calculated density of states can explain the experiments, such as the photoemission and optical spectra. On the basis of the results of the calculations, the effects of the pressure, substitution and irradiation to the transition were discussed.

Key words: band structure theory, sulphospinel compound, metal-insulator transition

1. INTRODUCTION

The electronic structure of the transition metal compounds has been a controversial issue. One model is based on the aspect that the motion of valence electrons are highly correlated. The valence electrons are localized around transition metal ions excluding other extra electrons by the strong Coulomb repulsion. This model has been often taken for the heavier 3d compounds. On the contrary, the band-structure theory insists that the valence electrons have more itineracy, which reduces the correlation between electrons and plays an important role in the physical properties. The advantage of this theory is precise calculation techniques on the basis of the first principles. This article reports the application of the latter theory to one of the transition metal compounds, CuIr_2S_4 .

CuIr_2S_4 is the spinel compound that exhibits the metal-insulator (M-I) transition: Nagata et al.[1] observed the M-I transition with an abrupt decrease of the electrical conductivity and a volume change at about 230 K. Its high-temperature (HT) metallic phase has the cubic structure with the Cu and Ir ions at the A and B sites, respectively. The initial x-ray experiment[2] reported the small deformation from the cubic symmetry at the transition. Recently, it has been shown and confirmed by the precise experiments [3-7] that the low-temperature (LT) phase has the triclinic $P\bar{1}$ symmetry accompanied by the cluster formation of the Ir ions. Following the structural determination of the LT phase, it was discovered that the triclinic structure becomes unstable and changes to the tetragonal one under the electron-beam[5] or x-ray [8,9] irradiation at temperatures below 50K. While the details of this instability is now being investigated, the ground state of this material must be

clarified to understand the mechanism of the M-I transition and the x-ray induced structural change. This article reports the results of the band-structure calculations for the LT phase of this compound, which were performed to provide the knowledge on the ground state from the first-principles.

The ionic picture can be a prototype of the electronic structure for the compounds between the metallic and non-metallic elements. The NMR experiment [10] has shown that the Cu ions do not have any localized moments, and thus are in a monovalent state. If we assume the divalent state of the S ions, the Ir ions are nominally in a +3.5 state. This picture makes us imagine that the $\text{Ir}^{+3.5}$ ions in the HT metallic phase would become separated into the two groups of Ir^{+3} and Ir^{+4} in the LT phase with an ordered configuration. The $\text{Ir}^{+4}(d^5)$ ion is considered to have a spin of $S=1/2$ under the octahedral crystal field if we assume the low-spin ground state. However, the LT insulating phase shows diamagnetism experimentally [1,11]. The x-ray diffraction analysis have indicated that the size of the primitive cell of the LT phase becomes four times of that of the HT phase and that the transition makes a half of the 16 Ir ions form dimers, changing the Ir-Ir distance from $\sim 3.5\text{\AA}$ in the HT phase to $\sim 3.0\text{\AA}$ [6,7]. That is, half of the Ir ions make dimers by this distortion. Radaelli et al.[6] suggested that the dimerization of Ir ions is due to the singlet-state formation between the Ir spins.

Oda et al.[12] have performed the density-functional band calculations for the HT metallic phase of CuIr_2S_4 . The calculated density of states is in good agreement with the x-ray emission experiment [13,14]. According to the calculations, the conduction bands are made up of the $\text{S}3p\text{-Ir}5d_y$ bonding orbitals and $\text{Ir}5d_e$ orbitals, and

the Fermi level is located in the Ir5d band. The calculations have also shown that the Cu ions are in the monovalent state as indicated by the experiment. The obtained the Stoner enhancement factor, which is comparable to the theoretical value for FCC Cu. Within these facts, the band-structure theory is acceptable to explain the electronic structure of the HT phase.

In the model suggested by Radaelli et al., the origin of the energy gap of the LT phase is to be in the correlation between electrons. In fact, the electrical and magnetic properties have been discussed as the strongly correlated system for sulphospinel 3d-transition-metal compounds. However, the 5d orbital of Ir^{3+} has larger extension than, for example, the Co^{3+} 3d orbital. As a reference, the former orbital extends about 1.5 times of the latter in the atomic structure calculations. For the HT phase, there is no remarkable discrepancy between the band calculations and experiments, as described above. Considering these facts, it is worthwhile to apply the band-structure theory to CuIr_2S_4 in the triclinic structure.

2. DETAILS OF CALCULATIONS

The band structures have been calculated within the density functional formalism: The exchange-correlation energy was evaluated with the local density approximation [15]. We used the pseudopotential method [16], by assuming the ionic cores of Cu, Ir and S as [Ar], [Xe]4f¹⁴ and [Ne], respectively. Since the Cu3d and Ir5d orbitals have a significant overlap with their core orbitals in the real space, the partial core correction [17] was incorporated in the evaluation of the exchange correlation energy. The wavefunctions were described in terms of the plane-wave basis sets for which the kinetic energy is less than 75 Ryd. The k-space integration was performed with the 6 special points in the irreducible wedge of the Brillouin zone. Convergence was verified to be better than 0.002 eV by changing the cutoff energy

for the basis sets from 50 to 75 Ryd and increasing the k-point sampling to 14. We used the lattice parameters, $a=11.959\text{\AA}$, $b=11.956\text{\AA}$, $c=6.988\text{\AA}$, $\alpha=91.01^\circ$, $\beta=91.11^\circ$, and $\gamma=108.48^\circ$ [7], and the internal parameters, which were refined experimentally. These parameters differ from the published data [6] by less than a few percent.

3. RESULTS AND DISCUSSIONS

Figure 1 shows the band structure calculated for CuIr_2S_4 in the observed triclinic structure. The k_x -, k_y - and k_z -axis are taken in accordance with the crystal axis defined above. It can be seen that the direct gap of about 0.2-0.3 eV appears at the Fermi energy. The magnitude of the indirect minimum energy gap was calculated to be 0.038 eV, which is comparable to the observed values, 0.047 eV [1, 11] and 0.041 eV [10]. Above the energy gap, the unoccupied band with the width of about 0.5 eV can be seen.

The density of states of the LT phase is depicted with that of the HT phase in Fig. 2. We also applied the same calculation methods to the HT phase and obtained the results almost same as the previous ones [12]. The density of states of the HT phase has the sharp peak structure about 1eV below the Fermi level, which comes from the Ir5d orbitals. In the present calculations for the LT phase, the corresponding peak is depressed due to its lower symmetry. The similar change can be observed in the UPS spectra by Matsuno et al. [13] and Kurmaev et al. [14]. Those spectra have been taken with the same incident photon energy at different temperatures. The spectrum taken by the latter group at the room temperature shows the shoulder structure at 1.3 eV below the Fermi level, which was attributed to the Ir5d orbital. Comparing the spectrum by the former group at the room temperature with it, we can see the depression of this structure at the LT phase. The former group also performed the bremsstrahlung-isochromat

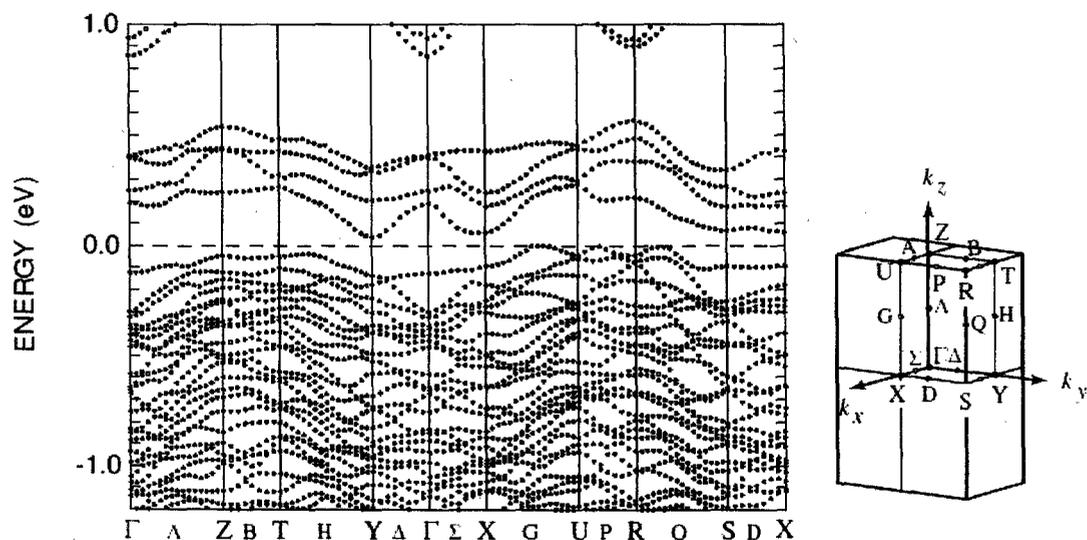


Fig. 1 The calculated band structures of the observed triclinic structure. The first Brillouin zone is also drawn. The broken line indicates the top of the valence band, which is set to be zero in the figure.

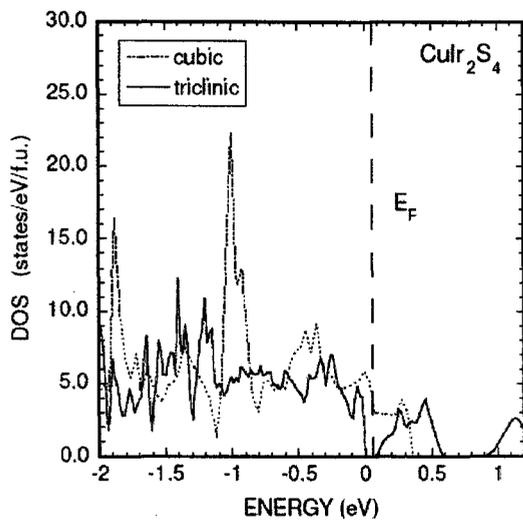


Fig. 2. The calculated density of states for the HT metallic and the LT insulating phases. The Fermi energy of the HT phase and the center of the energy gap of the LT phase are adjusted.

spectroscopy. The present results have shown a conduction band with the width of about 1eV, similar to the observed spectra. The optical reflection spectra measured by Hayashi et al. [18] clearly indicated the interband transitions around 0.4 and 0.7 eV. In the present calculations, these transitions will correspond to the excitation from the valence band to the upper conduction bands around 0.3 and 1 eV above the top of the valence band.

The energy gap opening can be analyzed in terms of the charge distribution. Figure 3 is the charge distribution plot for the four lowest unoccupied bands in

Fig.1. It can be seen that the charge distribution is prominent at around the Ir ions subject to the dimerization, and becomes very small at the center of each dimer (Fig3.(b)). This plot indicates that the unoccupied states correspond to the antibonding states between the Ir5d orbitals at the dimers hybridized with S3p orbitals: Therefore, the energy gap should be attributed to the splitting of the bonding and antibonding states between the Ir5d orbitals. Further analysis has shown that the highest occupied states and their vicinity have the amplitude at the Ir ions not dimerized, and thus the bonding states will be pushed away far from the Fermi level.

In the electronic structure of the HT metallic phase, a quarter of the non-bonding Ir5d bands are unoccupied, which corresponds to that each Ir ion has 0.5 holes in its 5d orbital. Since the primitive cell of the LT phase contains 16 Ir ions, the holes will fully occupy the four antibonding states of the dimerized 5d orbitals. That is, the holes are to be localized around the dimerized Ir ions. In such a sense, the structural change at 230 K causes the segregation of the charge distribution.

It is expected that the charge segregation makes the splitting of the core levels of the Ir ions. This effect will be approximated by the change of the potential at each Ir site. The present calculations gave us that the self-consistent total potentials differ about 60 meV between at the dimerized and non-dimerized Ir sites and scatters about 10 meV for each Ir group.

The experiments have revealed that the hydrostatic pressure raises the transition temperature [2,19]. If the pressure shorten the Ir-Ir distance at the dimmers effectively, the energy separation between the bonding and antibonding states of the Ir5d orbitals will increase. Thus, the Ir dimmers will be stabilized under this condition. Since the width of the hole band, which is mostly determined by the overlap between the dimers, does not seem to be sensitive with respect to the pressure, the energy gap will increase by the pressure.

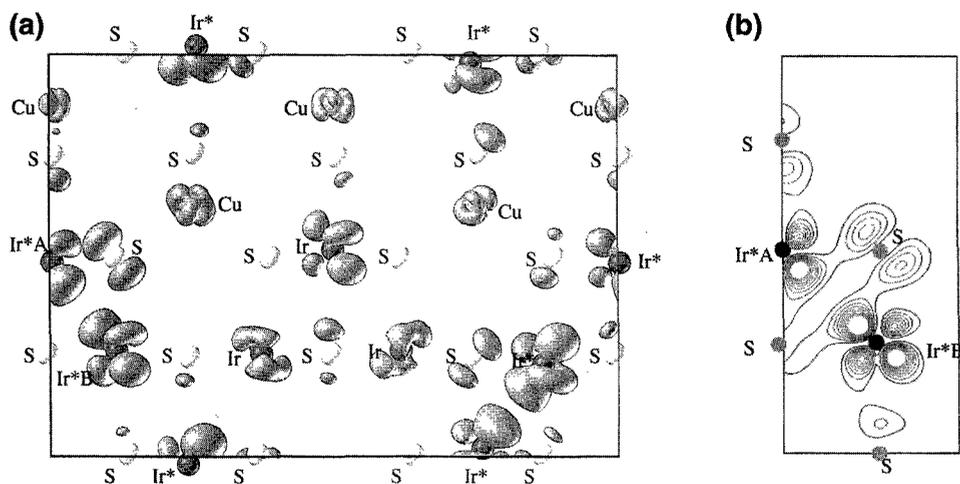


Fig. 3. The charge distribution plots of the four lowest unoccupied bands. The Ir sites subject to the dimerization are indicated by asteriks. (a) The iso-valued surface plot viewed from the (001) direction. The spherical balls indicate the atomic sites (b) The contour plot on the plane that includes the dimerized Ir sites denoted A and B in (a) and the nearest S sites.

It has been reported that the substitution of Cu by Zn reduces the transition temperature and, at the Zn content of 20-30%, the cubic metallic phase is stabilized in all temperature range exhibiting the superconductivity at about 3K [20,21]. Although the substitution is considered to make donor states below the conduction band at low concentration of Zn, the increase of the Zn content will cause the electron doping to the conduction band. In such a case, the bonding between the Ir ions will be weakened and finally the dimerized structure will become unstable.

In the electron diffraction experiments, Sun et al. [5] observed that the intensity of the characteristic additional diffraction spots of the LT phase decreases significantly at temperatures below 50 K. Recently, it was reported that the same change of the x-ray diffraction profile occurs and the change is induced by the incident x rays [8]. The experiments have shown that the induced profile can be accounted by the tetragonal $I4_1/amd$ space group and the structural change is accompanied by the reduction in the electrical resistivity by more than five decades [9]. Considering the energy range of the irradiation ($\sim 4\text{keV}$ for the electron beams and $\sim 9\text{keV}$ for the x rays), there is a possibility of that the core excitation is related to this instability of the triclinic structure. A simple idea is that the irradiation plays a role similar to the Zn substitution of Cu by the excitation of the Cu core electrons. If the excited electrons are relaxed into the conduction band, the similar electronic structure will be realized. In this explanation, however, the excited state must persist so long time that it could be detected by the resistivity or the diffraction measurements. Further investigation is required to establish the model for this issue.

A typical and famous example of the M-I transition of the spinel compounds is known as the Verwey transition of Fe_3O_4 . Its mechanism has been an unresolved question for a long time. From a point of view of that the Fe3d orbitals are more localized than the Ir5d ones, it is not clear whether the band theory can apply to the transition of Fe_3O_4 . The recent calculations [22] have shown that the properties of the HT phase can be explained well by the band theory. Unfortunately, since the atomic structure of the LT phase has not been elucidated yet, the band calculations for the LT phase has not been available.

4. SUMMARY

In summary, we have shown that the band-structure scheme is applicable to the LT insulating triclinic phase of CuIr_2S_4 , by showing the correspondences between the results of the band calculations and the experimental findings. This electronic structure of the LT insulating phase is contrary to the singlet formation between the spins localized at the Ir sites. In the calculated charge distribution, the inhomogeneity can be observed in accordance with the change of the atomic arrangement and the band structure.

The present calculations were performed with the Numerical Materials Simulator of NIMS.

- [1] S. Nagata, T. Hagino, Y. Seki, and T. Bitoh, *Physica B* **194-196**, 1077 (1994).
- [2] T. Furubayashi, T. Matsumoto, T. Hagino, and S. Nagata, *J. Phys. Soc. Jpn.* **63**, 3333 (1994).
- [3] H. Ishibashi, T. Sakai, and K. Nakahigashi, *J. Magn. Magn. Mater.*, **226-229**, 233 (2001).
- [4] K. Oikawa, T. Matsumoto, T. Furubayashi, N. Matsumoto, and S. Nagata, *J. Phys. Soc. Jpn.* **70**, Suppl. A 106 (2001).
- [5] W. Sun, T. Kimoto, T. Furubayashi, T. Matsumoto, S. Ikeda, and S. Nagata, *J. Phys. Soc. Jpn.* **70**, 2817 (2001).
- [6] P. G. Radaelli, Y. Horibe, M. J. Gutmann, H. Ishibashi, C. H. Chen, R. M. Ibberson, Y. Koyama, Y. S. Hor, V. Kiryukhin, and S. W. Cheong, *Nature*, **416**, 155 (2002).
- [7] T. Furubayashi, T. Matsumoto, and S. Nagata; private communication.
- [8] H. Ishibashi, T. Y. Koo, Y. S. Hor, A. Borissov, P. G. Radaelli, Y. Horibe, S. W. Cheong, and V. Kiryukhin, *Phys. Rev. B* **66**, 144424 (2002).
- [9] T. Furubayashi, H. Suzui, T. Matsumoto, and S. Nagata, *Solid State Commun.* **126**, 617 (2003).
- [10] K. Kumagai, S. Tsuji, T. Hagino, and S. Nagata, in *Spectroscopy of Mott Insulators and Correlated Metals, Springer Series in Solid-State Sciences*, Vol. 119, edited by A. Fujimori and Y. Tokura (Springer-Verlag, Berlin, 1995), p.255.
- [11] T. Hagino, T. Tojo, T. Atake, and S. Nagata, *Philos. Mag.* **B71**, 881 (1995).
- [12] T. Oda, M. Shirai, N. Suzuki, and K. Motizuki, *J. Phys.: Condens. Matter* **7**, 4333 (1995); *Cryst. Res. Technol.* **31**, 877 (1996).
- [13] J. Matsuno, T. Mizokawa, A. Fujimori, D.A. Zatssepina, V.R. Galakhov, E.Z. Kurmaev, Y. Kato, and S. Nagata, *Phys. Rev. B* **55**, R15979 (1997).
- [14] E.Z. Kurmaev, V.R. Galakhov, D.A. Zatssepina, V.A. Trofimova, S. Stadler, D.L. Ederer, A. Moewes, M.M. Grush, T.A. Callcott, J. Matsuno, A. Fujimori and S. Nagata, *Solid State Commun.* **108**, 235 (1998).
- [15] D. M. Ceperley and B. J. Alder, *Phys. Rev. Lett.* **45**, 566 (1980); J. P. Perdew and A. Zunger, *Phys. Rev. B* **23**, 5048 (1981).
- [16] N. Troullier and J. L. Martins, *Phys. Rev. B* **43**, 1993 (1990).
- [17] S. G. Louie, S. Froyen, and M. L. Cohen, *Phys. Rev. B* **26** 1738 (1982).
- [18] M. Hayashi, M. Nakayama, T. Nanba, T. Matsumoto, J. Tang, and S. Nagata, *Physica B* **281&282**, 631 (2000).
- [19] G. Oomi, T. Kagayama, I. Yoshida, T. Hagino, and S. Nagata, *J. Magn. Magn. Mater.* **140-144**, 157 (1995).
- [20] H. Suzuki, T. Furubayashi, G. Cao, H. Kitazawa, A. Kamimura, K. Hirata, and T. Matsumoto, *J. Phys. Soc. Jpn.* **68**, 2495 (1999).
- [21] G. Cao, T. Furubayashi, H. Suzuki, H. Kitazawa, and T. Matsumoto, and Y. Uwatoko, *Phys. Rev. B* **64**, 214514 (2001).
- [22] A. Yanase and N. Hamada, *J. Phys. Soc. Jpn.* **68**, 1607 (1999).