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Substitution effect on metal–insulator transition in $Cu(Ir_{1-x}M_x)_2S_4$ (M = Sn, Hf)

Naoto Koseki*, Shuji Ebisu, Shoichi Nagata[1]

Department of Materials Science and Engineering, Muroran Institute of Technology, 27-1 Mizumoto-cho, Muroran, Hokkaido, 050-8585 Japan

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ABSTRACT

A spinel $CuIr_2S_4$ exhibits a temperature-induced metal–insulator (M–I) transition at around 226 K. Non-magnetic substitution effect on the M–I transition, T_{M-I}, in $Cu(Ir_{1-x}M_x)_2S_4$ (M = Sn, Hf) has been studied on the focus of the rather low composition region of x. Magnetic property of $Cu(Ir_{1-x}M_x)_2S_4$ (M = Sn, Hf) has been examined experimentally. The T_{M-I} decreases with increasing x and the temperature hysteresis becomes unclear within the experimental errors. The step anomaly in the magnetic susceptibility smears out and the T_{M-I} becomes ill defined around $x = 0.20$ in $Cu(Ir_{1-x}Sn_x)_2S_4$, and $x = 0.10$ in $Cu(Ir_{1-x}Hf_x)_2S_4$, respectively. These substitutions play an important role in decoupling the spin-dimerization of Ir^{4+}–Ir^{4+} in $CuIr_2S_4$, and lead the destruction of the metal–insulator transition.

1. Introduction

A spinel $CuIr_2S_4$ shows the temperature-induced metal–insulator (M–I) transition at $T_{M-I} = 226$ K [1]. This $CuIr_2S_4$ has the mixed valence as $Cu^{+}Ir^{3+}Ir^{4+}S_4{}^{2-}$ and the intensive investigations have been carried out [2–4]. The M–I transition in $CuIr_2S_4$ is demonstrated as Fig. 1. A structural transformation is accompanied at 226 K, at which a simultaneous spin-dimerization with spin-singlet state and charge-ordering take place. The spin-dimerization does not occur in Ir^{3+} because of spin $S = 0$. The spin-dimerization of Ir^{4+}–Ir^{4+} forms below T_{M-I} which causes the low-temperature diamagnetism, while the Pauli paramagnetism has been observed above T_{M-I}. Many interesting substitution effects of B-site on the metal–insulator transition have been studied so far: $Cu(Ir_{1-x}Ti_x)_2S_4$ [5], $Cu(Ir_{1-x}V_x)_2S_4$ [6], $Cu(Ir_{1-x}Cr_x)_2S_4$ [7,8], $Cu(Ir_{1-x}Mn_x)_2S_4$ [9], $Cu(Ir_{1-x}Rh_x)_2S_4$ [10], $Cu(Ir_{1-x}W_x)_2S_4$ [9], and $Cu(Ir_{1-x}Pt_x)_2S_4$ [11].

The present work is an experimental original study of the metal–insulator transition on the focus of the magnetic properties in $Cu(Ir_{1-x}M_x)_2S_4$ (M = Sn, Hf). A systematic experimental investigation has been carried out with the emphasis on the sample preparation. The atoms of Sn and Hf are candidates of nonmagnetic to take 4+ ions of Sn^{4+} and Hf^{4+}, furthermore the difference between the two ionic radius is not significant because of 0.69 Å for Sn^{4+} ion and 0.71 Å for Hf^{4+} ion. A brief report for the magnetic results will be presented on the focus of the lower composition region of x less than 0.20. The behavior for the destruction of metal–insulator transition has been detected clearly.

2. Experimental methods

We have successfully synthesized high-purity specimens of $Cu(Ir_{1-x}Sn_x)_2S_4$ and $Cu(Ir_{1-x}Hf_x)_2S_4$. The polycrystalline specimens were prepared by a solid-state reaction. Mixtures of high-purity fine powders of Cu (purity 99.99%, melting point 1356 K), Ir (99.99%, 2716 K), Sn (99.9%, 505 K), Hf (99.8%, 2495 K), and S (99.999%, 392 K) with nominal stoichiometry were heated in sealed quartz ampules. These specimens were heated to 1223 K and kept at this temperature for 5 days, then were annealed at 673 K for 4 h. The identification of crystal structure and the determination of lattice constants were carried out by X-ray powder diffraction using Cu Kα radiation at room temperature. The XRD data were analyzed by the Rietveld simulation method with RIETAN-2000 [12].

The dc magnetization measurements of powder specimens were performed with a superconducting quantum interference device (rf-SQUID) magnetometer over the temperature range of 5.0–350 K.

3. Results and discussion

3.1. Lattice constant

X-ray data have been analyzed in terms of a cubic spinel structure with the space group $Fd\bar{3}m$ (No. 227). The X-ray powder diffraction patterns at room temperature give evidence that all the $Cu(Ir_{1-x}M_x)_2S_4$ (M = Sn, Hf) have the spinel type structure. Representative diffraction profiles are shown in Fig. 2. The Rietveld simulation method with RIETAN-2000 verifies the random distribution in the *A*- and *B*-sites, respectively [12]. The site preference is exactly examined and confirmed that Ir and Sn/Hf occupy at only B-sites. Occupation percentage and the randomness are ver-

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* Corresponding author.
E-mail address: nagatas@almond.ocn.ne.jp (S. Nagata).
[1] Present address: naga-sho@mmm.muroran-it.ac.jp.

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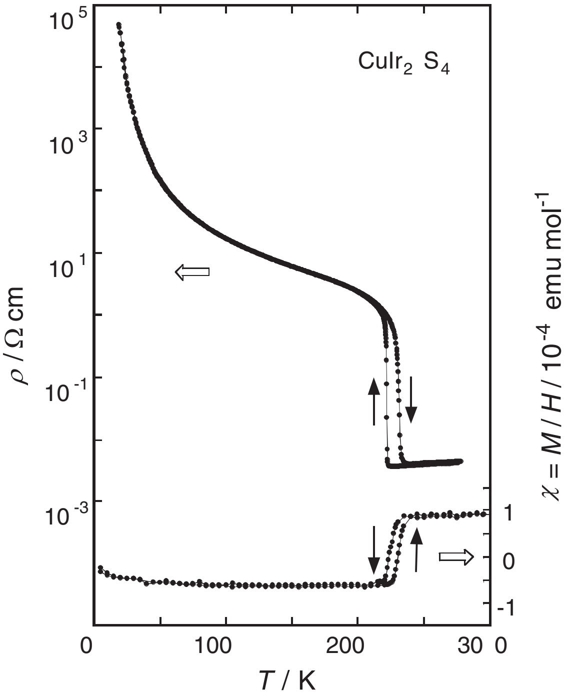

Fig. 1. Metal–insulator transition in $CuIr_2S_4$. The electrical resistivity and the magnetic susceptibility indicate the step anomaly at $T_{M\text{–}I} = 226$ K accompanied by the structural transformation.

ified. However, the Rietveld refinement to adjust the inter atomic distances has not been done in this substitution system.

The lattice constant, *a*, obtained by the least square method, varies as shown in Figs. 3 and 4 at room temperature. Here, these values of *x* are given by the initial stoichiometry of the reacting constituents. The lattice constant varies linearly with increasing Sn and Hf substitution and obeys Vegard's law. Nevertheless, it is difficult to synthesize the specimen with the higher value of *x* than 0.50 of $Cu(Ir_{1-x}Hf_x)_2S_4$ and impurity phases are included, except the end compound $CuHf_2S_4$.

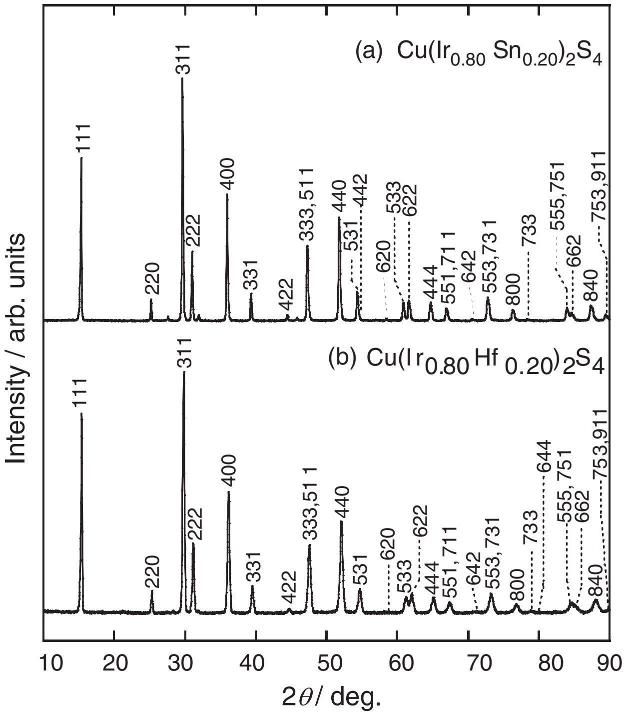

Fig. 2. X-ray diffraction profiles of (a) $Cu(Ir_{0.80}Sn_{0.20})_2S_4$ with the lattice constant $a = 9.977$ Å and (b) $Cu(Ir_{0.80}Hf_{0.20})_2S_4$, $a = 9.926$ Å for powdered specimens.

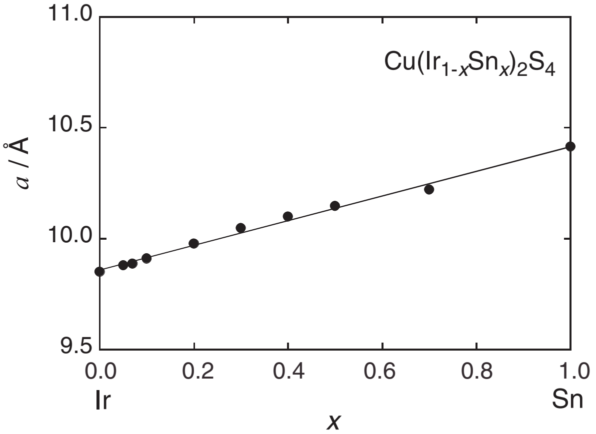

Fig. 3. Lattice constant *a* as functions of composition at room temperature, for $Cu(Ir_{1-x}Sn_x)_2S_4$, with $CuIr_2S_4$ ($a = 9.847$ Å) and $CuSn_2S_4$ ($a = 10.414$ Å).

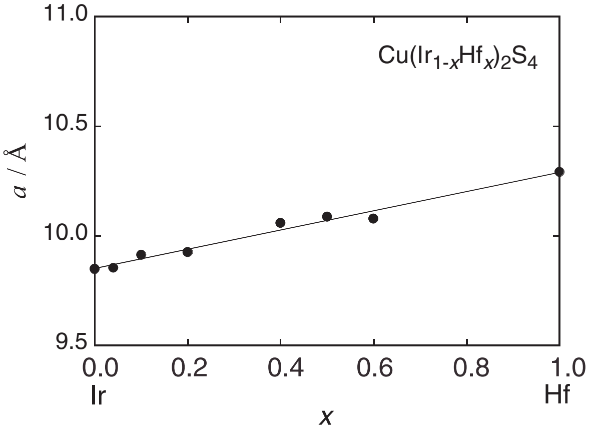

Fig. 4. Lattice constant *a* as functions of composition at room temperature, for $Cu(Ir_{1-x}Hf_x)_2S_4$, with $CuHf_2S_4$ ($a = 10.291$ Å).

3.2. Magnetic susceptibility

Figs. 5 and 6 display the temperature dependences of the susceptibility for the specimens of $Cu(Ir_{1-x}Sn_x)_2S_4$ and $Cu(Ir_{1-x}Hf_x)_2S_4$

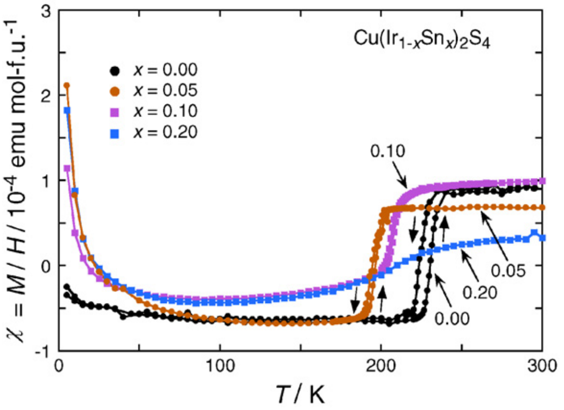

Fig. 5. Magnetic susceptibility $\chi = (M/H)$ as a function of temperature in a constant field of 1000 Oe for $Cu(Ir_{1-x}Sn_x)_2S_4$.

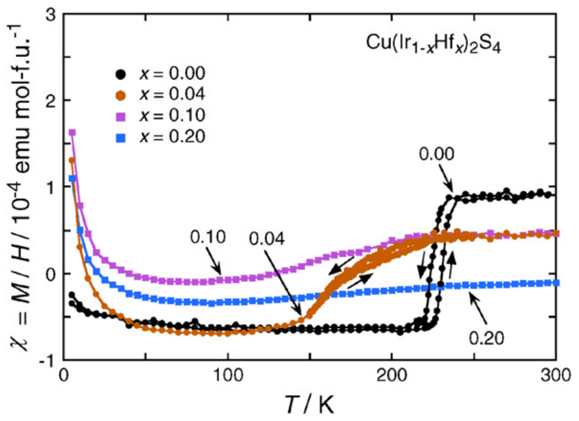

Fig. 6. Magnetic susceptibility $\chi = (M/H)$ as a function of temperature in a constant field of 1000 Oe for $Cu(Ir_{1-x}Hf_x)_2S_4$.

in a constant field of 1.000 kOe, respectively. The value of χ is defined as $\chi = (M/H)$. The susceptibility as a function of temperature exhibits the step anomaly at 226 K for $x = 0.00$, which is caused by the metal–insulator transition [2].

The metallic phase of $CuIr_2S_4$ indicates Pauli paramagnetism. The nature of the conduction electron in the metallic phase is characterized by means of the step-like difference $\Delta\chi$ in χ. The reduction of χ is due to the opening of the energy gap at $T_{M\text{–}I}$. The magnitude of the density of states at Fermi level, $D(\varepsilon_F)$, is estimated from the relation $\Delta\chi = \mu_B{}^2\, D(\varepsilon_F)$ where μ_B is the Bohr magneton. The value of $D(\varepsilon_F)$ is obtained to be 0.67 states $(\mathrm{eV\,atom})^{-1}$ for $CuIr_2S_4$. The change of the density of states at Fermi level has been modified delicately by the substitutions of Sn and Hf for Ir on the *B*-site. The different contribution to the $D(\varepsilon_F)$ is expected between Sn (5p-electrons) and Hf (5d-electrons). The detailed discussion of the gradual variation of the $D(\varepsilon_F)$ with the value of x has been presented for $Cu(Ir_{1-x}Ti_x)_2S_4$ [5] and $Cu(Ir_{1-x}V_x)_2S_4$ [6].

Below $T_{M\text{–}I}$, the presence of a temperature-independent diamagnetic contribution to the susceptibility, which is evaluated experimentally to be -6.33×10^{-5} emu mol^{-1} for $CuIr_2S_4$. The core orbital diamagnetism for $Cu^+Ir^{3+}Ir^{4+}S_4{}^{2-}$ is estimated by Pascal's additive law to be -2.26×10^{-4} emu mol^{-1}, these values could be reasonable because they are extremely small [13]. The negative value of χ below $T_{M\text{–}I}$ has very marked influence in changing from the metallic phase to insulating phase. The lack of the conduction electron, then, the Pauli paramagnetic contribution cannot exceed the low magnitude of χ from the core orbital diamagnetism.

The low-temperature increase in the χ does not seem to be intrinsic moment in this system. It may arise from the existence of extrinsic localized moments at non stoichiometry sites or another kind of lattice imperfection. The similar behavior at low temperature has been observed in many compounds, see examples [14,15]. The numerical value extracted from the susceptibility at lower temperatures using Curie–Weiss law is estimated to be approximately $0.10\mu_B$ (formula unit)$^{-1}$. This Curie tail gives an approximate 6% with $S = 1/2$. This interpretation and the numerical evaluation have already been in our earlier works [5,6], and then the detailed discussion is omitted in this paper.

The substitution of Sn and Hf for Ir atom on *B*-site has given a fairly strong modification of the step feature in the susceptibility. The variation of $T_{M\text{–}I}$ is not regular, but irregular a little, presumably which comes from the appreciable experimental errors. The temperature hysteresis becomes unclear with increasing x. Broad and gradual changes in the χ are seen for $x = 0.20$ in $Cu(Ir_{1-x}Sn_x)_2S_4$, and $x = 0.10$ in $Cu(Ir_{1-x}Hf_x)_2S_4$. The step anomaly in the χ smears out and the $T_{M\text{–}I}$ becomes ill defined.

These non-magnetic ions Sn^{4+} and Hf^{4+} have no spin, therefore the spin-dimerizatin of Ir^{4+}–Ir^{4+} is destroyed by this substitution. At the same time, the shrinkage of distance between Ir^{4+} and Ir^{4+} is also relieved by the substitution from the shorter length to the mean one. The overlapping of the wave function between the nearest atoms recovers the conduction paths. Then the itinerant electrons can emerge from insulating background. Consequently the electrons can move through the broken-dimers and can itinerant in the whole crystal. They have a tendency toward the metallic property and suppress the diamagnetic nature. Below $T_{M\text{–}I}$, the absolute values of the diamagnetism becomes smaller with increasing x except some irregularity, which is presumably experimental errors because of the low magnitude. The suppression of sharp M–I transition by Hf substitution for Ir is more sensitive than that of Sn. The difference between the two ions could originate from the value ionic radius for 0.69 Å for Sn^{4+} ion and 0.71 Å for Hf^{4+} ion. The general features of the obtained results are reasonable to understand the substitution influence on the M–I transition in $CuIr_2S_4$.

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