

OPTICAL RESPONSE OF $\text{Cu}_{1-x}\text{Zn}_x\text{Ir}_2\text{S}_4$ DUE TO METAL-INSULATOR TRANSITION*

L. CHEN, M. MATSUNAMI, T. NANBA

Graduate School of Science and Technology, Kobe University
Nada-ku, Kobe 657-8501, Japan

G. CAO, H. SUZUKI, M. ISOBE AND T. MATSUMOTO

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

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The mother material CuIr_2S_4 of the thiospinel system $\text{Cu}_{1-x}\text{Zn}_x\text{Ir}_2\text{S}_4$ undergoes a temperature-induced metal-insulator (MI) transition. We report the temperature dependence of the optical reflection spectra of $\text{Cu}_{1-x}\text{Zn}_x\text{Ir}_2\text{S}_4$ ($x \leq 0.5$) at the temperatures of 8–300 K in the energy regions of 0.005–30 eV in order to study the change in the electronic structure due to the Zn substitution for Cu. Zn substitution induced mainly the splitting of the hybridization band between the Ir-5d(t_{2g}) and S-3p states crossing the E_F . Obtained optical conductivity (σ) spectrum is discussed in relation to the change in the electronic structure close to the E_F .

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1. Introduction

Spinel compounds, CuIr_2S_4 was found to undergo a metal-insulator (MI) transition from a high temperature metallic phase (cubic symmetry) to a low temperature insulating phase (tetragonal symmetry) at around 226 K [1]. Recent X-ray diffraction experiment revealed the existence of some superstructure spots in the low temperature phase that cannot be assigned by tetragonal symmetry [2, 3]. The detail of the crystal structure is now on progress. X-ray photoemission spectroscopy revealed also that the valence state of Cu ion is almost monovalent [4]. This means that the ionic configuration is $\text{Cu}^+\text{Ir}^{3+}\text{Ir}^{4+}\text{S}_4^{2-}$. Ir^{3+} is non-magnetic (t_{2g}^6 , $S = 1$) and Ir^{4+}

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has a local moment of $S = 1/2$ in the low spin-state (t_{2g}^5). Dimerization of neighboring two magnetic ions Ir^{4+} at the low symmetry phase which leads to non-magnetic property by forming a spin singlet pair is pointed out as one prevalent mechanism of the MI transition. The Zn substitution for Cu corresponds to a hole-filling in the valence band due to an excess electron of Zn which results in prominent properties of the complete suppression of the MI transition for $x \geq 0.4$ and also of the appearance of superconductivity for $x \geq 0.25$ [5]. Up to now, however, study on electronic structure close to the Fermi level (E_F) has not been done. In this work, we performed an infrared spectroscopic study in order to know a precise change in the electronic structure due to Zn substitution.

2. Experimental

Single phase polycrystalline sample of $\text{Cu}_{1-x}\text{Zn}_x\text{Ir}_2\text{S}_4$ was prepared by chemical reaction method [5]. Subsequently, the powder was reground and pressed under pressure of 2000 kg/cm^2 at 1123 K for 48 h . The surface of obtained sample was metal-polished and mounted to the cold head of the refrigerator in a high-vacuum chamber of $3 \times 10^{-6} \text{ Pa}$. For measurements of reflectivity ($R\omega$) between 0.007 eV and 2 eV , a rapid-scan Fourier interferometer Bruker IFS66v was used with a suitable beam splitter in each available region combined with a Si-bolometer, mercury-cadmium-telluride and Si photo-diode detector, respectively. The reference signal was measured *in-situ* on Au which was coated on the sample surface immediately after the measurement with sample. Above 2 eV , measurement was performed at the beamline BL7B of UVSOR Facility, Institute for Molecular Science (IMS) at Okazaki. The whole ($R\omega$) was obtained by an extrapolation of the lower energy part to a Hagen-Rubens' equation, $(R\omega) = 1 - aE^{-2}$ and the higher energy part to $(R\omega) = bE^{-4}$. Finally, optical conductivity σ was obtained by a Kramers-Kronig analysis of ($R\omega$).

3. Results and discussion

Temperature dependences of σ -spectra of $\text{Cu}_{1-x}\text{Zn}_x\text{Ir}_2\text{S}_4$ ($x \leq 0.5$) are shown in Fig. 1 in a logarithmic scale. The lower energy part of each σ -spectrum undergo a large temperature dependence in contrast with that the higher energy part does not almost change. In order to analyze these results more quantitatively, we fitted each σ -spectrum with a classical Drude oscillator model (Drude components, D) that denotes an intra-band transition of free and a Lorentz oscillator model (Lorentz ones, L) that denotes an inter-band transitions [6]. In $x = 0.1$ sample, the Drude part lost its intensity with the decrease in temperature, and instead of it the lowest band-to-band

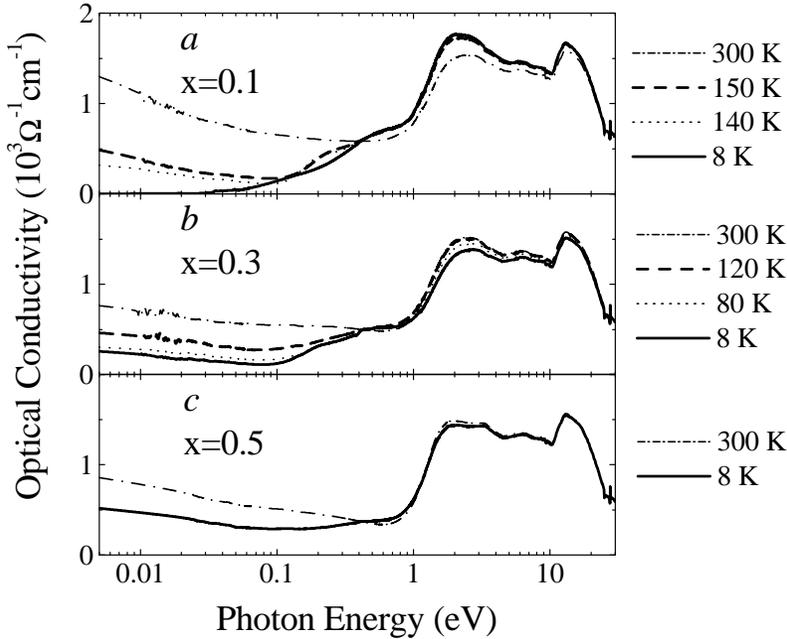


Fig. 1. Optical conductivity spectra of $\text{Cu}_{1-x}\text{Zn}_x\text{Ir}_2\text{S}_4$ (a) for $x=0.1$, (b) for $x = 0.3$ and (c) for $x = 0.5$ at different temperatures.

peaks grew at around 0.5 eV. In $x = 0.5$, the spectra have little temperature dependence and the intensity of the Drude part remained even at 8 K which corresponds to the disappearance of the MI transition.

Typical examples of the fitting in the low energy part are shown in Fig. 2. In the σ -spectrum in the metallic state above T_{MI} , the Drude part was found in common to be composed of two components which correspond to the two branches around Γ point at BZ across the E_{F} in the energy band calculation [7]. With Zn substitution for Cu, the lowest Lorentz peak (named as L) for $x = 0$ sample below T_{MI} was found to split into two components at 0.24 (L_1) and 0.52 eV (L_2) for $x = 0.1$ and $x = 0.3$ samples (see curves (b) and (c)). The intensities of these L_1 and L_2 peaks hardly changed with the Zn concentration. This means that Zn does not participate in the electronic state close to the E_{F} which is mainly composed of Ir-5d and S-3p, and that the role of Zn is to change the degree of the hybridization of the both states through following two effects. One is the decrease in the numbers of Ir⁴⁺ ion which contributes to the formation of a singlet pair at the low temperature phase and the other is the induced distortion by the Zn substitution because of the difference of the ionic radius of Cu and Zn.

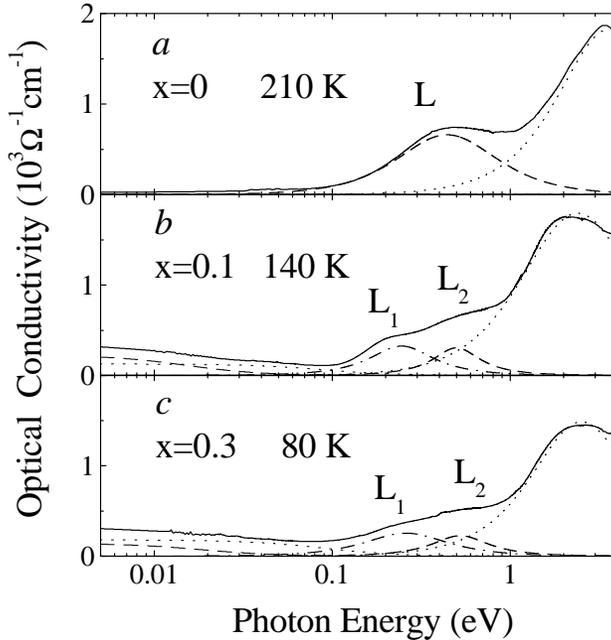


Fig. 2. Decomposition of the low energy part in the spectrum at each sample to Drude and Lorentz components.

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