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Metal-insulator transition in the spinel-type Cu(Ir$_{1-x}$V$_x$)$_2$S$_4$

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Abstract

The spinel CuIr$_2$S$_4$ exhibits a temperature-induced metal-insulator (M-I) transition at around $T_{MI} = 226$ K with a structural transformation, at which a simultaneous bond-dimerization with spin-singlet state and charge-ordering transition takes place. Conversely, CuV$_2$S$_4$ exhibits two step anomalies at about 92 K and 56 K, reflecting the CDW state. High-purity spinel-type Cu(Ir$_{1-x}$V$_x$)$_2$S$_4$ specimens have been synthesized. The lattice constant does not obey Vegard’s law, but looks like a parabolic curve. The d-electrons on the octahedral B-sites play a dominant role in determining the physical properties. A low substitution ($x \approx 0.04$) of V for Ir leads to disappearance of the step-like sharp M-I transition, and vice versa, a low substitution of Ir for V destroys the CDW transition. The local structural and orbital degrees of freedom in Cu(Ir$_{1-x}$V$_x$)$_2$S$_4$ couple to the spin system and the electronic state. The M-I transition and the CDW state are incompatible with each other in Cu(Ir$_{1-x}$V$_x$)$_2$S$_4$. In the metallic phase, a novel relationship, namely “a mirror image effect” has been manifestly found between the residual resistivity and the electronic energy density-of-states $D(E_F)$ at the Fermi level. The lower is the resistivity, the higher is the value of $D(E_F)$. Furthermore, a composition-induced gradual M-I transition is found over the range of $0.00 \leq x \leq 1.00$, where the most insulating behavior is displayed around $x \approx 0.2$–0.3.

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keywords: Spinel-type CuIr$_2$S$_4$; CuV$_2$S$_4$; Cu(Ir$_{1-x}$V$_x$)$_2$S$_4$; Metal-insulator transition; Electrical conductivity; Magnetic properties

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1. Introduction

The thiospinel compound \( \text{CuIr}_2\text{S}_4 \) has spinel structure at room temperature where Cu ions occupy the A (tetrahedral) site and Ir ions occupy the B (octahedral) site, as shown in Fig. 1. \( \text{CuIr}_2\text{S}_4 \) exhibits a metal-insulator (M-I) transition at around \( T_{M-I} = 226 \text{ K} \) with structural transformation, showing hysteresis on heating and cooling. The resistivity of \( \text{CuIr}_2\text{S}_4 \) varies abruptly by nearly a factor 300 at \( T_{M-I} \) [1-69]. The striking feature is the absence of localized magnetic moment below \( T_{M-I} \). A comprehensive review of this M-I transition is provided in ref [67]. Recently, orbital induced Peierls state concerned with the origin of M-I transition in \( \text{CuIr}_2\text{S}_4 \) has been investigated in detail using X-ray photoemission spectroscopy (XPS) [68, 69].

Fig. 1. The cubic unit cell of the spinel structure. Cu ions occupy the A (tetrahedral) sites, and Ir and V ions occupy the B (octahedral) sites. Large white circles indicate S ions.

On the other hand, \( \text{CuV}_2\text{S}_4 \) has the same spinel structure and shows two-step anomalies at about 92 \text{ K} and 56 \text{ K}, in the resistivity and in the magnetic susceptibility [70-83]. These anomalies are related to a charge density wave (CDW) state. The observation of CDW in only a very few three-dimensional cubic structure makes \( \text{CuV}_2\text{S}_4 \) notable, so intensive investigations have been carried out. The recent work reported that the two-step transitions came from the structural modulations and Fermi-liquid behavior for strongly correlated electrons was observed at low temperatures [81].

This paper will present the variation of the M-I transition in \( \text{CuIr}_2\text{S}_4 \) and the change of the anomalies in \( \text{CuV}_2\text{S}_4 \) in the substituted system \( \text{Cu(}\text{Ir}_{1-x}\text{V}_x\text{)}_2\text{S}_4 \). We have successfully synthesized high-quality specimens of \( \text{Cu(}\text{Ir}_{1-x}\text{V}_x\text{)}_2\text{S}_4 \). Systematical study of structural, electrical, and magnetic properties has been made. The variation in the M-I transition with V composition \( x \) is examined. The sharp step-like transition varies drastically with \( x \) and disappears around \( \text{Cu(}\text{Ir}_{0.06}\text{V}_{0.94}\text{)}_2\text{S}_4 \). The transition temperature \( T_{M-I} \) is fairly sensitive to the value of \( x \). Conversely, the two-step anomaly of \( \text{CuV}_2\text{S}_4 \) becomes ill defined, because the resistivity and the susceptibility jumps are not clear at around the composition \( \text{Cu(}\text{Ir}_{0.02}\text{V}_{0.98}\text{)}_2\text{S}_4 \) and disappear completely around \( \text{Cu(}\text{Ir}_{0.05}\text{V}_{0.95}\text{)}_2\text{S}_4 \). A basic characteristic of the phase diagram of temperature vs. composition \( x \) is provided experimentally for \( \text{Cu(}\text{Ir}_{1-x}\text{V}_x\text{)}_2\text{S}_4 \) system. The M-I transition and the CDW state are strictly incompatible with each other in \( \text{Cu(}\text{Ir}_{1-x}\text{V}_x\text{)}_2\text{S}_4 \).
2. Experimental methods

The polycrystalline specimens were prepared by a solid-state reaction. Mixtures of high-purity fine powders of Cu (purity 99.99 %, melting point 1357.5 K), Ir (99.99 %, 2716 K), V (99.9 %, 2190 K), and S (99.999 %, 385.8 K) with normal stoichiometry were heated in sealed quartz tubes to 1123 K and kept at this temperature for 10 days. The resultant powder specimens were reground and pressed to rectangular bars and then were heated to 1123 K for 2 days.

The identification of the crystal structure and the determination of the lattice constants were carried out by X-ray powder diffraction using CuK$\alpha$ radiation at room temperature. The resistivity $\rho$ of sintered specimens with dimensions of about $2\times2\times10$ mm$^3$ was measured by a standard DC four-probe method over the temperature range 4.2 K to room temperature. The DC magnetic susceptibility $\chi$ of powder specimens was measured with a Quantum Design superconducting quantum interference device (rf-SQUID) magnetometer over the temperature range 4.2-300 K at intervals of 5.0 K in an applied magnetic field of 10.000 kOe.

3. Results and discussion

3.1. Lattice constant of Cu(Ir$_{1-x}$V$_x$)$_2$S$_4$

Powder X-ray diffraction patterns at room temperature confirm that Cu(Ir$_{1-x}$V$_x$)$_2$S$_4$ has the spinel type structure in all the V-composition range. Representative results of the X-ray diffraction patterns are presented in Fig. 2. The indices, the $d$ spacings, and the intensities are listed in Tables 1 to 3. The lattice constant, $a$, obtained by the least square method, varies as shown in Fig. 3 at room temperature. The composition dependence of the lattice constant $a$ does not obey the Vegard’s law, but looks like a parabolic curve. The values of $a$ are listed in Table 4, $a$ decreases with V substitution to a broad minimum at around $x = 0.55$; then from $x = 0.55$ to $x = 1.00$ $a$ increases smoothly. The ionic radius of V (0.65 Å for V$^{3+}$) is slightly smaller than that of Ir (0.66 Å for Ir$^{3+}$) for the same valence. A similar behavior of the variation of the lattice constant $a$ with composition, has been observed in the Cu(Ir$_{1-x}$Ti$_x$)$_2$S$_4$ system by Nagata et al. [51] and in the Cu(Ir$_{1-x}$Cr$_x$)$_2$S$_4$ system by Endoh et al. [57]. A reasonable interpretation of the parabolic curve for the lattice constant in Fig. 3 has been proposed by previous researchers [51, 57]. Two effects can be superimposed: the first effect is that the ionic radius decreases with $x$ obeying the Vegard’s law, the second one is the influence originating from the cohesive energy of the conduction electrons in the electron $d$-band. The latter effect is caused by the delocalized nature of $d$ electrons in Cu(Ir$_{1-x}$V$_x$)$_2$S$_4$. Presumably, the influence the second effect is much stronger than that of the former one. Here it should be pointed out that the characteristic parabolic curve can be found manifestly only in special circumstances, where the number of $d$ electron of the substituting atoms on the B-site is much different from that of an Ir atom, such as in the Cu(Ir$_{1-x}$M$_x$)$_2$S$_4$ (M = Ti, V, and Cr) systems. The variation of the lattice constant as indicated in Fig. 3 may influence the electrical and magnetic properties.
Table 1. Indices, observed and calculated values of $d$ spacings and observed intensities for Cu(Ir$_{1-x}$V$_x$)$_2$S$_4$, $x = 0.03$ with lattice constant $a = 9.841$ Å

| $h$ | $k$ | $l$ | $d_{\text{obs}}$(Å) | $d_{\text{cal}}$(Å) | $I_{\text{obs}}$ |
|-----|-----|-----|---------------------|---------------------|--------------|
| 1   | 1   | 1   | 5.7048              | 5.6817              | 58           |
| 2   | 0   | 2   | 3.4848              | 3.4793              | 9            |
| 3   | 1   | 1   | 2.9723              | 2.9672              | 100          |
| 2   | 2   | 2   | 2.8448              | 2.8409              | 36           |
| 4   | 0   | 0   | 2.4636              | 2.4603              | 62           |
| 3   | 1   | 1   | 2.2597              | 2.2577              | 16           |
| 2   | 2   | 2   | 2.0103              | 2.0088              | 3            |
| 3   | 3   | 3   | 1.8953              | 1.8939              | 50           |
| 5   | 1   | 1   | 1.8939              |                     |              |
| 4   | 4   | 0   | 1.7410              | 1.7397              | 69           |
| 3   | 3   | 3   | 1.6643              | 1.6634              | 20           |
| 6   | 2   | 0   | 1.5571              | 1.5560              | 1            |
| 5   | 3   | 3   | 1.5017              | 1.5007              | 15           |
| 6   | 2   | 2   | 1.4844              | 1.4836              | 18           |
| 4   | 4   | 4   | 1.4212              | 1.4204              | 15           |
| 5   | 5   | 1   | 1.3786              | 1.3780              | 12           |
| 7   | 1   | 1   | 1.3780              |                     |              |
| 6   | 4   | 2   | 1.3155              | 1.3151              | 2            |
| 5   | 5   | 3   | 1.2817              | 1.2812              | 23           |
| 7   | 3   | 1   | 1.2812              |                     |              |
| 8   | 0   | 0   | 1.2306              | 1.2301              | 10           |
| 7   | 3   | 3   | 1.2026              | 1.2023              | 1            |
| 6   | 6   | 0   | 1.1602              | 1.1598              | 1            |
| 8   | 2   | 2   | 1.1598              |                     |              |
| 5   | 5   | 5   | 1.1367              | 1.1363              | 13           |
| 7   | 5   | 1   | 1.1363              |                     |              |
| 6   | 6   | 2   | 1.1292              | 1.1288              | 7            |
| 8   | 4   | 0   | 1.1005              | 1.1003              | 17           |

Table 2. Indices, observed and calculated values of $d$ spacings and observed intensities for Cu(Ir$_{1-x}$V$_x$)$_2$S$_4$, $x = 0.50$ with lattice constant $a = 9.768$ Å

| $h$ | $k$ | $l$ | $d_{\text{obs}}$(Å) | $d_{\text{cal}}$(Å) | $I_{\text{obs}}$ |
|-----|-----|-----|---------------------|---------------------|--------------|
| 1   | 1   | 1   | 5.6541              | 5.6396              | 40           |
| 2   | 2   | 0   | 3.4582              | 3.4535              | 16           |
| 3   | 1   | 1   | 2.9492              | 2.9452              | 100          |
| 2   | 2   | 2   | 2.8220              | 2.8198              | 13           |
| 4   | 0   | 0   | 2.4442              | 2.4420              | 59           |
| 3   | 3   | 1   | 2.2425              | 2.2409              | 8            |
| 4   | 2   | 2   | 1.9952              | 1.9939              | 5            |
| 3   | 3   | 3   | 1.8813              | 1.8799              | 45           |
| 5   | 1   | 1   | 1.8799              |                     |              |
| 4   | 4   | 0   | 1.7275              | 1.7268              | 69           |
| 5   | 3   | 1   | 1.6521              | 1.6511              | 9            |
| 6   | 2   | 0   | 1.5448              | 1.5445              | 1            |
| 5   | 3   | 3   | 1.4904              | 1.4896              | 10           |
| 6   | 2   | 2   | 1.4734              | 1.4726              | 5            |
| 4   | 4   | 4   | 1.4105              | 1.4099              | 11           |
| 5   | 5   | 1   | 1.3683              | 1.3678              | 6            |
| 7   | 3   | 1   | 1.3678              |                     |              |
| 6   | 4   | 2   | 1.3058              | 1.3053              | 2            |
| 5   | 5   | 3   | 1.2720              | 1.2717              | 15           |
| 7   | 3   | 1   | 1.2717              |                     |              |
| 8   | 0   | 0   | 1.2214              | 1.2210              | 8            |
| 7   | 3   | 3   | 1.1936              | 1.1934              | 1            |
| 5   | 5   | 5   | 1.1282              | 1.1279              | 6            |
| 7   | 3   | 1   | 1.1279              |                     |              |
| 8   | 4   | 0   | 1.0924              | 1.0921              | 5            |

Fig. 2. Powder X-ray diffraction patterns for $x = 0.03$, 0.50 and 0.98 at room temperature.

Fig. 3. The lattice constant $a$ as a function of V composition $x$ at room temperature.
Table 3. Indices, observed and calculated values of \( d \) spacings and observed intensities for Cu(Ir\(_1-x\) V\(_x\))\(_2\)S\(_4\), \( x = 0.98 \) with lattice constant \( a = 9.805 \) Å

| \( h \) | \( k \) | \( l \) | \( d_{\text{obs}}(\text{Å}) \) | \( d_{\text{calc}}(\text{Å}) \) | \( I_{\text{obs}} \) |
|---|---|---|---|---|---|
| 1 | 1 | 1 | 5.6757 | 5.6609 | 6 |
| 2 | 2 | 0 | 3.4715 | 3.4666 | 47 |
| 3 | 1 | 1 | 2.9607 | 2.9563 | 100 |
| 2 | 2 | 2 | 2.8342 | 2.8305 | 5 |
| 4 | 0 | 0 | 2.4545 | 2.4513 | 54 |
| 2 | 2 | 2 | 2.0027 | 2.0014 | 16 |
| 3 | 3 | 3 | 1.8878 | 1.8870 | 43 |
| 5 | 1 | 1 | | 1.8870 | |
| 4 | 4 | 0 | 1.7342 | 1.7333 | 75 |
| 5 | 3 | 1 | 1.6560 | 1.6573 | 1 |
| 6 | 2 | 0 | 1.5514 | 1.5503 | 4 |
| 5 | 3 | 3 | 1.4960 | 1.4952 | 9 |
| 6 | 2 | 2 | 1.4788 | 1.4782 | 2 |
| 4 | 4 | 4 | 1.4158 | 1.4152 | 7 |
| 5 | 5 | 1 | 1.3732 | 1.3730 | 1 |
| 7 | 1 | 1 | | 1.3730 | |
| 6 | 4 | 2 | 1.3105 | 1.3102 | 5 |
| 5 | 5 | 3 | 1.2767 | 1.2765 | 11 |
| 7 | 3 | 1 | | 1.2765 | |
| 8 | 0 | 0 | 1.2258 | 1.2256 | 9 |
| 8 | 2 | 2 | 1.1559 | 1.1555 | 2 |
| 5 | 5 | 5 | 1.1324 | 1.1322 | 5 |
| 7 | 5 | 1 | | 1.1322 | |
| 8 | 4 | 0 | 1.0964 | 1.0962 | 6 |

Table 4. Lattice constant \( a \) of spinel-type Cu(Ir\(_1-x\) V\(_x\))\(_2\)S\(_4\) at room temperature.

| \( x \) | \( a (\text{Å}) \) |
|---|---|
| 0.00 | 9.847 |
| 0.03 | 9.841 |
| 0.05 | 9.834 |
| 0.10 | 9.817 |
| 0.15 | 9.801 |
| 0.20 | 9.794 |
| 0.25 | 9.788 |
| 0.30 | 9.779 |
| 0.35 | 9.775 |
| 0.40 | 9.771 |
| 0.45 | 9.767 |
| 0.50 | 9.768 |
| 0.55 | 9.766 |
| 0.60 | 9.767 |
| 0.65 | 9.767 |
| 0.70 | 9.777 |
| 0.75 | 9.773 |
| 0.80 | 9.781 |
| 0.85 | 9.787 |
| 0.90 | 9.793 |
| 0.95 | 9.800 |
| 0.98 | 9.805 |
| 1.00 | 9.808 |

3.2. Variation of the metal-insulator and CDW transitions in Cu(Ir\(_1-x\) V\(_x\))\(_2\)S\(_4\)

Fig. 4 shows the temperature dependence of the electrical resistivity for the sintered specimens. With increasing V-composition \( x \), \( T_{M-I} \) decreases steeply and the height of the resistivity jump at \( T_{M-I} \) becomes smaller as shown in Fig. 5. The temperature dependence of the resistivity below \( T_{M-I} \) is semiconductive. The resistivity jump becomes ill defined around \( x = 0.05 \). With increasing \( x \) over \( x = 0.30 \), the resistivity becomes lower and the metallic state is recovered at still higher compositions. Figs. 5 and 6 present the results for the region \( 0.00 \leq x \leq 0.10 \) and \( 0.90 \leq x \leq 1.00 \), respectively.

Pure CuV\(_2\)S\(_4\) shows strong sample dependence of the resistivity so far [70-83]. Recently the results of the resistivity for CuV\(_2\)S\(_4\) converge on the representative datum by H. Okada et al. [81]. The single crystals of CuV\(_2\)S\(_4\) are not always of high purity and high quality [74, 82-83].

Fig. 7 shows the temperature dependence of the magnetic susceptibility \( \chi \) for the powder specimens. The value of \( \chi \) is defined as \( \chi = M / H \): the magnetization \( M \) divided by the applied magnetic field \( H \). Measurements were carried out at a constant applied magnetic field of 10 kOe. Figs. 8 to 10 present the results for the V-composition region of \( 0.00 \leq x \leq 0.15 \), \( 0.20 \leq x \leq 0.70 \) and the higher \( x \) region of \( 0.90 \leq x \leq 1.00 \). The resistivity jump due to the \( T_{M-I} \) corresponds exactly to the step-like anomaly of the susceptibility for \( x = 0.00 \) and 0.03. For \( x \geq 0.05 \), no step-like anomaly is observed. With increasing V-composition \( x \), the temperature dependence of the susceptibility becomes rather steeper below \( T_{M-I} \) as seen in Fig. 8. It should be noticed that the magnetic susceptibility of CuIr\(_2\)S\(_4\), in the low
Fig. 4. Temperature dependence of the electrical resistivity $\rho$ for sintered Cu(Ir$_{1-x}$V$_x$)$_2$S$_4$ specimens.

Fig. 5. Temperature dependence of the electrical resistivity $\rho$ for sintered Cu(Ir$_{1-x}$V$_x$)$_2$S$_4$ specimens for $0.00 \leq x \leq 0.10$.

Fig. 6. Temperature dependence of the electrical resistivity $\rho$ for sintered Cu(Ir$_{1-x}$V$_x$)$_2$S$_4$ specimens for $0.90 \leq x \leq 1.00$.

Fig. 7. Magnetic susceptibility versus temperature of Cu(Ir$_{1-x}$V$_x$)$_2$S$_4$. The applied magnetic field is 10 kOe.
temperature insulating phase, indicates basically a non-magnetic state except a paramagnetic behavior and small amount of diamagnetism due to the core atomic orbitals. Fig. 9 shows the paramagnetic behavior with temperature-independent constant value \( \chi_0 \) which is defined in the next section.

The susceptibility of CuV\(_2\)S\(_4\) (\( x = 1.00 \)) exhibits two step anomalies around \( T = 90 \) K and 55 K due to the CDW transition, as can be seen in Fig 10. The absolute value of the susceptibility for CuV\(_2\)S\(_4\) and the general feature of the temperature dependence with the two-step anomaly are in agreement with the result of the previous researchers [81]. With \( x \) decreasing a little below \( x = 1.00 \), the CDW transition becomes ill defined. For \( x = 0.98 \), no step-like anomaly is observed at 55 K and the sharp jump smears out around 90 K. The sharp anomaly disappears beyond the extremely little substitution of Ir atom for V.

3.3. The value of effective magnetic moment

The magnetic susceptibility can be fitted to a modified Curie-Weiss law, \( \chi = C / (T - \theta) + \chi_0 \) where \( \chi_0 \) is the temperature independent term, \( C \) the Curie constant, and \( \theta \) the Weiss temperature. Table 5 provides the summary of the magnetic data. The second column from the right in Table 5 indicates the value calculated assuming that only the V ions possess a magnetic moment. It is hard to draw the definite conclusion that the induced magnetic moment originates from the substitution of Ir by V. The effective magnetic moment per V ion in the low temperature region is much less than the value corresponding to \( s = 1/2 \), leading to \( \sqrt{s(s+1)} = 1.73 \). There is no indication of any systematic variation of the effective magnetic moment. Therefore, there seems to be no intrinsic localized magnetic moment in this system. The low temperature increase in the susceptibility may arise from the existence of extrinsic localized moments at impurity sites or at other kind of lattice imperfections due to e.g. nonstoichiometry.
Table 5. Summary of the magnetic properties of Cu(Ir$_{1-x}$V$_x$)$_2$S$_4$. These numerical values are extracted from the magnetic susceptibility at lower temperatures based on the modified Curie-Weiss law $\chi = C / (T - \theta) + \chi_0$. The value of $\chi_0$ includes appreciable experimental errors.

| $x$   | $\chi_0$ (emu mol$^{-1}$) | $C$ (emu K mol-f.u.$^{-1}$) | $\theta$ (K) | $p_{eff}$ (f.u.$^{-1}$) | $p_{eff}$ (V-ion$^{-1}$) | Temperature (K) |
|-------|---------------------------|-----------------------------|--------------|--------------------------|--------------------------|-----------------|
| 0.03  | -7.28 $\times$ 10$^{-6}$  | 1.47 $\times$ 10$^{-3}$     | -2.541       | 0.108                    | 0.443                    | 10 - 50         |
| 0.05  | 2.77 $\times$ 10$^{-5}$   | 1.34 $\times$ 10$^{-3}$     | -0.429       | 0.103                    | 0.327                    | 10 - 50         |
| 0.10  | -1.45 $\times$ 10$^{-5}$  | 4.78 $\times$ 10$^{-3}$     | -0.598       | 0.195                    | 0.437                    | 4.2 - 100       |
| 0.15  | -1.17 $\times$ 10$^{-5}$  | 2.80 $\times$ 10$^{-3}$     | -2.506       | 0.150                    | 0.273                    | 10 - 50         |
| 0.20  | -2.78 $\times$ 10$^{-5}$  | 3.66 $\times$ 10$^{-3}$     | -1.241       | 0.171                    | 0.270                    | 10 - 100        |
| 0.30  | -5.90 $\times$ 10$^{-5}$  | 3.59 $\times$ 10$^{-2}$     | 5.420        | 0.535                    | 0.691                    | 55 - 300        |
| 0.50  | 1.90 $\times$ 10$^{-4}$   | 7.30 $\times$ 10$^{-2}$     | 4.380        | 0.764                    | 0.764                    | 55 - 300        |
| 0.70  | 5.83 $\times$ 10$^{-4}$   | 4.19 $\times$ 10$^{-2}$     | 7.493        | 0.579                    | 0.489                    | 55 - 200        |
| 0.90  | 1.01 $\times$ 10$^{-3}$   | 1.28 $\times$ 10$^{-2}$     | -6.354       | 0.320                    | 0.238                    | 4.5 - 100       |
| 0.95  | 9.95 $\times$ 10$^{-4}$   | 9.96 $\times$ 10$^{-3}$     | -7.853       | 0.282                    | 0.205                    | 10 - 50         |
| 0.98  | 9.15 $\times$ 10$^{-4}$   | 6.85 $\times$ 10$^{-3}$     | -9.549       | 0.234                    | 0.167                    | 10 - 65         |

Fig. 10. Magnetic susceptibility versus temperature of Cu(Ir$_{1-x}$V$_x$)$_2$S$_4$ for $0.90 \leq x \leq 1.00$. The applied magnetic field is 10 kOe.

Fig. 11. Comparison of the resistivity and the magnetic susceptibility at 280 K for $0.00 \leq x \leq 1.00$. 
3.4. A mirror image effect between the residual resistivity and the Pauli susceptibility

Fig. 11 presents the composition dependence of the resistivity and the magnetic susceptibility at 280 K. Below 230 K, the $M-I$ transition occurs for low values of $x$, moreover the Curie like behavior arises for all the compositions $x$. Therefore it is hard to extract the metallic property. Indeed, for the composition region $x \geq 0.10$, the metallic state is not verified from the temperature dependence of the resistivity. Nevertheless, Fig. 11 gives a rough sketch of the general relation between the magnitude of the residual resistivity and the Pauli paramagnetic contribution. The Pauli paramagnetic susceptibility is proportional to the electronic energy density-of-states at the Fermi level, $D(\varepsilon_F)$. The measured susceptibility, shown in Fig. 11, lower panel, has a minimum value at around $x = 0.20$, and shows two approximately linear parts, with opposite signs.

Figs. 12 and 13 indicate the expanded plots for the composition dependences of the resistivity and the susceptibility at 280 K for $0.00 \leq x \leq 0.20$ and $0.70 \leq x \leq 1.00$, respectively. It should be noted that the susceptibility corresponds inversely to the height of resistivity, say, “a mirror image effect” or “an alligator mouth”. This mirror image effect between the residual resistivity and $D(\varepsilon_F)$ can be clearly seen in Figs. 12 and 13: the lower is the resistivity, the higher is the value of $D(\varepsilon_F)$.

Almost the same effect has been observed and reported in detail for the Cu(Ir$_{1-x}$Pt$_x$)$_2$S$_4$ system by Matsumoto et al. [41] and also for the Cu(Ir$_{1-x}$Ti$_x$)$_2$S$_4$ system by Nagata et al. [51]. Over the range of $0.20 \leq x \leq 0.70$, the metallic state at 280 K is not confirmed. Consequently, the precise comparison itself does not make sense for the results of Fig. 11, although the mirror effect is present for $x > 0.3$.

![Fig. 12. Comparison of the resistivity and the magnetic susceptibility at 280 K for $0.00 \leq x \leq 0.20$.](image1)

![Fig. 13. Comparison of the resistivity and the magnetic susceptibility at 280 K for $0.70 \leq x \leq 1.00$.](image2)
3.5. Phase diagram of Cu(Ir$_{1-x}$V$_x$)$_2$S$_4$

Fig. 14 shows a crude sketch of a phase diagram for $T$ versus $x$, which displays only an extremely low composition region ($x \leq 0.10$) and a high one ($x \geq 0.98$) in the Cu(Ir$_{1-x}$V$_x$)$_2$S$_4$ system. The $M$-$I$ transition and the CDW state are incompatible with each other in Cu(Ir$_{1-x}$V$_x$)$_2$S$_4$. The temperature induced sharp $M$-$I$ transition is seen for $x \leq 0.03$ and is smeared at around $x = 0.05$. The shaded area of $0.03 \leq x \leq 0.05$ shows a weak indication of the $M$-$I$ transition. With increasing $x$, the temperature dependence of the resistivity changes from metallic to semiconducting. Weakly doped CuIr$_2$S$_4$ can lie on either side of the $M$-$I$ transition induced by electron correlation. Furthermore, a composition induced gradual $M$-$I$ transition is found over the range of $0.00 \leq x \leq 1.00$, where the more insulating behavior is found around the composition region of $x \approx 0.2$–$0.3$.

Solid circles for $x = 1.00$ show a two-step transition at $T_{C1}$ and $T_{C2}$. The discovery of the CDW transition in the cubic spinel CuV$_2$S$_4$ has attracted intensive researches [70]. In contradistinction to this trend, a recent study indicates a two-step structural modulation and Fermi liquid behavior [81]. The transition at $T_{C1}$ (92 K) is reversible from cubic to tetragonal, while the transition at $T_{C2}$ (56 K) exhibits a thermal hysteresis at which the lattice constant is modulated, a discontinuity without changing the symmetry [81]. The origin of the two anomalies in CuV$_2$S$_4$ may remain controversial, but is not the main subject in the present study. Here, we refer to the two-step transitions $T_{C1}$ and $T_{C2}$ as CDW transitions. The sharp two-step transitions are smeared out at around $x = 0.98$. The shaded areas, for the range of $0.97 \leq x \leq 1.00$, show weak indications of $T_{C1}$ and $T_{C2}$. Extensive theoretical effort to understand the present experimental results is required.
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