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著者	BURKOV A.T., NAKAMA T., HEDO M., SHINTANI K., YAGASAKI K., MATSUMOTO N., NAGATA Shoichi
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Anomalous resistivity and thermopower of the spinel-type compounds CuIr_2S_4 and CuIr_2Se_4

A. T. Burkov

Department of Physics, University of the Ryukyus, Okinawa 903-01, Japan
and A. F. Ioffe Physical-Technical Institute, Russian Academy of Sciences, St. Petersburg 194021, Russia

T. Nakama, M. Hedo, K. Shintani, and K. Yagasaki

Department of Physics, University of the Ryukyus, Okinawa 903-01, Japan

N. Matsumoto, and S. Nagata

Department of Materials Science and Engineering, Muroran Institute of Technology, Muroran, Hokkaido 050-8585, Japan

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Resistivity (ρ) and thermopower (S) of spinel-type compounds CuIr_2S_4 and CuIr_2Se_4 have been measured at temperatures from 2 to 900 K under magnetic field from 0 to 15 T. The thermopower is positive in the metallic phase of both compounds at high temperatures, as well as in the low-temperature insulating state of CuIr_2S_4 . The positive thermopower of the insulating phase implies p -type charge carriers, in agreement with the recent photoemission results. The low-temperature resistivity of CuIr_2S_4 is in good agreement with the Efros-Shklovskii variable-range hopping conductivity mechanism: $\rho = \rho_0 \exp[(T^*/T)^{1/2}]$. The most striking result is that the resistivity of the metallic phases is well described by an exponential-type temperature dependence in a wide temperature range from 2 K to at least 900 K. This unusual result for metals type of the resistivity temperature dependence, as well as other features in the transport properties, imply a nonconventional conductivity mechanism. The magnetoresistivity $\Delta\rho$ is positive and proportional to H^2 , while magnetothermopower $\Delta S = S(H, T) - S(0, T)$ is very small for both compounds at all temperatures.

I. INTRODUCTION

Spinel-type compound CuIr_2S_4 is known for the metal-insulator transition (MIT) which it displays at $T \approx 230$ K.^{1,2} The MIT in CuIr_2S_4 is associated with a structural transition from the high-temperature cubic symmetry to the low-temperature tetragonal symmetry. The isostructural (cubic) compound CuIr_2Se_4 remains metallic at ambient pressure at temperatures down to 0.5 K.³ However, the MIT can be induced in CuIr_2Se_4 by the application of pressure of about 4 GPa.⁴ Despite rather extensive studies¹⁻⁷ the precise driving force of the transition in CuIr_2S_4 remains unknown. Recent photoemission results⁷ suggest that the metallic phase of CuIr_2S_4 and the isostructural compound CuIr_2Se_4 have unusual features in their electronic structure, which may have an important impact on the electronic transport. Additionally, the instability of the metallic phase due to the closeness of both these compounds to the MIT may result in a nontrivial transport property behavior.⁸ Nevertheless, no attempt has been made to appreciate whether the transport properties in the metallic state of the compounds can be described within the framework of a conventional metallic conductivity mechanism, or they have some unusual features. The only transport property, which has been investigated for these compounds, is the resistivity (recently thermopower and thermal conductivity of CuIr_2S_4 and CuIr_2Se_4 were measured at 10 to 300 K,⁹ but the results have not been published yet). The resistivity of CuIr_2S_4 has been measured from about 20 K to room temperature,¹ whereas the resistivity of CuIr_2Se_4 is known from room temperature down to 0.5 K.³ No data have been available above room temperature. The resistivity was used as the tool to detect the insulating phase and to determine the activation energy, or band gap, in the

insulating phase. It is clear from the literature data, however,^{1,5} that in the insulating phase of CuIr_2S_4 the conductivity does not show a simple activation variation with temperature, and therefore the meaning of the extracted parameters is questionable. The goal of this study is the investigation of thermopower and resistivity of CuIr_2S_4 and CuIr_2Se_4 in an extended temperature range as an attempt to clarify the conductivity mechanism in the metallic phase of both compounds, and in the insulating phase of CuIr_2S_4 . We have measured two transport coefficients, which provide complimentary information about transport mechanism: resistivity is primarily dependent on the magnitude of conduction electron mobility, whereas thermopower is dependent on the energy derivative of the mobility. The measurements were made in a broad temperature range from 2 to 900 K, with temperature varying by more than two orders of magnitude. Temperature-induced scattering gives the main contribution to the transport properties in this temperature range. This is cardinal when one wants to extract information from the temperature-dependent transport properties concerning the underlying physical mechanism. In the previous investigations it was found that despite the fact that both compounds are nonmagnetic, the magnetic susceptibility shows a Curie-like variation at low temperatures, presumably due to magnetic impurities.⁵ To examine whether there is an effect of residual magnetic impurities on the transport properties, both resistivity and thermopower below room temperature were measured in magnetic fields of 0 to 15 Tesla.

II. EXPERIMENTAL PROCEDURES

The transport property measurements were made with polycrystalline sintered samples. The sample preparation

procedures were described elsewhere.¹ A four-probe dc method was used for the electrical resistivity measurements; for the thermopower measurements a differential method was utilized. At low temperatures (from 2 to 300 K) the thermopower was measured using a setup with a modulation of temperature gradient.¹⁰ Both resistivity and thermopower in this temperature range were measured in magnetic fields from 0 T to 15 T with the magnetic field directed along the current, or the temperature gradient direction, respectively. At high temperatures (from 100 to 900 K) the resistivity and thermopower were measured simultaneously. The estimated error in the determination of absolute value of the electrical resistivity is $\pm 1\%$. The thermopower was measured with an accuracy of $\pm(0.5 \mu\text{V K}^{-1} + 3\%)$.

III. EXPERIMENTAL RESULTS AND DISCUSSION

A. Resistivity

The resistivity of CuIr_2Se_4 and of CuIr_2S_4 at temperatures from 2 K up to 900 K is shown in Fig. 1. Two characteristic features of the resistivity are obvious from the experimental data. First, the resistivity of both compounds at high temperatures shows a pronounced saturation tendency. And, second, the magnitude of ρ considerably exceeds 0.2 m Ω cm, which value is commonly accepted as an approximate limit for the metallic conductivity.¹¹ In the high-temperature limit, $T \gg \Theta_D$ (Θ_D is the Debye temperature), theory predicts that resistivity of a metal linearly increases with the temperature. But the experimental resistivity of most of the metals displays at high temperatures essential deviations from the linear dependency, following from theory.^{12,13} Particularly, the saturation of resistivity at high temperatures is not uncommon for high-resistivity metals, such as transition metals and compounds. Therefore, the saturation in itself cannot be considered as an unusual feature of a metallic resistivity temperature dependency (yet, there is no universal explanation of the saturation). A reason for the large magnitude of the resistivity can be in part a lower (than the theoretical) density of the sintered samples (the density of our samples was about 75% of the theoretical density). But, only the lower density of the samples cannot account for the large magnitude of the resistivity, especially in the case of CuIr_2S_4 .

At low (much lower than Θ_D) temperatures the resistivity of a conventional metal, according to the theory, is expected to vary as $\rho - \rho_0 = aT^m$, with m in the range from 2 to 5, depending on the scattering mechanism.¹¹ Experimentally the power dependency of resistivity on temperature, predicted by theory, has been observed for many metals, although in a rather limited temperature range, usually below 10 K.¹² The temperature-dependent part of the resistivity of CuIr_2Se_4 from 2 K to about 10 K does vary approximately as $\rho \propto T^4$. In the framework of the conventional metallic conductivity model this implies that the main conductivity mechanism in this low-temperature range is due to electron-phonon scattering. The resistivity in this temperature range increases, however, by less than 1 $\mu\Omega$ cm, i.e., about 0.25% of its room-temperature value. This raises the question whether a simple law exists, to which the temperature-dependent resistivity follows as it increases from the values of about 1 $\mu\Omega$ cm at 10 K, to about 1 m Ω cm at 1000 K. A more elaborate analysis reveals that the resistivity indeed has

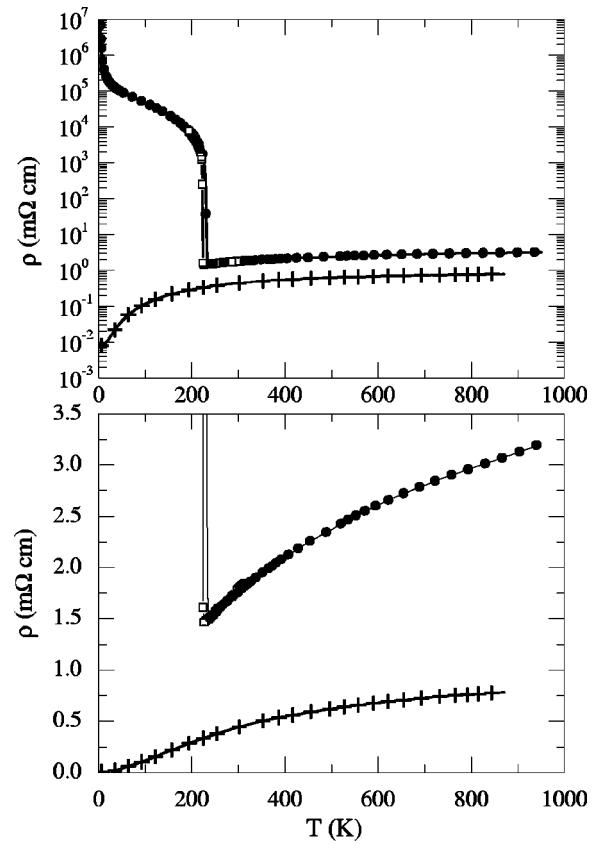


FIG. 1. Temperature dependence of the resistivity of CuIr_2Se_4 (+) and of CuIr_2S_4 (□ on cooling and ● on heating) in zero magnetic field. The upper panel shows the resistivity in logarithmic scale, whereas in the lower panel the resistivity is presented in linear scale.

overall temperature dependence, which is rather different from the conventional power law. In Fig. 2 the logarithmic temperature derivative of the resistivity, $[1/(\rho - \rho_0)] \times (d\rho/dT)$, is plotted as a function of temperature in double logarithmic scale. For a power dependence of resistivity on temperature: $\rho = aT^m + \rho_0$, the logarithm of the derivative is expressed as $\ln\{[1/(\rho - \rho_0)] (d\rho/dT)\} = \ln m - \ln T$, i.e., is a linear function of $\ln T$ with the gradient of -1. The experimental dependence, shown in Fig. 2, displays two regions of a linear variation with $\ln T$: below approximately 200 K it has the gradient of about $-3/2$; whereas at higher temperatures the gradient is close to -2 . These values of the gradient of $\ln\{[1/(\rho - \rho_0)] (d\rho/dT)\}$ versus $\ln T$ dependence correspond to an exponential temperature dependence of the resistivity: $\rho - \rho_0 = a \exp[-(T^*/T)^n]$ with $n = 1/2$ and $n = 1$, respectively. This type of temperature dependency of the resistivity looks very unusual for a metal. Hence, the first question is whether this exponential behavior is a real fact. In the present case it seems that the experimental evidence is rather clear in favor of the exponential temperature dependence of the resistivity. As can be seen in Fig. 2, the difference between the exponential temperature dependence and a power dependence is well beyond the experimental uncertainty in the range of temperatures covering about two orders of magnitude from at least 10 to 900 K. Note, the power temperature dependence of the resistivity for conventional metals has been observed in a far more limited temperature

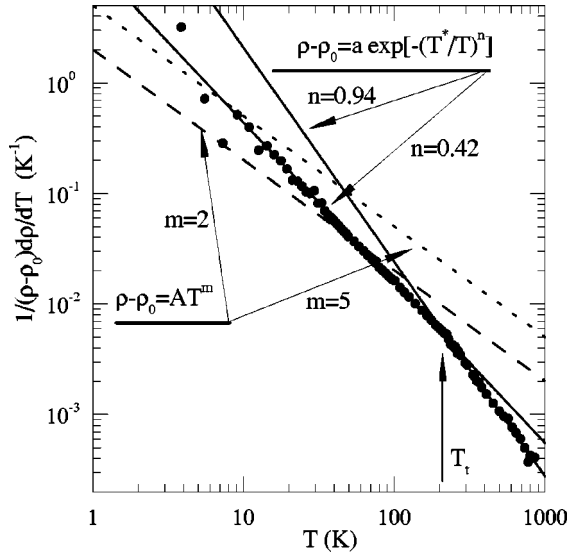


FIG. 2. Derivative of resistivity $[1/(\rho(T) - \rho_0)](d\rho/dT)$ of CuIr_2Se_4 against temperature in double logarithmic scale. Solid lines show the derivative for the function $\rho = a \exp[-(T^*/T)^n]$ with $n = 0.42$ and $n = 0.94$. The broken and dotted lines display the derivative for a power dependence of resistivity on temperature: $\rho - \rho_0 = b T^m$. There is a change of the gradient of the experimental temperature dependence at $T = T_t$.

range, usually of 1 to 10 K.¹² Furthermore, the present observation is not an isolated fact. Experimentally, the existence of the exponential resistivity temperature dependence was initially noticed in Nb_3Sn compound,¹⁴ and recently, a similar exponential behavior of the resistivity was found in CuRh_2Se_4 and CuRh_2S_4 compounds.¹⁵ We want to emphasize that the result presented in Fig. 2 implies a conductivity mechanism, which is fundamentally different from the conventional picture of metallic conductivity. The latter suggests that the resistivity of a metal obeys a power temperature dependency at low- and high-temperature limits, being a more complex function at intermediate temperatures. Physically, this picture is based on a nonactivated scattering of conduction electrons, i.e., the scattering which magnitude is nonzero at any nonzero temperature. In contrast, Fig. 2 indicates that the resistivity of CuIr_2Se_4 follows the exponential dependency on temperature in the whole temperature range from at least 10 K to at least 900 K. This fact also has a clear physical meaning: the main temperature-induced scattering mechanism for conduction electrons is of an activation type, i.e., the magnitude of the scattering is exponentially small below some characteristic temperature. From a theoretical point of view, the possibility of such a resistivity temperature variation has been anticipated and few mechanisms, which can lead to an exponential dependence of resistivity on temperature, have been discussed. The most familiar is Mott's s - d scattering model.¹⁶ It is assumed in this model that s electrons carry the bulk of current. Impurities, phonons, and other scattering mechanisms cause scattering of the s electrons into vacant s or d states, so that the contribution to total resistivity, originating from the i th scattering mechanism can be expressed as $\rho_i = \rho_i^{s-s} + \rho_i^{s-d}$. Each of these contributions is proportional to the corresponding scattering probability which depends upon the density of states $N(\varepsilon_F)$ into which the electrons are scattered.¹⁷ In transition metals and

transition-metal-based compounds the d -electron contribution to the density of states at the Fermi energy can be much larger than the contribution of s electron states: $N_d(\varepsilon_F) \gg N_s(\varepsilon_F)$, therefore the s - d scattering occurs much more frequently than the s - s scattering. As the result of this, the s - d scattering may give a main contribution to the resistivity. Furthermore, the scattering probability also depends upon Fermi surface geometry through the conservation law of crystal momentum. If the d -like and s -like parts of the Fermi surface are separated in k space then only the phonons with a wave vector larger than some minimum wave vector k_{\min} will be effective for s - d scattering. As a result, at low temperatures, when no such phonons exist, the s - d scattering contribution to the resistivity exponentially decreases. This mechanism was discussed already in 1938 by Wilson.¹⁶ One should expect a similar exponential variation of the s - d resistivity when the d -electron contribution to the density of states (DOS), $N_d(\varepsilon)$, vanishes at ε_F , having a gap at the Fermi energy. Other mechanisms of the activation-type temperature dependence of resistivity include scattering on localized states split by a crystal field,¹⁸ or low-dimensional models of conductivity.¹⁴

Since the DOS of CuIr_2S_4 at the Fermi energy has a large contribution from Ir $5d$ states,⁶ and it is plausible that the same is true for CuIr_2Se_4 , it would be reasonable to assume that s - d Mott's scattering is relevant in the present case. Yet, there is a difficulty with this model: it predicts (at least in its simple form) the resistivity varying as $\rho = a \exp(-T^*/T)$. The experimental resistivity does follow this simple exponential dependency only at high temperatures, whereas below about 200 K the resistivity varies as $\rho = a \exp[-(T^*/T)^n]$ with $n \approx 1/2$, which is in an apparent contradiction to the s - d model. The resistivity behavior of CuIr_2S_4 , presented below, probably gives a hint to an alternative conductivity mechanism. The change of the resistivity temperature dependency of CuIr_2Se_4 around $T = 200$ K will be discussed in more detail later.

Figure 3 presents the dependence of $(1/\sigma)(d\sigma/dT)$ and $(1/\rho)(d\rho/dT)$ on T in double logarithmic scale for CuIr_2S_4 . In the high-temperature range, above the MIT, the resistivity of CuIr_2S_4 varies as $\rho = a \exp[-(T^*/T)^{1/2}]$, similar to the resistivity of CuIr_2Se_4 below 200 K. In contrast to CuIr_2Se_4 , the resistivity of CuIr_2S_4 does not show the simple exponential temperature dependency $\rho = a \exp(-T^*/T)$ in the investigated temperature range. It is a possibility that the change of the resistivity temperature dependency from $\rho = a \exp(-T^*/T)$ to $\rho = a \exp[-(T^*/T)^{1/2}]$ is a precursor of the MIT, and it occurs in CuIr_2S_4 at a higher temperature.

Below the MIT the conductivity $\sigma = 1/\rho$ of CuIr_2S_4 does not follow the simple activation temperature dependence $\sigma = b \exp(-\Delta/T)$ expected for an insulator. At temperatures below 50 K the temperature dependence is well described by $\sigma = b \exp[-(T^*/T)^{1/2}]$. The dependence conforms to the Efros-Shklovskii hopping mechanism with long-range Coulomb correlations.¹⁹ Therefore, we conclude that hopping represents the principal conductivity mechanism in CuIr_2S_4 at low temperatures, and that Coulomb correlations are likely important in stabilization of the insulating phase. It is interesting that in the low-temperature range the temperature dependence of $[(1/\sigma)(d\sigma/dT)]$ for CuIr_2S_4 has a strong resem-

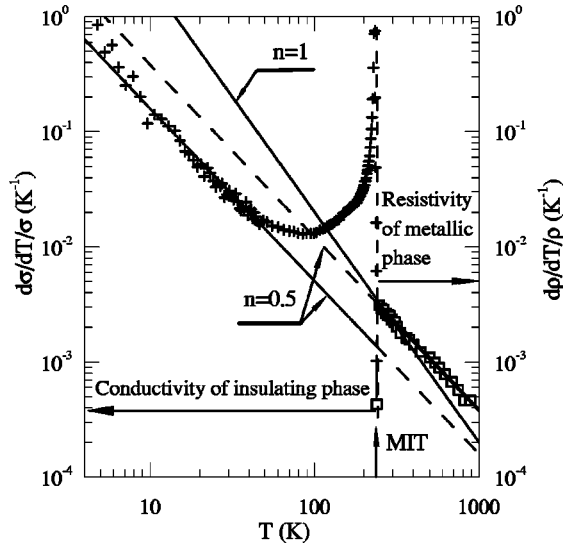


FIG. 3. The derivative of the resistivity $[1/\rho(T)](d\rho/dT)$ (\square), and the derivative of the conductivity $[1/\sigma(T)](d\sigma/dT)$ ($+$) of CuIr_2S_4 against temperature in double logarithmic scale. In the temperature range below the MIT, the derivative of the conductivity of insulating CuIr_2S_4 is displayed (left y axis). Above the MIT the derivative of the resistivity of the metallic phase is depicted (right y axis). Solid and broken lines show the derivative for function $f = a \exp[-(T^*/T)^n]$ with $n = 1/2$ and $n = 1$.

blance to the dependence of $[(1/\rho)(d\rho/dT)]$ in the metallic phase of CuIr_2S_4 , and in CuIr_2Se_4 below 200 K; see Fig. 3. This parallelism suggests that similar mechanisms are operating in the conductivity of the low-temperature insulating phase of CuIr_2S_4 , and in the resistivity of the metallic phase of CuIr_2S_4 and in CuIr_2Se_4 . We speculate that some temperature-induced, very low mobility electron excitations are present in both insulating and metallic phases of the compounds. In the insulating material these excitations are responsible for the conductivity. On the other hand, in the metallic phase the high mobility conduction electrons carry the charge current. The temperature-induced electron excitations represent in this case the most important scattering channel for the conduction electrons. With increasing temperature, the number of the low mobility excitations increases, leading to the increase of the conductivity of the insulating CuIr_2S_4 . Whereas in the metallic CuIr_2Se_4 , the increasing number of the excitations results in a more intense scattering of the conduction electrons, thus increasing the resistivity.

The resistivity of CuIr_2Se_4 changes the type of temperature dependency from $\rho = a_L \exp[-(T_L^*/T)^{1/2}]$ to $\rho = a_H \exp(-T_H^*/T)$ at temperature T_t ; see Fig. 2. This change suggests a change in the conductivity mechanism. Indications of the change are present also in the thermopower and in the magnetoresistivity. dS/dT of CuIr_2Se_4 has a minimum, related to the high-temperature shoulder, at the same temperature $T_t \approx 200$ K at which $\ln[(1/\rho)(d\rho/dT)]$ has the kink; see Fig. 4. This coincidence implies that the shoulder in the thermopower and the change of the gradient of $\ln[(1/\rho)(d\rho/dT)]$ against $\ln T$ dependence both have the same origin. Further confirmation that at T_t the conductivity mechanism changes gives the magnetoresistivity temperature dependence, shown in the lower panel of Fig. 4: it also re-

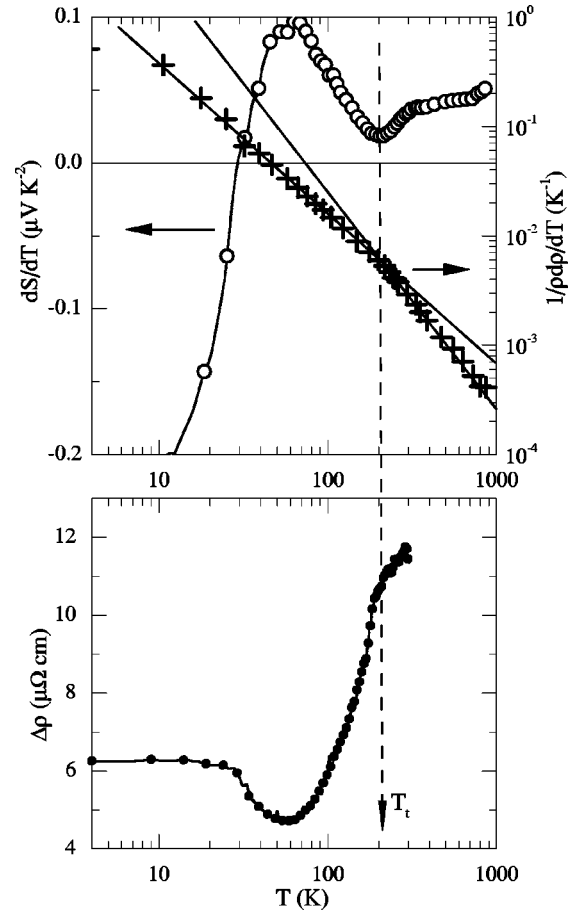


FIG. 4. Resistivity, thermopower, and magnetoresistivity all reveal peculiar behavior near to temperature $T_t \approx 200$ K. The upper panel displays the temperature dependence of the derivative of resistivity $[1/\rho(T)](d\rho/dT)$ ($+$) and of the thermopower dS/dT of CuIr_2Se_4 (\circ). There is a change of the gradient of the derivative of the resistivity at T_t , whereas the derivative of thermopower has a minimum at this temperature. The lower panel shows the magnetoresistivity $\Delta\rho = \rho(T, H) - \rho(T, 0)$ ($\mu_0 H = 15$ T). The magnetoresistivity exhibits a kink near to T_t .

veals a kink around T_t . It is worth mentioning here that the photoemission spectra for CuIr_2Se_4 , measured at 30 and 250 K,⁷ indicate a larger DOS at the Fermi level at 250 K in comparison with the DOS at 30 K. It is also interesting that the value of T_t is very close to the temperature of the MIT in CuIr_2S_4 . Whether the peculiarities in the transport of CuIr_2Se_4 around T_t have some relation to the MIT in CuIr_2S_4 is, however, an open question.

B. Thermopower

Figure 5 presents the thermopower of CuIr_2Se_4 and CuIr_2S_4 from 4 to 900 K. At high temperatures the thermopower of both compounds is nearly linear in the temperature and has large positive values. The MIT in CuIr_2S_4 manifests itself by the abrupt change of the thermopower. Figure 6 shows the variation of S and ρ in a vicinity of the MIT. Note that the transition in the thermopower is more smooth than in the resistivity. The different width of the transition area in the thermopower and in the resistivity may reflect a coexistence of the metallic and insulating phases in a rather

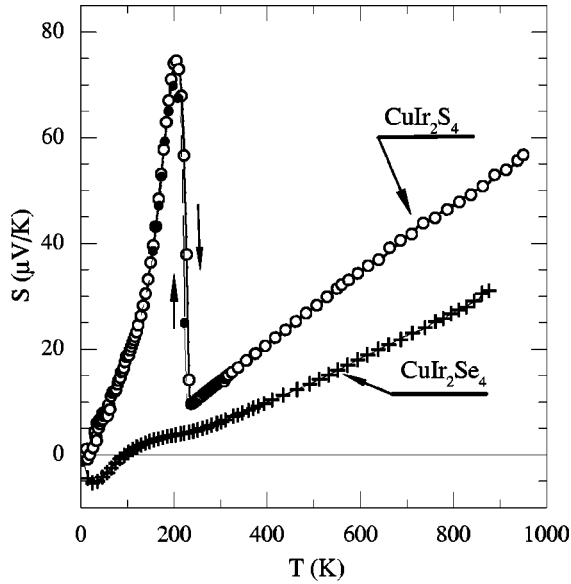


FIG. 5. Temperature dependence of the thermopower of CuIr_2Se_4 (+), and of CuIr_2S_4 (\circ and \bullet) in zero magnetic field.

broad temperature region below the MIT. It was shown that the thermopower of a two-component mixture is mainly determined by the low-resistivity component, whereas the resistivity, depending strongly on microstructure, can be of the same magnitude as the resistivity of high-resistivity component.²⁰ The different behavior of the thermopower and

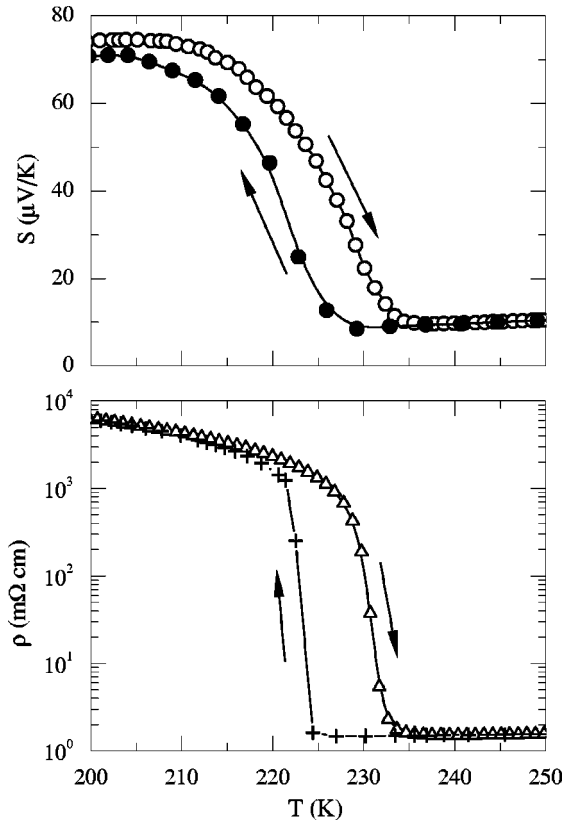


FIG. 6. Temperature dependence of the thermopower (upper panel) and resistivity (lower panel) of CuIr_2S_4 in the vicinity of the MIT. The arrows indicate the direction of the variation of temperature.

of the resistivity in the vicinity of MIT can be understood assuming that immediately below the MIT a considerable fraction of the sample material is still in the metallic state, and that the amount of this metallic phase continuously decreases with decreasing temperature. This conjecture is also in agreement with the more rapid (than it should be for a normal semiconductor) decrease of the resistivity as temperature increases above 50 K.

Thermopower generally consists of two contributions: diffusion thermopower S_d , the origin of which is an energy dependence of conduction-electron mobility, and phonon drag thermopower S_g , which arises due to a transfer of non-equilibrium momentum from a phonon system to the conduction electrons. Total thermopower can be represented as $S = S_d + S_g$. The diffusion thermopower of metals is predicted to be a linear function of temperature. Experimentally the linear temperature dependency of diffusion thermopower is almost never observed in a broad temperature range, owing to a competition between different scattering mechanisms and to effects of energy band structure.^{13,21} Yet, in the limit of low temperatures, when a single scattering mechanism dominates conductivity, the diffusion thermopower of a conventional metal should be linear in the temperature. The phonon drag thermopower varies as $S_g \propto T^3$ at $T \ll \Theta_D$ and as $S_g \propto 1/T$ in the high-temperature limit, having a maximum at intermediate temperatures.²²

The thermopower of CuIr_2Se_4 reveals features which could be considered similar to those of some transition metals. But, a closer inspection reveals anomalous behavior of the thermopower. At high temperatures the combination of a large magnitude of the thermopower with its almost linear temperature dependence over a broad temperature range (although it does not contradict to transport theory) is rather unusual for metals.^{13,21} At low temperatures there are two peculiarities in the temperature dependence of the thermopower: a minimum at $T_m = 30$ K, and a shoulder, centered at about 100 K. Phonon drag thermopower would be a routine interpretation of the minimum. A characteristic feature of phonon drag is that at low temperatures its contribution to the thermopower should be proportional to T^3 . Therefore, for a conventional metallic conductor the thermopower at low temperatures includes a linear in the temperature diffusion thermopower and the phonon drag thermopower and can be expressed as²² $S = \alpha_d T + \alpha_g T^3$. Contrary to this expression, the data presented in Fig. 7 indicate that below about 13 K $S(T) \propto T^{1.5}$. Usually,²² to separate the phonon drag contribution one uses a plot of S/T against T^2 . Such a plot, shown in Fig. 8, confirms that the thermopower below 13 K cannot be represented as $S = \alpha_d T + \alpha_g T^3$. Instead, S/T in this low-temperature region can be expressed as $S/T = \alpha_d + \beta \sqrt{T}$. The parameter values in this expression can be estimated from the plot in Fig. 8: $\alpha_d = 0.002 \mu\text{V K}^{-2}$, $\beta = -0.088 \mu\text{V K}^{-2.5}$. Because of the very small value of α_d , there is actually no usual linear diffusion contribution to the thermopower at low temperatures. Hence, the thermopower in this temperature range is given by a simple single-term expression: $S = \beta T^{1.5}$. This type of thermopower temperature dependence has not been known for metallic conductors. The observed dependence cannot be accounted for by a competition between different scattering mechanisms. In the temperature range below 13 K in which S

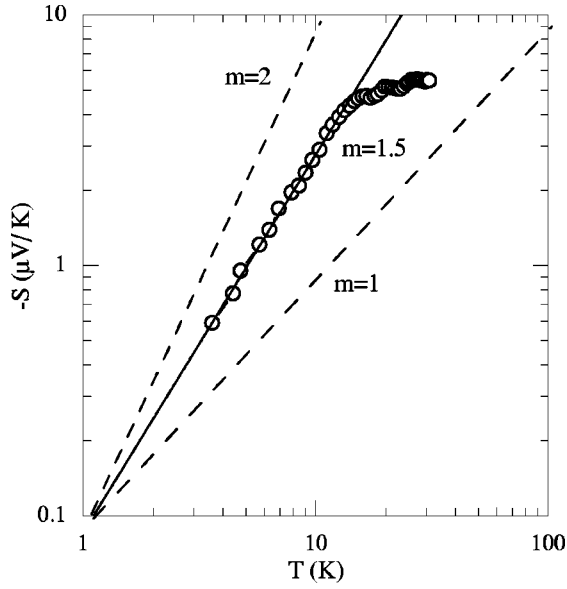


FIG. 7. Temperature dependence of the thermopower of CuIr_2Se_4 in double logarithmic scale. The thermopower below about 13 K (in the temperature range where the resistivity is almost independent of temperature) varies as $S = \beta T^m$. The function with $m = 1.5$ is shown by the solid line. The broken lines depict the function for $m = 1$ and $m = 2$.

$= \beta T^{1.5}$ is observed, the temperature-dependent part of the resistivity is virtually zero in comparison with the temperature-independent (impurity) contribution. Therefore, the temperature-independent impurity scattering is the dominating scattering mechanism in this whole temperature

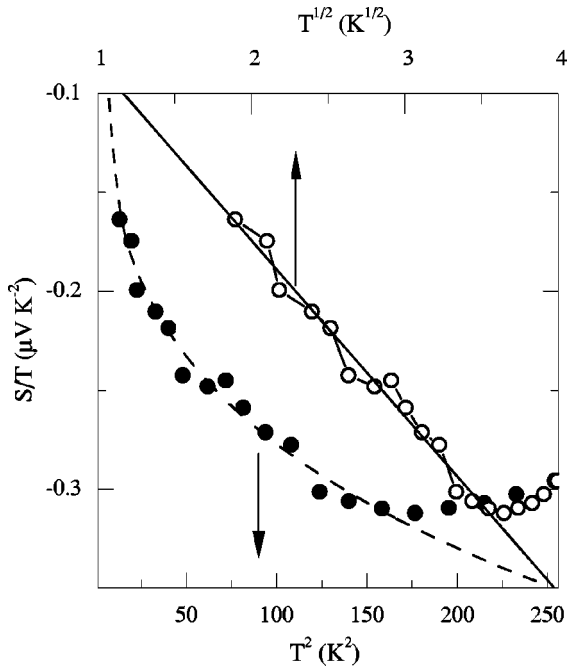


FIG. 8. Dependence of S/T against T^2 (bottom x axis) and against $T^{1/2}$ (top x axis) of CuIr_2Se_4 from 1 to 16 K. The solid and broken lines depict the function $S = \xi T^{1.5}$ for the top and bottom x axes, respectively. The plot clearly shows that the thermopower at low temperatures cannot be represented as a sum of a linear diffusion term and of a phonon drag term, proportional to T^3 .

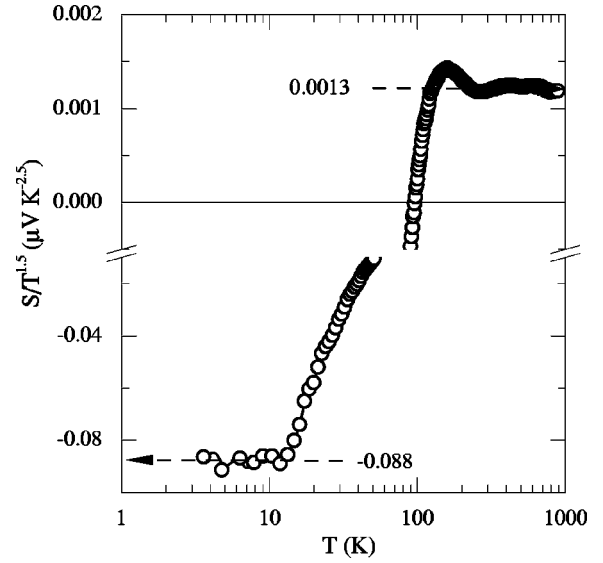


FIG. 9. Temperature dependence of $S/T^{1.5}$ of CuIr_2Se_4 . Below 13 K and above 200 K, $S/T^{1.5}$ is independent of temperature, i.e., $S = \beta T^{1.5}$. The low-temperature value of β, β_L , and the high-temperature value β_H are indicated by the arrows.

range. Another interesting feature is seen in Fig. 9: the thermopower at high temperatures—above about 200 K—exhibits a temperature dependence similar to that found at low temperatures: $S = \beta_H T^{1.5}$. This last observation implies that the proportionality of S to $T^{1.5}$ is an intrinsic property of the compound related to basic features of its electronic structure, since it is independent of a particular scattering mechanism. And, second, it suggests that the complex temperature variation of the thermopower between 13 and 200 K is a result of transition from the negative thermopower, related to the temperature-independent scattering at low temperatures, to the positive thermopower, related to the temperature-dependent one at high temperatures. To appreciate this suggestion, we notice that the diffusion thermopower in the presence of several scattering mechanisms can be expressed as²² $S = \sum_i S_i \rho_i / \rho$, where S_i and ρ_i are partial thermopower and resistivity due to the i th scattering mechanism, and $\rho = \sum \rho_i$. In the present case it is reduced to

$$S = S_{\text{imp}} \frac{\rho_{\text{imp}}}{\rho} + S_T \frac{\rho_T}{\rho}, \quad (1)$$

with $S_{\text{imp}}, \rho_{\text{imp}}$ being the impurity thermopower and resistivity, and ρ_T and S_T denoting the temperature-dependent part of the resistivity and corresponding thermopower. According to the previous discussion, $S_{\text{imp}} = \beta_L T^{1.5}$ and $S_T = \beta_H T^{1.5}$, where β_L and β_H can be estimated from the plot in Fig. 9: $\beta_L = -0.088 \mu\text{V K}^{-2.5}$ and $\beta_H = 0.0013 \mu\text{V K}^{-2.5}$. Equation (1) can be obtained from the Mott's formula for the thermopower of metals,²²

$$S = \frac{\pi^2}{3} \frac{k_B}{e} k_B T \left[\frac{1}{\rho} \frac{d\rho}{d\varepsilon} \right]_{\varepsilon = \varepsilon_F}. \quad (2)$$

It predicts a linear temperature dependence for the thermopower. Since Mott's formula in the low-temperature limit has a rather general nature, it is reasonable to assume that some kind of Mott-like expression is also valid for the ther-

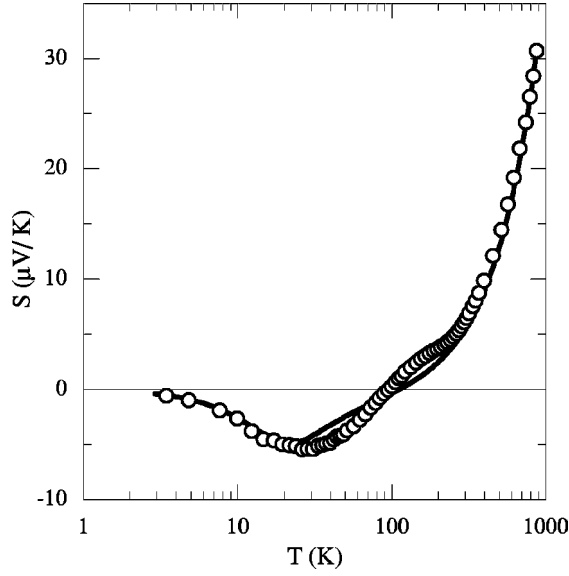


FIG. 10. Temperature dependence of the thermopower of CuIr_2Se_4 calculated with formula (4), solid line, and the experimental data, \circ .

mopower of the present compound. As follows from the experimental data for the thermopower, it should contain $T^{1.5}$ temperature dependence: $S = (\pi^2/3)(k_B/e)k_B T^{1.5}[\dots]$. Now, to keep the correct units for thermopower the formula should be modified as

$$S = \frac{\pi^2}{3} \frac{k_B}{e} (k_B T)^{1.5} \left[\frac{1}{\rho} \frac{d\rho}{d\varepsilon} \right]_{\varepsilon = \varepsilon_F}^{1.5}. \quad (3)$$

Formula (3) by the routine procedure yields

$$S = S_{\text{imp}} \left(\frac{\rho_{\text{imp}}}{\rho} \right)^{1.5} + S_T \left(\frac{\rho_T}{\rho} \right)^{1.5}. \quad (4)$$

We calculate the thermopower with the help of Eq. (4) using the experimental resistivity $\rho(T) = \rho_{\text{imp}} + \rho_T(T)$, where $\rho_{\text{imp}} = 8 \mu\Omega \text{ cm}$ and S_{imp} and S_T are defined above. The result, presented in Fig. 10 shows surprisingly good agreement with the experimental thermopower. Particularly, it indicates that the low-temperature minimum in the thermopower is not due to a phonon drag effect, rather it originates from the competition between the negative impurity thermopower and the positive thermopower related to the temperature-dependent conductivity mechanism.

The thermopower of CuIr_2S_4 at temperatures above the MIT, in the metallic phase, is considerably larger than the thermopower of CuIr_2Se_4 and increases with temperature slower than by the linear rate. These features correlate with the larger magnitude (than in CuIr_2Se_4), of the resistivity, and with the different temperature dependency of the resistivity: $\rho = a \exp[-(T^*/T)^{1/2}]$, whereas the resistivity of CuIr_2Se_4 varies at high temperatures as $\rho = a \exp(-T^*/T)$. At low temperatures, according to the electrical conductivity analysis, the principal conductivity mechanism in CuIr_2S_4 is Efros-Shklovskii hopping with long-range Coulomb correlations.¹⁹ The thermopower of a semiconductor with hopping conductivity is expected to depend on temperature as $S = \xi \sqrt{T}$.²³ The experimental data on the thermopower at

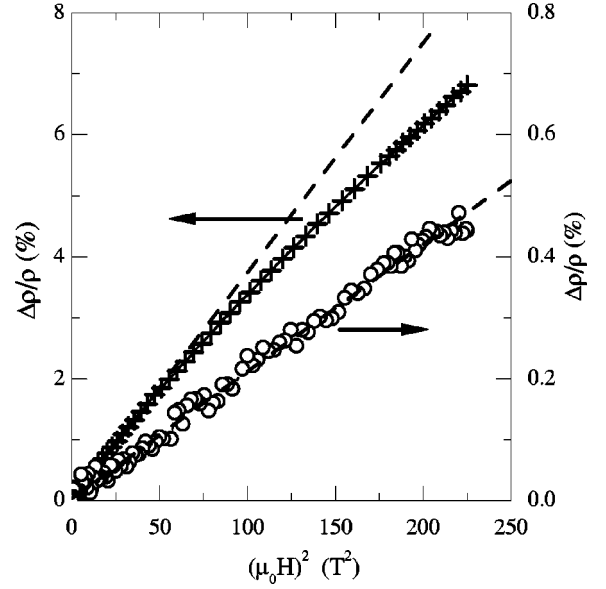


FIG. 11. The magnetoresistivity of CuIr_2S_4 (\circ) and of CuIr_2Se_4 ($+$) at 50 K against H^2 . The broken lines depict $\Delta\rho/\rho \propto H^2$. Note, the magnetoresistivity of CuIr_2S_4 is about an order of magnitude smaller than the magnetoresistivity of CuIr_2Se_4 .

low temperatures do not rule out this type of temperature dependence, but the quality of the experimental data is not good enough (owing to the high resistance of the sample at low temperatures) to make a certain conclusion.

C. Magnetoresistivity and magnetothermopower

The magnetoresistivity of CuIr_2Se_4 and of CuIr_2S_4 , measured at 50 K, is presented in Fig. 11. The magnetoresistivity is positive, proportional to H^2 in weak fields and exhibits a saturation tendency with the increasing field strength. This behavior is in agreement with theoretical results for the longitudinal magnetoresistivity of conductors. Magnetothermopower is very small for both compounds at all temperatures in the range of 4 to 300 K. These results show that the effect of the external magnetic field on the transport properties arises solely due to Lorentz force, acting on the conduction electrons. We have found no definite indication of an effect of magnetic impurities on the transport properties.

IV. CONCLUSIONS

The resistivity and the thermopower of spinel-type compounds CuIr_2S_4 and CuIr_2Se_4 have been measured at temperatures from 2 to 900 K under magnetic field from 0 T up to 15 T. Both the resistivity and the thermopower in the metallic state of the compounds have features unusual for metals. The experimental data on the resistivity suggest that the compounds are nonconventional metals with a low mobility of the charge carriers, presumably due to the d -character DOS at the Fermi level. The most striking feature is that the resistivity of both compounds follows to an exponential-type temperature dependence in a very broad temperature range from 2 K to at least 900 K.

The resistivity of CuIr_2Se_4 (which has a metallic type of conductivity) has two temperature regions with a different variation in dependence on temperature: below about 200 K

it follows to $\rho = a_L \exp[-(T_L^*/T)^{1/2}]$, whereas above 200 K the resistivity varies as $\rho = a_H \exp(-T_H^*/T)$. The thermopower and the magnetoresistivity of CuIr_2Se_4 also display anomalous temperature dependencies around 200 K, indicating that there is a change of the conductivity mechanism around this temperature.

The conductivity of CuIr_2S_4 in the temperature range of 4 to 50 K is well described by the Efros-Shklovskii hopping conductivity mechanism with long-range Coulomb correlations: $\sigma = b \exp[-(T^*/T)^{1/2}]$, with the characteristic temperature $T^* \approx 90$ K. This implies that the Coulomb correlations play an essential role in the formation of the insulating phase of CuIr_2S_4 . Above the MIT the resistivity shows an exponential temperature dependence $\rho = a \exp[-(T^*/T)^{1/2}]$ with $T^* \approx 600$ K. It is interesting that in the insulating phase of CuIr_2S_4 the conductivity reveals the same type of temperature dependence as the resistivity of the metallic CuIr_2Se_4 .

The thermopower is positive in the metallic phase of both compounds at high temperatures, as well as in the low-

temperature insulating state of CuIr_2S_4 . The positive thermopower of the insulating phase implies *p*-type charge carriers, in agreement with recent photoemission results.⁷

The thermopower of CuIr_2Se_4 has anomalous temperature dependency. At low- and at high-temperature limits it is proportional to $T^{3/2}$; this type of thermopower temperature dependency has not been known for metallic conductors.

The magnetoresistivity of CuIr_2S_4 and CuIr_2Se_4 is positive and follows the relation $\Delta\rho \propto H^2$. Magnetothermopower [$\Delta S = S(H, T) - S(0, T)$] is very small for both compounds at all temperatures. No clear indications of an effect of residual magnetic impurities on transport properties have been found.

The results of the present work give the distinct experimental evidence that the metallic state of CuIr_2S_4 and CuIr_2Se_4 compounds is very unusual. This is in accord with the general tendency that the metallic conductors near the insulating transition exhibit nontrivial properties.⁸ Further studies are necessary to understand the mechanism of this peculiar behavior.

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