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ELECTRICAL CONDUCTIVITY, HALL COEFFICIENT AND THERMOELECTRIC POWER OF ICOSAHEDRAL i-$Al_{62}Cu_{25.5}Fe_{12.5}$ AND i-$Al_{63}Cu_{25}Fe_{12}$ QUASICRYSTALS

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Dedicated to Professor Boran Leontić on the occasion of his 70$^{\text{th}}$ birthday

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The electrical conductivity, Hall coefficient and thermoelectric power of icosahedral i-$Al_{62}Cu_{25.5}Fe_{12.5}$ quasicrystal samples in the temperature range 2 K – 340 K are measured, and comparison with icosahedral i-$Al_{63}Cu_{25}Fe_{12}$ quasicrystal samples is made. We have analysed the temperature dependence of the conductivity below 70 K and the results of this analysis are consistent with the predictions of the weak-localisation and the electron-electron interaction theories. The temperature dependence of the electrical conductivity, Hall coefficient and thermoelectric power above 40 K are consistently explained by a two-band model. Although the overlapping of the valence and conduction bands at Fermi level is responsible for the coexistence of both types of carriers, and it enables us to describe quasicrystals as semi-metals, the temperature variation of the electrical conductivity is determined by that of carrier density which makes the situation essentially the same as that in normal semiconductors.

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1. Introduction

The discovery of quasicrystals fifteen years ago [1] has stimulated a good deal of interest in the physics of these materials. They have structures intermediate between periodic and random. Particularly interesting among them are the highly ordered, thermodynamically stable, quasicrystals with an icosahedral structure i-AlCu(Fe, Ru, Os) [2], which is aperiodic in all three dimensions of space. An important problem in the condensed-matter physics is whether the quasiperiodic structure leads to new and unexpected physical properties. In particular, it is observed that transport properties, such as electric conductivity, are strongly affected by the nonperiodic order. Many quasicrystalline alloys are characterized by very low values of electrical conductivity, by a negative temperature coefficient of resistivity and by a low electronic contribution to the specific heat, which points to a small density of states at the Fermi energy [3]. Among the thermodynamically stable quasicrystals, icosahedral i-AlCuFe quasicrystals are highly suitable for the study of elementary excitations of electrons and phonons. The available information on transport and thermodynamical properties of these materials includes data on electrical transport properties [4–6], low-temperature thermodynamic and magnetic properties [7–9] and results from tunneling spectroscopy [10]. Below, we describe the results of our measurements of the electrical conductivity $\sigma(T)$, Hall coefficient $R_{\mathrm{H}}(T)$, and thermoelectric power $S(T)$ of icosahedral i-$Al_{62}Cu_{25.5}Fe_{12.5}$ and i-$Al_{63}Cu_{25}Fe_{12}$ quasicrystals over a wide temperature range. This set of data supplements previous investigations of thermoelectric power of i-$Al_{63}Cu_{25}Fe_{12}$, thus providing a better insight into the ground state of such materials.

2. Experimental procedure

We have investigated two samples of slightly different composition i-$Al_{63}Cu_{25}Fe_{12}$ and i-$Al_{62}Cu_{25.5}Fe_{12.5}$, which were made from large polyquasicrystalline ingots prepared by conventional casting and subsequent annealing at CECM (CNRS-Vitry, France). It has been verified by X-ray diffraction that the samples are single-phased icosahedral. The characterisation, the specific heat and the low-temperature thermal conductivities of i-$Al_{63}Cu_{25}Fe_{12}$ and i-$Al_{62}Cu_{25.5}Fe_{12.5}$, have been reported in Refs. [8] and [9] and the study of electronic properties by tunnelling spectroscopy of i-$Al_{63}Cu_{25}Fe_{12}$ in Ref. [10]. The specimens of i-$Al_{63}Cu_{25}Fe_{12}$ and i-$Al_{62}Cu_{25.5}Fe_{12.5}$ used for electrical conductivity, Hall coefficient and thermopower measurements were cut from the ingots by electroerosion in the form of prisms (the shape close to a rod) with dimensions 13 mm $\times$ 2 mm^2 and 7 mm $\times$ 1.3 mm^2, respectively. The contacts for the transport measurements were made by evaporating 500 nm of Au onto certain spots and fixing wires onto them with silver paint. The electrical conductivity was measured by a standard four-probe technique [11] with applied currents of 0.1 mA to 1 mA. The thermoelectric power was measured with respect to highly-purity leads wires, using a differential technique [12], and the Hall coefficient was measured by the five-lead method in a magnetic field of up to 1 T, using a permanent magnet. The Hall coefficient was measured at selected temperatures from 4.2 K to 340 K, and the sample currents ranged from 1 mA up to 10 mA at higher temperatures.

3. Results and discussion

The electrical conductivities $\sigma(T)$ of i-$Al_{63}Cu_{25}Fe_{12}$ and i-$Al_{62}Cu_{25.5}Fe_{12.5}$ quasicrystals are shown in Fig. 1. We see a strong variation of the conductivity for the very small change in composition. This fact has already been reported in literature [4]. However, we should mention that our samples are further characterised by measurements of the Hall coefficient and thermoelectric power, as discussed below. The conductivity values exhibit a different but, for a system of only metallic constituents, always a very small increase in absolute conductivity with temperature. The occurrence of a minimum at 18 K and 25 K for the higher and lower conductiv-

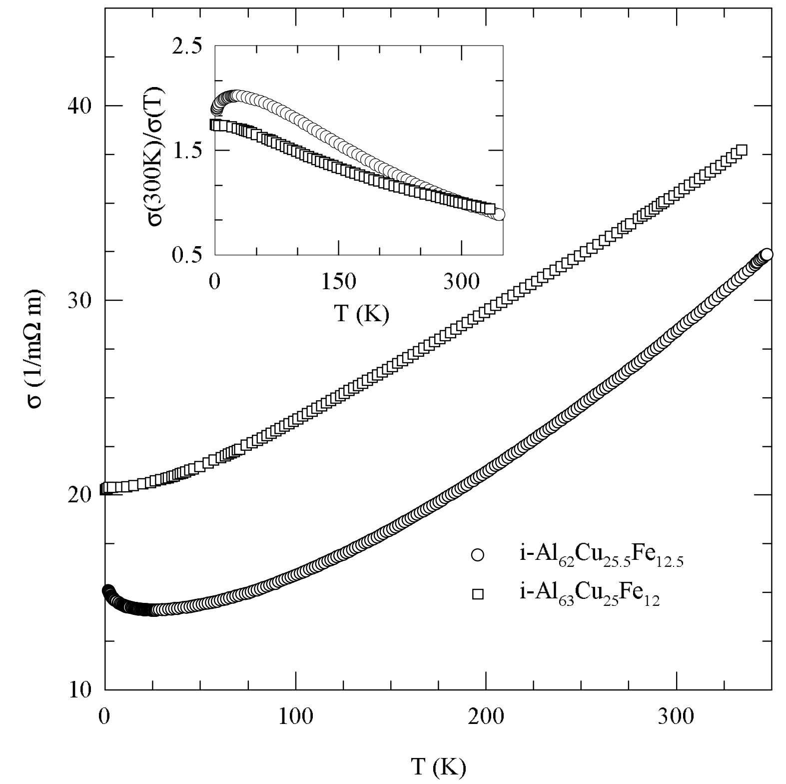

Fig. 1. Temperature variation of the electrical conductivity $\sigma(T)$ for the i-$Al_{62}Cu_{25.5}Fe_{12.5}$ and i-$Al_{63}Cu_{25}Fe_{12}$ samples. The inset shows the electrical conductivities for the same samples normalised to their room temperature value.

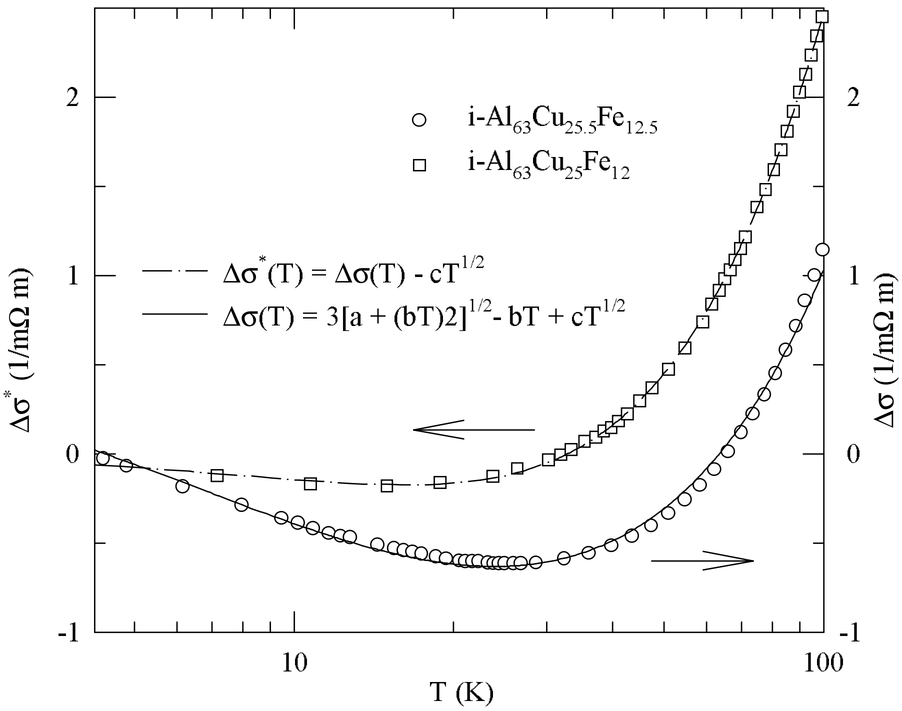

Fig. 2. Variation of the electrical conductivity $\Delta\sigma(T)$ as a function of temperature for the samples of compositions i-$Al_{62}Cu_{25.5}Fe_{12.5}$ *and* i-$Al_{63}Cu_{25}Fe_{12}$*. The symbols denote the experimental data, the lines are the fit to weak localisation theory described in the text; parameters of fits are given in Table 1.*

ity samples (Fig. 2) is due to the quantum corrections. Indeed, the low-temperature variation of the electrical conductivities, $\Delta\sigma(T) = \sigma(T) - \sigma_{4.2\mathrm{K}}$ of i-$Al_{62}Cu_{25.5}Fe_{12.5}$ and $\Delta\sigma^*(T) = \sigma(T) - \sigma_{4.2\mathrm{K}} - c\sqrt{(T)}$ of i-$Al_{63}Cu_{25}Fe_{12}$, can be well described using a fitting procedure of the form $\Delta\sigma(T) = 3\sqrt{a + b^2T^2} - bT + c\sqrt{T}$, where the two first terms refer to the weak localisation (WL) effects [13] and the third one is attributed to the electron-electron interactions (EEI) [14]. Parameters a, b and c are related to the spin-orbit scattering time (τ_{so}), the inelastic scattering time (τ_{i}), the screening factor λF_σ and the diffusivity D:

$$a = \left(\frac{e^2}{2\pi^2 h}\right)^2 \frac{1}{D\tau_{\mathrm{so}}}, \quad bT = \sqrt{\left(\frac{e^2}{4\pi^2 h}\right)^2 \frac{1}{D\tau_{\mathrm{i}}}}, \quad \text{and} \quad c = \frac{2.1(4/3 - 1.5\lambda F_\sigma)}{\sqrt{D}},$$

where λ is a parameter introduced to take into account the band-structure effects, $e = 1.6 \times 10^{-19}$ As and $h = 6.626 \times 10^{-34}$ Js. We have estimated the diffusivity, D, by using the measured value of the density of states, $N(E_F)$, at the Fermi level from the specific heat measurements performed on the samples taken from the same ingots [8], $D = \sigma/(e^2 N(E_F))$, and we then get the spin-orbit scattering time (τ_{so}), the inelastic scattering time (τ_i) and the screening factor λF_σ (see Table 1). Note, by fitting the conductivity data, we obtain a negative value of the c coefficient for i-$Al_{62}Cu_{25.5}Fe_{12.5}$ as is observed in highly doped semiconductors, which is at variance with a positive value of c in the case of

TABLE 1. Characteristic values for the quasicrystals i-$Al_{62}Cu_{25.5}Fe_{12.5}$ *and* i-$Al_{63}Cu_{25}Fe_{12}$ *as derived from the fit to experimental data of the theory of weak-localization [13] and electron-electron interactions [14].*

	Units	i-$Al_{62}Cu_{25.5}Fe_{12.5}$	i-$Al_{63}Cu_{25}Fe_{12}$
$\sigma_{4.2K}$	$\Omega^{-1}m^{-1}$	14700	20400
$\rho_{4.2K}/\rho_{300K}$	–	1.93	1.74
D	10^{-5} m^2s^{-1}	2.5	3.0
τ_i/T^2	10^{-9} s	2.1	1.8
τ_{so}	10^{-12} s	2.5	34
λF_σ	–	1.59	0.69

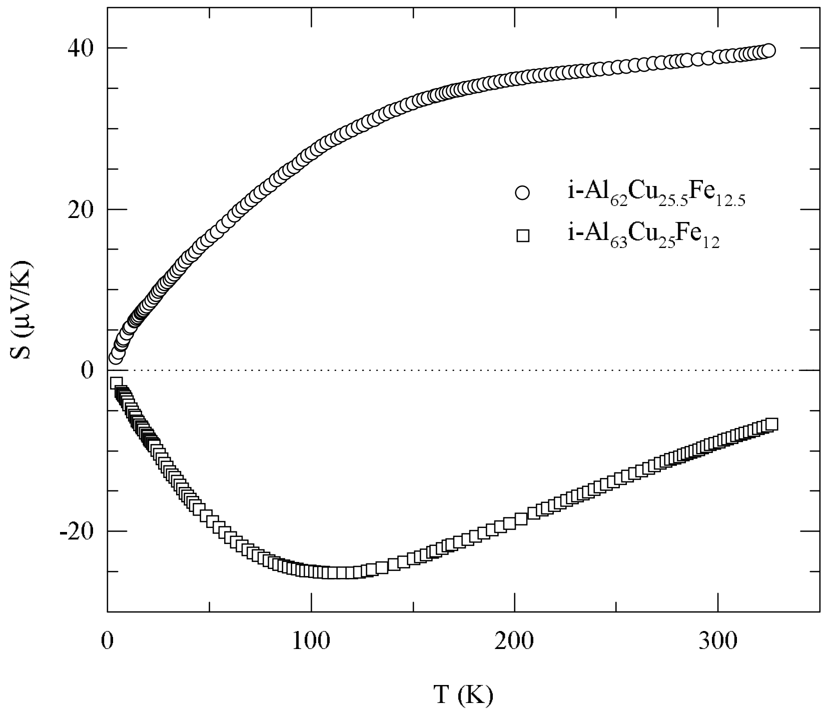

Fig. 3. Temperature dependence of the thermopower S(T) for the samples of compositions i-$Al_{62}Cu_{25.5}Fe_{12.5}$ *and* i-$Al_{63}Cu_{25}Fe_{12}$.

i-$Al_{63}Cu_{25}Fe_{12}$. The consequence of that is a decrease of the screening factor with increasing conductivity and/or a lower value of the band-structure parameter λ in the higher-conductive sample (see Table 1).

The thermoelectric power for the same samples is shown in Fig. 3. It is, in general, large and, in addition, we see a change from a negative to a positive value as the content of iron increases, as previously reported for differently annealed samples of i-AlCuFe [5].

The temperature dependence of the Hall coefficient $R_H(T)$ is presented in Fig. 4 for i-$Al_{62}Cu_{25.5}Fe_{12.5}$ and i-$Al_{63}Cu_{25}Fe_{12}$ quasicrystals, respectively. As in the case of the thermoelectric power, we see a change from a negative to a positive value in the i-AlCuFe system with increasing iron content, which is related to an increase of the resistivity (Fig. 1), often interpreted as due to an improvement of the quasicrystalline structural quality.

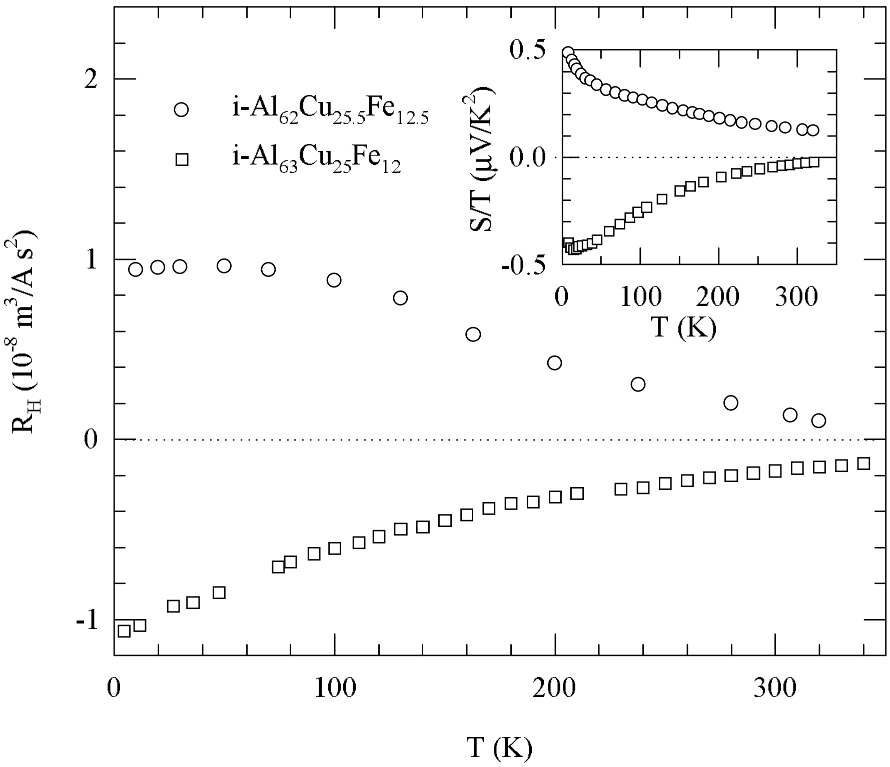

Fig. 4. Hall coefficient $R_H(T)$ as a function of temperature for the samples of compositions i-$Al_{62}Cu_{25.5}Fe_{12.5}$ *and* i-$Al_{63}Cu_{25}Fe_{12}$. *Inset shows ratio of the thermopower S(T)/T over the temperature as a function of temperature for the same samples.*

Looking at the conductivities of the different samples, the most striking feature is their similar change with temperature accompanied by a different value of the absolute conductivity. At low temperature, there is some density $n_{e,h}$ of electrons and/or holes depending on the composition and the quality of the quasicrystalline structure. The mechanism for the dependence of described properties on the composition is the balance between the size of the pseudo-Brillouin zone and the Fermi sphere in the frame of Hume-Rothery alloys. A small change in the composition varies the size of the latter by altering the average number of electrons per atom, while the pseudo Brillouin zone should not be disturbed. As seen in Fig. 3, a shift of 1% from Al with 3 electrons per atom to 0.5% Cu with one electron per atom reduces the size of the Fermi sphere in a manner that the thermoelectric power changes sign. Therefore, these two samples should be very near to the ideal quasicrystals. If we assume a two-band model consisting of electrons and holes, $R_{\mathrm{H}}(T)$ can be written as

$$R_{\mathrm{H}} = \frac{1}{e} \frac{n_e(\tau_e/m_e^*)^2 - n_h(\tau_h/m_h^*)^2}{(n_e\tau_e/m_e^* + n_h\tau_h/|m_h^*|)^2} \,. \tag{1}$$

The density and the effective mass of the electrons and the holes, and the scattering time are $n_{e,h}$, $m_{e,h}^*$, and $\tau_{e,h}$, respectively. As a first estimate, we can assume an increase of the carrier densities by excitation over a pseudogap E_G, $n_{e,h} = n_{e_0,h_0} + C\exp(-E_G/k_{\mathrm{B}}T)$, $k_{\mathrm{B}} = 1.38 \times 10^{-23}$ Js. A doubling of the hole density and a generation of a corresponding number of electrons would be sufficient to describe $R_{\mathrm{H}}(T)$ and $\sigma(T)$

$$\sigma = e^2 \left(\frac{\tau_e n_e}{m_e^*} + \frac{\tau_h n_h}{|m_h^*|} \right) , \tag{2}$$

assuming a constant mobility for each carrier type. The thermoelectric power $S(T)$ for a two-band system can be extracted from the basic formula

$$S = \frac{\pi^2}{3} \frac{k_{\mathrm{B}}^2}{e} T \left(\frac{\mathrm{d} \ln \sigma(E)}{\mathrm{d}E} \right)_{E=E_G} .$$

With a free electron and hole behaviour for the energy dependence of the carrier density

$$n_{e,h} = \frac{1}{3\pi^2} \left(\frac{8\pi^2 m}{h^2} \right)^{3/2} E_{\mathrm{F}}^{3/2} ,$$

we get

$$S = \left(\frac{\pi}{3}\right)^{2/3} \frac{4\pi^2 k_{\mathrm{B}}^2}{eh^2} T \left(\frac{n_e^{1/3}\tau_e - n_h^{1/3}\tau_h}{n_e\tau_e/m_e^* + n_h\tau_h/|m_h^*|} \right) . \tag{3}$$

This formula is similar to Eq. (1) for the Hall-coefficient, therefore, the temperature dependence of the ratio S/T (shown in the inset of Fig. 4) is similar to the temperature dependence of the Hall coefficient. The reason for that is the compensation of electrons and holes. We have made a common fit to the measured conductivity, the Hall effect and the thermoelectric power using Eqs. (1–3) for i-$Al_{62}Cu_{25.5}Fe_{12.5}$ and i-$Al_{63}Cu_{25}Fe_{12}$. The results are shown for $\sigma(T)$, $R_H(T)$ and $S(T)$ as solid and dashed lines in Fig. 5, respectively, while the additional parameters are written in Table 2. Moreover, the temperature-dependent carrier densities for electrons and holes are given in Fig. 6. We show that the applied model can give the sign, the value, and the temperature dependence of all transport properties.

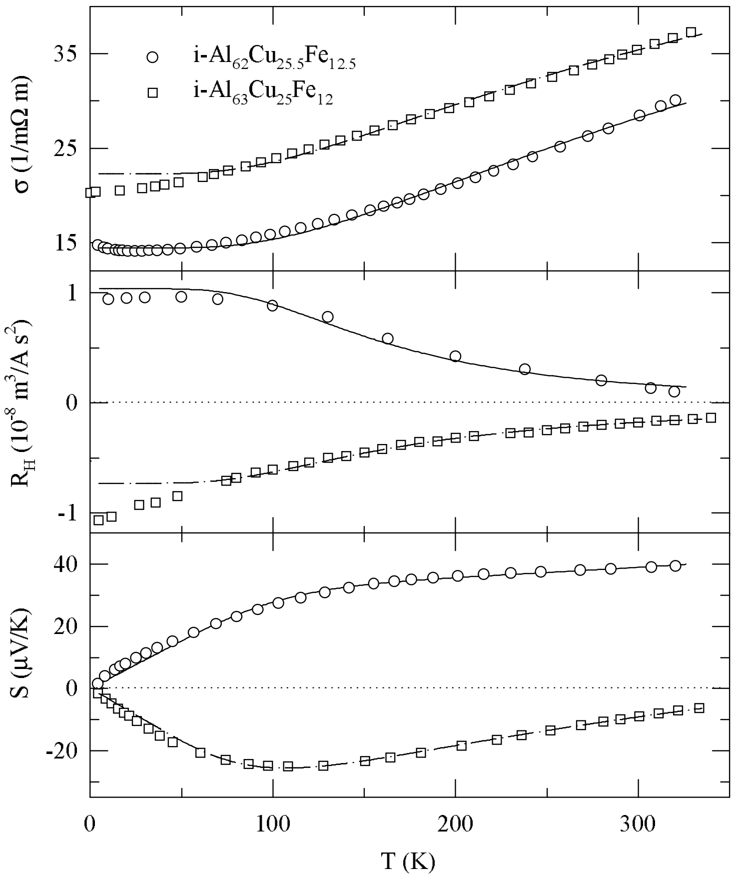

Fig. 5. Electrical conductivity $\sigma(T)$, Hall coefficient $R_H(T)$ and thermopower $S(T)$ data for the samples of compositions i-$Al_{62}Cu_{25.5}Fe_{12.5}$ *and* i-$Al_{63}Cu_{25}Fe_{12}$*. The symbols denote the experimental data, the lines are the fit to the two band model described in the text; parameters of fits are given in Table 2.*

TABLE 2. Additional parameters for the common fit of the electrical conductivity, the Hall coefficient and the thermoelectric power. Note that pseudogap E_G value and the data from tunneling spectroscopy Ref. [10] are in good agrement.

	Units	i-$Al_{62}Cu_{25.5}Fe_{12.5}$	i-$Al_{63}Cu_{25}Fe_{12}$
E_G	(K; meV)	406; 35	348; 30
τ_e	$(10^{-14}$ s)	1.6	1.0
τ_h	$(10^{-14}$ s)	2.6	8.0
n_{e_0}	$(10^{26}$ m$^{-3})$	2.40	0.78
n_{h_0}	$(10^{26}$ m$^{-3})$	0.48	1.30
C	$(10^{26}$ m$^{-3})$	8.2	5.7
$\|m_h^*\|/m_e^*$	–	2.1	5.0
m_e^*/m_e	–	1.2	1.0

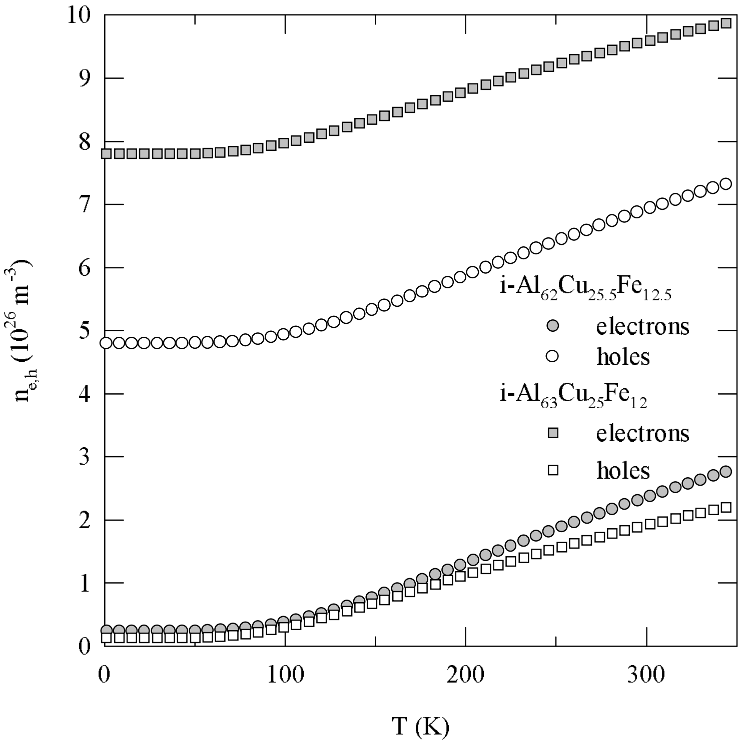

Fig. 6. Temperature dependence of carrier densities for electrons $n_e(T)$ and holes $n_h(T)$ as derived from the fit to the two-band model for the samples of compositions i-$Al_{62}Cu_{25.5}Fe_{12.5}$ *and* i-$Al_{63}Cu_{25}Fe_{12}$.

4. *Conclusion*

The high structural quality i-AlCuFe samples of slightly different composition show a very low electrical conductivity and an unusual temperature dependence of the conductivity, the Hall coefficient and the thermoelectric power. The low temperature ($T < 70$ K) behaviour of the conductivity is well described by the quantum interference effects (QIE). The orders of magnitude of the relevant parameters deduced from the weak-localisation analysis are similar to those of amorphous materials ($\tau_{\mathrm{i}} \approx (10^{-9}/T^2)$ s, $\tau_{\mathrm{so}} \approx 10^{-12}$ s. At very low temperatures, the conductivity, σ, exhibits a $\sqrt{T}$ dependence ($\Delta\sigma = c\sqrt{T}$) which is attributed to the electron-electron interactions. However, we have observed a change of sign of the coefficient c from a positive to a negative value as the conductivity of the samples decreases. The electron-electron interaction theories predict that $c \approx (\frac{4}{3} - \frac{3}{2}F_\sigma\lambda)/\sqrt{D}$, where the screening factor $0 < F_\sigma < 0.93$ and λ is a parameter introduced to take into account the band structure effects (intervalley scattering, mass anisotropy etc.) The coefficient c is thus usually positive in an amorphous system ($\lambda = 1$), but can also be negative due to an increase of the screening factor close to band structure effects ($\lambda > 1$) in the more resistive samples. This change of sign can thus be associated with the proximity of metal-insulator transition in our samples. In addition, the pseudo-gap at the origin of the temperature dependence of n_e and n_h (Fig. 6) is in good agreement with the value of 20–22 meV for the zero-bias anomaly determined by tunnelling and point-contact spectroscopy [10]. The small values of the conductivity and, particularly, the temperature dependence of the conductivity, Hall coefficient and thermoelectric power above 40 K can be explained by a two-band model based on the Hume-Rothery mechanism. We have applied a quantitative model to the three transport properties with common parameters. As a result, we get the values for the carrier densities, the scattering times and the effective masses. The extracted carrier densities are smaller than the values estimated from a one-band model which is insufficient to explain the value and the temperature dependence of the Hall coefficient and thermoelectric power for the quasicrystals of the high structural quality used here. It should be mentioned that the small values of conductivity arise not only from the small carrier densities, but also from the high effective masses caused by the flat bands near the edge of the pseudo-Brilloiun zone and the short elastic scattering times. All these properties can be explained by a strong interaction between the electronic system and the atomic structure, as expected for the Hume-Rothery mechanism.

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ELEKTRIČNA VODLJIVOST, HALLOV KOEFICIJENT I TERMOELEKTRIČNA SNAGA IKOSAEDARSKIH i-$Al_{62}Cu_{25.5}Fe_{12.5}$ I i-$Al_{63}Cu_{25}Fe_{12}$ KVAZIKRISTALA

Mjerili smo električnu vodljivost, Hallov koeficijent i termoelektričnu snagu uzorka ikosaedarskog kvazikristala i-$Al_{62}Cu_{25.5}Fe_{12.5}$ u području temperature 2 K – 340 K i usporedili s uzorkom ikosaedarskog kvazikristala i-$Al_{62}Cu_{25.5}Fe_{12.5}$. Analizirali smo temperaturnu ovisnost električne vodljivosti ispod 70 K i ustanovili da su rezultati u skladu s predviđanjima teorija slabe lokalizacije i međudjelovanja elektron-elektron. Ovisnost električne vodljivosti, Hallovog koeficijenta i termoelektrične snage o temperaturi iznad 40 K uspješno se objašnjava modelom dviju vrpci. Iako je predodžba o preklapanju valentne i vodljive vrpce na Fermijevoj razini odgovorna za istovremeno postojanje dviju vrsta nositelja i za opis kvazikristala kao polumetala, temperaturna ovisnost električne vodljivosti je, kao i kod normalnih poluvodiča, određena promjenon gustoće nositelja.