1 INTRODUCTION

The family of icosahedral \(i\)-Al-Cu-Fe quasicrystals is currently one of the most studied, due to its excellent thermal stability. Most studies reported so far were performed on polycrystalline samples, and include investigations of the electrical resistivity and magnetoresistance,\(^1\)\(^\text{-}\)\(^9\) thermoelectric power,\(^9\)\(^\text{-}\)\(^12\) thermal conductivity,\(^2\)\(^,\)\(^3\)\(^,\)\(^8\) magnetism,\(^3\)\(^,\)\(^3\)\(^,\)\(^14\) and Hall coefficient.\(^1\)\(^,\)\(^5\)\(^,\)\(^7\)\(^,\)\(^8\) Though polycrystalline samples may acquire quite a high structural perfection through a proper thermal annealing procedure, rapid quenching to room temperature after annealing inevitably results in a strained material that contains high thermal vacancy concentration for the much higher temperature of annealing). In addition, grain boundaries may hinder the propagation of electrons and phonons, thus affecting long-range electrical and heat-transport phenomena. In order to test for the true intrinsic properties of \(i\)-Al-Cu-Fe quasicrystals, it is desirable to compare the physical properties of the polycrystalline material with those measured on high-quality monocrystalline samples, where structural imperfections are largely absent. Therefore, we have performed a study by investigating the electrical resistivity, the thermoelectric power and the thermal conductivity of a monocrystalline \(i\)-Al\(_{64}\)Cu\(_{23}\)Fe\(_{13}\) and a polycrystalline \(i\)-Al\(_{63}\)Cu\(_{25}\)Fe\(_{12}\) quasicrystal.
shaped in the form of a prism, with dimensions 3.9 mm × 1.5 mm × 1.4 mm (i-Al64Cu23Fe13) and 7.2 mm × 1.6 mm × 1.2 mm (i-Al63Cu25Fe12). The electrical resistivity was measured by a standard four-probe technique with applied currents of 0.1 mA to 1 mA, while the thermoelectric power was measured with respect to high-purity gold lead wires, using a differential technique. The thermal conductivity was measured using an absolute steady-state heat-flow method. The thermal flux was generated by a 1 kΩ RuO2 chip-resistor glued to one end of the sample, while the other end was attached to a copper heat sink. The temperature gradient across the sample was monitored by a chromel-constantan differential thermocouple.

3 RESULTS AND ANALYSIS

3.1 Electrical resistivity and thermopower

The electrical resistivity (ρ(T)) and thermopower (S(T)) of i-Al64Cu23Fe13 and i-Al63Cu25Fe12 were measured in the temperature range from 4 K to 300 K. The results are shown in Figure 1 and Figure 2. The resistivities of i-Al64Cu23Fe13 and i-Al63Cu25Fe12 exhibit a negative temperature coefficient, the room temperature resistivities of i-Al64Cu23Fe13 and i-Al63Cu25Fe12 at 300 K are 2200 µΩ cm and 2900 µΩ cm respectively and the total increases of resistivity by factors of R = ρ300K/ρ0K = 1.8 and R = ρ300K/ρ0K = 1.7, respectively. In addition, ρ(T) of the i-Al64Cu23Fe13 exhibits a weakly pronounced maximum with the peak value ρ300K = 4040 µΩ cm, at 20 K. The thermopowers S(T) are, in general, large and, in addition, exhibit an interesting feature of a sign reversal (Figure 2) in the case of i-Al64Cu23Fe13. Below 120 K, S(T) is negative with a negative slope, whereas around 120 K it exhibits a minimum and the slope is reversed. Consequently, the

\[ S(T) \text{ of i-Al64Cu23Fe13 changes sign to positive at } T = 278 K. \]

For the analysis of ρ(T) and S(T) we used the spectral resistivity model of Landauro and Solbrig,11,12,16 where both quantities are analyzed simultaneously by presuming a specific structure- and composition-related form of the energy-dependent spectral resistivity function ρ(ε) (or its inverse, the spectral conductivity σ(ε)=1/ρ(ε)). Using the Kubo-Greenwood formalism, the temperature-dependent electrical conductivity is calculated according to

\[ \sigma(ε) = \int dε \sigma(ε) \left( -\frac{∂f(ε, T)}{∂ε} \right) \]

whereas the thermopower is obtained from

\[ S(T) = -\frac{k_B}{ε_f} \int dε \sigma(ε) \left( \frac{ε - μ(T)}{k_B T} \right) \left( -\frac{∂f(ε, T)}{∂ε} \right) \]

Here, f(ε,T) = {exp[(ε − μ)/k_BT] + 1}−1 is the Fermi-Dirac function and μ(T) is the chemical potential, which is written in the low-temperature representation as17

\[ μ(T) = ε_f − (k_BT)^2 \frac{π^2}{6} \left( \frac{d ln n(ε)}{dε} \right)_{ε_f} = ε_f - \frac{2}{3} T^2 \]

The electronic density of states n(ε) is related to the spectral conductivity via the Einstein relation σ(ε)=(ε^2/V)n(ε)D(ε) with D(ε) being the electronic spectral diffusivity. The only material-dependent quantity in Eqs. (1–3) is σ(ε), so that a proper model of the spectral conductivity should reproduce both σ(T) and S(T) at the same time.

The ab-initio-derived spectral resistivity could be modeled by the superposition of two Lorentzians
\[
\rho(\varepsilon) = A \left( \frac{1}{\pi} \frac{\gamma_1}{(\varepsilon - \delta_1)^2 + \gamma_1^2} + \frac{1}{\pi} \frac{\gamma_2}{(\varepsilon - \delta_2)^2 + \gamma_2^2} \right)
\]

(4)

where \(1/\pi \gamma_1\) is the height of a Lorentzian, \(2\gamma_1\) its FWHM, \(\delta_1\) its position with respect to the Fermi energy \(\varepsilon_F\) (taken to be at the origin of the energy scale; \(\varepsilon_F = 0\)) and \(\alpha\) is the relative weight of the Lorentzians. The position of the narrow resistivity peak with respect to the Fermi energy \(\varepsilon_F\) is responsible for the anomalous electronic transport properties. As this peak is due to a specific distribution of Fe atoms in the structure, quasiperiodicity alone cannot account for the anomalous transport properties of i-Al-Cu-Fe quasicrystals; a right chemical decoration is also needed. The Fermi energy can be shifted on the scale of a few 100 meV by deviations in the stoichiometry and/or by defects in both structure and chemical decoration,18,19 so that the relative position of the narrow peak can change on this energy scale in samples of slightly different composition and annealing treatment. Consequently, solely on the basis of small shifts of \(\varepsilon_F\), the thermopower of i-Al-Cu-Fe samples of similar composition can switch between large positive and large negative values and it may also change sign with temperature, as demonstrated for the i-Al\textsubscript{62}Cu\textsubscript{25.5}Fe\textsubscript{12} polycrystalline sample.9,10,12

The fits of both \(\rho(T)\) and \(S(T)\) data were performed simultaneously with Eqs. (1-4) by adjusting the set of parameters \((A, \alpha, \delta_1, \delta_2, \gamma_1, \gamma_2)\) to the shape of the spectral resistivity \(\rho(\varepsilon)\). The starting value of the parameter \(\xi\) entering the temperature-dependent chemical potential of Eq. (3) was determined by recognizing that in the case when the spectral variation of the electronic diffusivity can be neglected, one can replace \(n(\varepsilon)\) by \(\sigma(\varepsilon)\) in Eq. (3). The initial value was obtained by using the Mott formula

\[
S^\text{Mott}(T) = \frac{\pi^2 k_B^2}{3} \left( \frac{d \ln \sigma(\varepsilon)}{d \varepsilon} \right)_{\varepsilon=0} T
\]

so that \(\xi = -0.5 \left| S^\text{Mott}(T)/T \right|\). The fits for the spectral and transport properties, respectively, are collected in Table 1. The fits of both \(\rho(T)\) and \(S(T)\) are excellent in the whole investigated temperature range.

The magnitude of the electrical resistivity of the monocrystalline i-Al\textsubscript{63}Cu\textsubscript{25}Fe\textsubscript{12} is in-line with the values reported for the polycrystalline i-Al-Cu-Fe. In polycrystalline i-Al-Cu-Fe the total variation of \(\rho(T)\) over the relevant Fe range is merely a factor of two,2 so that the material is best classified as a semi-metal over the whole icosahedral concentration range with no indication of a large resonant increase of the resistivity. The \(\rho_4K\) resistivity value of our i-Al\textsubscript{63}Cu\textsubscript{25}Fe\textsubscript{12} matches well with that of the polycrystalline samples from the study\textsuperscript{9} with the same Fe concentration. However, since the Fermi energy of our i-Al\textsubscript{63}Cu\textsubscript{25}Fe\textsubscript{12} is located nearly at the maximum of the spectral resistivity\textsuperscript{20}, further shifts of \(\varepsilon_F\) over the resistivity peak due to a small variation of the Fe composition would not result in an additional increase of the resistivity, but can only make it smaller. This hints that the factor-of-two larger peak resistivity of the polycrystalline i-Al-Cu-Fe material at the Fe 12.5\% concentration,\textsuperscript{6} as compared to the monocrystalline i-Al\textsubscript{63}Cu\textsubscript{25}Fe\textsubscript{12}, could originate in extrinsic factors like grain boundaries and other lattice imperfections that act as additional scattering centers for the conduction electrons.

### 3.2 Thermal conductivity

The measured thermal conductivities \(\kappa(T)\) of i-Al\textsubscript{64}Cu\textsubscript{23}Fe\textsubscript{13} and i-Al\textsubscript{64}Cu\textsubscript{23}Fe\textsubscript{12} are displayed in Figure 3. The conductivity value at room temperature of i-Al\textsubscript{64}Cu\textsubscript{23}Fe\textsubscript{13} amounts \(\kappa_{300K} = 1.7W/mK\), whereas in the case of the i-Al\textsubscript{63}Cu\textsubscript{25}Fe\textsubscript{12} is \(\kappa_{300K} = 2.9 W/mK\). These values are surprisingly low for an alloy of regular metals and are comparable to the thermal conductivities of known thermal insulators, amorphous fused silica\textsuperscript{21} and the technologically widespread thermally insulating material, yttrium-doped zirconia ceramics\textsuperscript{22}. The \(\kappa(T)\) data were analyzed with a semi-quantitative model, appropriate for icosahedral quasicrystals and their approximants\textsuperscript{22-29}. The thermal conductivity parameter \(\kappa(T)\) is divided into three terms.

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<th>Table 1: Parameters of the spectral resistivity (\rho(\varepsilon)) of Eq. (4), obtained from the simultaneous fits of (\rho(T)) and (S(T)) for i-Al\textsubscript{64}Cu\textsubscript{23}Fe\textsubscript{13} (monocrystalline) and i-Al\textsubscript{64}Cu\textsubscript{23}Fe\textsubscript{12} (polycrystalline)</th>
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<th>Table 2: Fit parameters of the thermal conductivity (\kappa(T)) for i-Al\textsubscript{64}Cu\textsubscript{23}Fe\textsubscript{13} (monocrystalline) and i-Al\textsubscript{64}Cu\textsubscript{23}Fe\textsubscript{12} (polycrystalline) respectively</th>
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The electronic contribution $\kappa_e$ is obtained using the empirical Wiedemann-Franz law ($\kappa_e=\ell T/\sigma(T)$) with a temperature-dependent effective Lorenz number

$$L(T) = \frac{\kappa_e(T)}{T \times \sigma(T)}$$

The lattice contribution ($\kappa - \kappa_e$) is analyzed by considering (i) the propagation of long-wavelength acoustic phonons (for which the quasicrystal structure is an elastic continuum) within the Debye model and (ii) hopping of localized vibrations within the icoshedral cluster substructure, which participate in the heat transfer via thermally activated hopping. In the simplest model, the hopping of localized vibrations is described by a single activation energy $E_a$, yielding a contribution to the thermal conductivity

$$\kappa_H = \kappa_{H0} \exp\left(-\frac{E_a}{k_B T}\right)$$

where $\kappa_{H0}$ is a constant. The Debye thermal conductivity is written as

$$\kappa_D = C_D T^3 \int_0^{\theta_D/T} \tau(x) \frac{x^4 e^x}{(e^x-1)^2} \, dx$$

where $C_D = k_B^4/(2\pi^3 m^3)$, $\theta_D$ is the average sound velocity, $\theta_D$ the Debye temperature, $\tau$ the phonon relaxation time and $x = \hbar \tau/k_B T$, where $\hbar$ is the phonon energy. The different phonon-scattering processes are incorporated into the relaxation time $\tau(x)$ and we assume that Matthiessen’s rule is valid, $\tau^{-1} = \sum_j \tau_j^{-1}$, where $\tau_j^{-1}$ is the scattering rate related to the $j$-th scattering channel. In analogy with the Al-Pd-Mn approximant and quasicrystal phases, we consider two dominant scattering processes in the investigated temperature range: (1) the scattering of phonons on structural defects of stacking-fault type with the scattering rate $\tau^{-1}_sf = A \tau^2 T^2$ and (2) umklapp processes with the phenomenological form of the scattering rate pertinent to quasicrystals, $\tau^{-1}_um = B T^{4-d}$, so that $\tau^{-1} = \tau^{-1}_sf + \tau^{-1}_um$. The Debye temperature of $i$-Al-Cu-Fe was estimated from the specific heat $32$ as $\theta_D = 560$ K and the Debye constant $C_D$ was determined from ultrasonic data $30$. The fits (solid lines in Figure 4) are excellent and the fit parameters are collected in Table 2. The electronic ($\kappa_e$), Debye ($\kappa_D$) and hopping ($\kappa_H$) contributions are shown separately on the graph. The temperature-dependent effective Lorenz number $L(T)$ of $i$-Al$_6$d$_{Cu_23}Fe_{13}$ and $i$-Al$_6$d$_{Cu_23}Fe_{12}$ deviates considerably from the Wiedemann-Franz value $L_0$, amounting $L/L_0 \approx 2.1$ and $L/L_0 \approx 2.5$ at 300 K, respectively, and the electrons carry around 40 % of the total heat in both cases. The Debye contribution exhibits a maximum at about 30 K and declines above this temperature, whereas the hopping contribution becomes significant at elevated temperatures. The activation energy for the hopping of $i$-Al$_6$d$_{Cu_23}Fe_{13}$ and $i$-Al$_6$d$_{Cu_23}Fe_{12}$ was determined as $E_a = 16$ meV and $E_a = 16$ meV, respectively. These energies correlate with the inelastic neutron and X-ray scattering experiments on $i$-Al-Pd-Mn quasicrystals, where dispersionless vibrational states were identified for energies higher than 12 meV. Such dispersionless states indicate localized vibrations and are considered to be a consequence of a dense distribution of energy gaps in the phonon excitation spectrum of quasicrystals. The parameters $B$ and $\beta$ define phonon scattering by umklapp processes in a phenomenological way. The fit-determined $\beta = 3.2$ value for $i$-Al$_6$d$_{Cu_23}Fe_{13}$ yields

![Figure 3: Thermal conductivity $\kappa(T)$ of the monocrystalline $i$-Al$_6$d$_{Cu_23}Fe_{13}$ and the polycrystalline $i$-Al$_6$d$_{Cu_23}Fe_{12}$, respectively.](image)

![Figure 4: Thermal conductivity $\kappa(T)$ with the fits to the total $\kappa(T)$, of the monocrystalline $i$-Al$_6$d$_{Cu_23}Fe_{13}$ and the polycrystalline $i$-Al$_6$d$_{Cu_23}Fe_{12}$. The three contributions to the total $\kappa(T)$, electronic $\kappa_e$, Debye $\kappa_D$ and hopping $\kappa_H$, are shown separately.](image)
the frequency- and temperature dependence of the umklapp term \( \tau_{\text{umklapp}}^{-1} \propto \omega^{2} T^{-0.8} \) indicates similarity with the modified quasi-umklapp scattering rate \( \tau_{\text{quasi}}^{-1} \propto \omega^{2} T^{-2} \), used for the analysis of the thermal conductivity of i-Zn-Mg-Y quasicrystals, while for the polycrystalline sample, the fit-determined \( \beta = 2.0 \) \( \tau_{\text{quasi}}^{-1} \propto \omega^{2} T^{-2} \) indicates the quasi-umklapp scattering rate obtained for the i-Al-Pd-Mn quasicrystals. Here it should be mentioned that the Debye and hopping contributions slightly compensate for each other in the fit procedure, so that the parameter values characterizing \( \kappa_{D} \) and \( \kappa_{H} \) should be considered at the qualitative level.

Regarding the comparison of the thermal conductivity of monocrystalline and polycrystalline i-Al-Cu-Fe, we are not aware of other quantitative analyses of \( \kappa(T) \) of polycrystalline samples in the sense of Eqs. (5–8), so that the comparison has to be made at the level of experimental thermal conductivities. The room-temperature value for i-Al63Cu25Fe12 amounts to \( \kappa_{300K} = 1.7 \text{ W/mK} \), whereas for the i-Al60Cu23Fe13 it is \( \kappa_{300K} = 2.9 \text{ W/mK} \). Though the scatter of the known values of thermal conductivity of i-Al-Cu-Fe is relatively large, there seems to be no systematic difference between the polycrystalline and monocrystalline samples.

4 CONCLUSION

We performed investigations of electrical resistivity, thermoelectric power and thermal conductivity on a monocrystalline i-Al60Cu23Fe13 and a polycrystalline i-Al63Cu25Fe12 icosahedral quasicrystal, for comparison. The electrical resistivity and thermopower analysis shows that the Fermi energy is located at the minimum of the pseudogap in the spectral conductivity \( \sigma(\varepsilon) \). All this gives evidence that we are dealing with icosahedral quasicrystals of exceptional quality, so that its magnetic properties may be considered as intrinsic to the i-Al-Cu-Fe phase. A comparison of the investigated monocrystalline i-Al60Cu23Fe13 to the polycrystalline i-Al63Cu25Fe12, however, shows that there are no pronounced differences between the two forms of the material. While there are essentially no differences in the magnetic properties of the monocrystalline and polycrystalline materials, the electrical resistivity of the polycrystalline material is larger by a factor of two. This difference can be easily accounted for by the grain boundaries and other lattice imperfections that act as additional scattering centers for the conduction electrons. Comparing the thermopowers of the monocrystalline and polycrystalline i-Al-Cu-Fe materials, in general, the \( S(T) \) magnitude and temperature dependence depend strongly on the position of \( \xi_{F} \) relative to the spectral resistivity peak, so that slight differences in the samples' stoichiometry and structural perfection may lead to very different thermopowers in both magnitude and sign.

A quantitative comparison of the thermal conductivities of monocrystalline and polycrystalline i-Al-Cu-Fe is less straightforward due to the random scatter of the reported values, but \( \kappa_{300K} \) of the monocrystalline i-Al60Cu23Fe13 fits within the range of values for the polycrystalline i-Al63Cu25Fe12. To conclude, we found no systematic differences in the electrical resistivity, thermoelectric power and thermal conductivity between the high-quality monocrystalline and polycrystalline i-Al-Cu-Fe quasicrystals, and the reported physical properties of the other i-Al-Cu-Fe quasicrystals appear to be intrinsic to this family of icosahedral quasicrystals.

Acknowledgements

We would like to thank Y. Yokoyama and Y. Calvayrac for giving us the samples of monocrystalline i-Al60Cu23Fe13 and polycrystalline i-Al63Cu25Fe12 icosahedral quasicrystal, respectively. This work was done within the activities of the 6th Framework EU Network of Excellence "Complex Metallic Alloys" (Contract No. NMP3-CT-2005-500140), and has been supported in part by the Ministry of Science, Education and Sports of Republic of Croatia through the Research Projects Nos. 035-0352826-2848 and 177-0352828-0478.

5 REFERENCES

I. SMILJANIĆ ET AL.: THERMOELECTRICAL PROPERTIES OF A MONOCRYSTALLINE Al_{64}Cu_{23}Fe_{13} QUASICRYSTAL

32 J. C. Lassjaunias, Y. Calvayrac, H. Yang, J. Physique 17 (1997), 959–976
34 A. Bilušič, D. Pavuna, A. Smontara, Vacuum 61 (2001), 345–348