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Conduction Mechanisms in Some Icosahedral and Amorphous Phases

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Quasicrystalline icosahedral and amorphous phases prepared as thin films or bulk samples in the systems Al–Pd–Re, Al–Cu–Fe and Ti–Zr–Ni, have been investigated with respect to their temperature dependence of conductance and thermopower, in the range between 10 and 300 K. Various conduction mechanisms yield different exponent values in the power-law temperature dependence of conductance, T^ζ . A semi-metal behaviour ($\zeta \cong 1.5$) is found in the amorphous phase and in the disordered icosahedral Al–Pd–Re film and Ti–Zr–Ni ribbons, as well as in icosahedral Al–Cu–Fe films. Lower ζ values found in the quasi-perfect icosahedral Al–Pd–Re bulk sample and in two of the icosahedral Al–Cu–Fe films suggest that electron localization in a hierarchy of clusters is the main conduction mechanism in these samples. The thermopower data support the existence of a pseudo-gap at the Fermi level and suggest a similar short-range order in both amorphous and icosahedral phases. The special sensitivity of the thermopower to the DOS details at E_F is responsible for the strong variation of its magnitude with the degree of icosahedral order.

1. Introduction

The origin of the high electrical resistivity in icosahedral phases is still a matter of debate. Two facts seem to be generally recognised:

- the existence of a pseudo-gap in the electron density of states (DOS) near the Fermi level (E_F);
- the localization tendency of electrons in states near E_F .

The presence of the pseudo-gap confers a Hume-Rothery-type energetical stabilisation to icosahedral phases. The corresponding model is the standard two-band picture, with electron and hole pockets at the Fermi surface. Topological defects can however induce partial superposition of valence and conduction bands along certain crystallographic directions, causing a semi-metal-like behaviour of the conductivity $\sigma \sim T^{3/2}$. This dependence is attributed [1] to an increasing concentration of electrons being transferred into the conduction band with increasing temperature.

On the other hand, short-range order is expected to strongly influence the conduction mechanism [2]. Recent models [3, 4] validated by diffraction experiments, describe

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icosahedral phases as a hierarchy of isomorphous clusters, with spatial extent on length scales related by τ ($\tau = 1 + \sqrt{5}/2$). This peculiar structure has direct consequences on the DOS “fractal” shape [3] and causes localization of electrons in a series of potential wells, described as recurrently localised (“critical”) states. At low temperatures, variable-range hopping between these localised electron states is expected [4]. Taking into account the power law decay of “critical states” with distance R between isomorphous clusters,

$$|\Psi| = \alpha R^{-\nu},$$

a variable-range hopping argument leads to

$$\sigma = \sigma_0 + AT^{B\nu} \quad (1)$$

with B taking the value $2/3$ [1] or 1 [5].

The parameter ν , which defines the spatial range of the critical states is governed [5] by the increase rate of the number of atoms in clusters with distance R , i.e. by the topology of icosahedral clusters. An evaluation based on the i-Al–Pd–Mn structure [5] resulted in $B\nu \cong 1.3$.

The power-law dependence predicted by Eq. (1) supports the experimental law

$$\sigma = \sigma_0 + CT^\zeta \quad (2)$$

generally reported in well-structured icosahedral phases ($0.5 \leq \zeta \leq 1.5$), with C and ζ being empirical parameters.

The present work reports on $\sigma(T)$ dependences measured in three icosahedral systems (Al–Pd–Re, Al–Cu–Fe and Ti–Zr–Ni), with various degrees of icosahedral order. Films, prepared by different methods were investigated to this respect and results were compared, wherever possible with those obtained on bulk samples. In order to gather additional information concerning the DOS gap at E_F , thermopower data were also measured. The effect of structural disorder on the conduction mechanisms was a point of particular concern in our experiments. This prompted us to compare data obtained on icosahedral and amorphous samples of similar compositions.

2. Experimental

2.1 Sample preparation

Thin films (≈ 2000 Å thick) in the system Al–Pd–Re were prepared by sputtering on substrates kept at a temperature of 77 K (Table 1).

Al–Cu–Fe films were obtained by sequential flash evaporation at 4.2 K (Table 1). The films are amorphous, as shown by electron diffraction (ED). Annealing up to about 750 K induced transformation into well-structured icosahedral phases, showing narrow spots in ED patterns.

Bulk icosahedral Al_{70.5}Pd₂₁Re_{8.5} (Table 1) was prepared by arc melting, followed by an annealing procedure at about 1210 K. Its high structural quality was assessed by X-ray diffraction.

Ti–Ni–Zr amorphous and icosahedral phases were prepared as melt-spun ribbons (Table 1). Details about preparation are given in [6]. Ribbon cross sections were

Table 1

Structure, composition and conductance exponent ζ (see Eq. (2)) for the samples investigated

sample	type	structure	composition	ζ
1	film	amorphous	Al ₆₄ Pd ₂₄ Re ₁₂	1.44
2	film	amorphous	Al ₆₅ Pd ₂₄ Re ₁₁	1.45
3	film	amorphous	Al ₆₅ Pd ₂₅ Re ₁₀	1.49
4	film	amorphous	Al ₇₁ Pd ₂₁ Re ₈	1.51
5	film	icosahedral	Al ₇₁ Pd ₂₁ Re ₈	1.50
6	bulk	icosahedral	Al _{70.5} Pd ₂₁ Re _{8.5}	1.23
7	film	icosahedral	Al _{62.5} Cu ₂₅ Fe _{12.5}	1.14
8	film	icosahedral	Al _{62.5} Cu ₂₅ Fe _{12.5}	1.66
9	film	icosahedral	Al _{63.5} Cu ₂₄ Fe _{12.5}	1.14
10	film	icosahedral	Al _{63.5} Cu ₂₄ Fe _{12.5}	1.64
11	ribbon	amorphous	Ti ₄₄ Zr ₁₉ Ni ₃₇	1.27 (low temp.) 0.68 (high temp.)
12	ribbon	disordered icosahedral	Ti ₅₃ Zr ₂₆ Ni ₂₁	1.50 (low temp.) 0.66 (high temp.)
13	ribbon	icosahedral + Laves	Ti ₄₇ Zr ₃₃ Ni ₂₀	1.47 (low temp.) 0.59 (high temp.)

around $1.5 \text{ mm} \times 45 \text{ }\mu\text{m}$. Their degree of icosahedral order was investigated by X-ray diffraction [7] as a function of composition and quenching rate.

2.2 Electrical measurements

Samples were measured in an Oxford Instruments continuous-flow cryostat in the temperature range between 10 and 300 K.

Thermopower was measured by the integrated method, the temperature gradient ΔT being computer-controlled at a constant value of 2 K. We used as a reference a chromel–alumel thermocouple. Resistance measurements were performed in the classical four-probe geometry.

All contacts were made by means of silver paint. Because the temperature was better controlled during the heating process than during cooling, all measurements were performed at a heating rate of 1 K/min up to about 50 K and 2 K/min above this temperature. Only the resistance of the bulk Al–Pd–Re sample was measured during the cooling process, due to the particular construction of the cryostat used. To ensure reliable results, the cooling rate at low temperatures was kept as low as 0.5 K/min.

3. Results

The variation of normalized conductance G_N with temperature is shown in Fig. 1a to c for the three classes of icosahedral phases investigated. Since the sample geometry parameters were difficult to be determined precisely, we used the conductance data, as we are primarily concerned with the temperature dependence and not with the absolute value of the conductivity.

The conductance ratio $G_N = G(T)/G(300 \text{ K})$ shows a general increasing trend with increasing T (Fig. 1). In order to confirm the power dependence on T (Eq. (2)) we

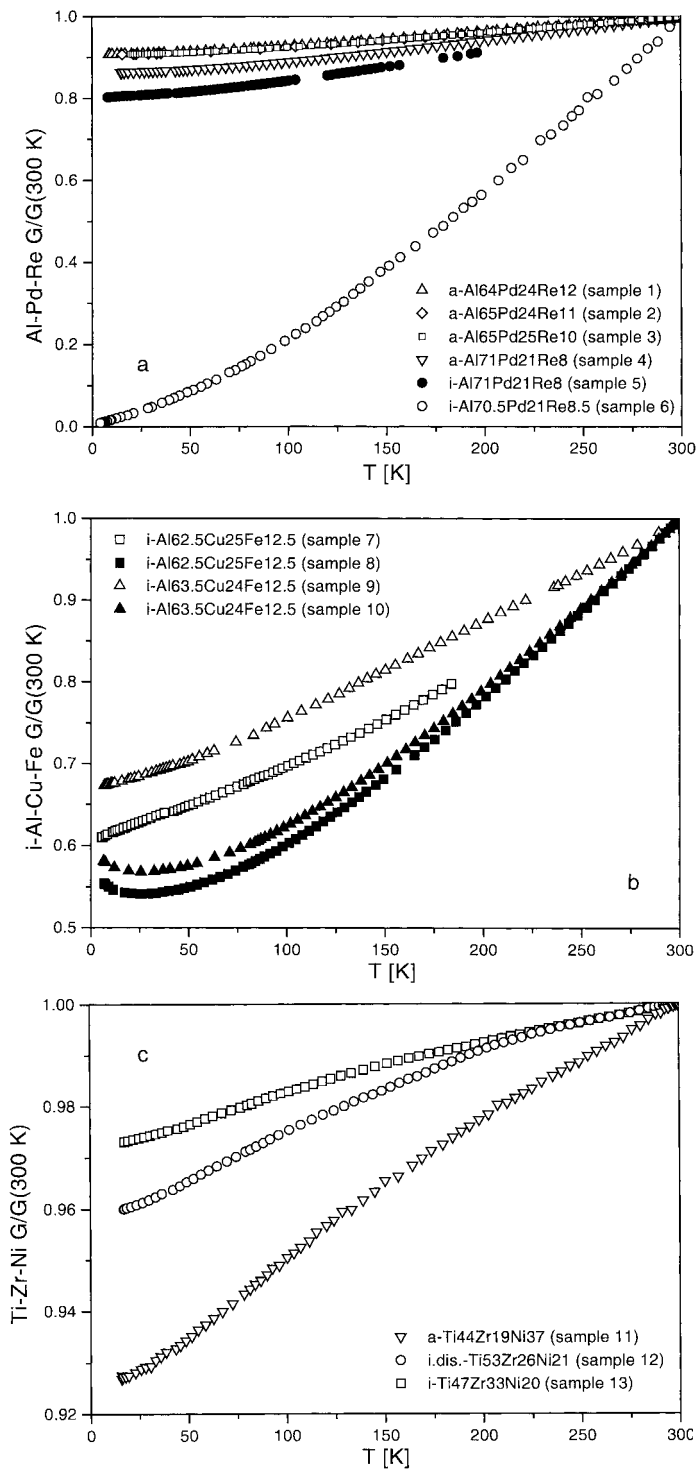


Fig. 1. Normalized conductance data $G/G(300\text{ K})$ vs. temperature for a) Al-Pd-Re, b) Al-Cu-Fe, and c) Ti-Zr-Ni in amorphous (a) and icosahedral (i) states. Dis means disordered

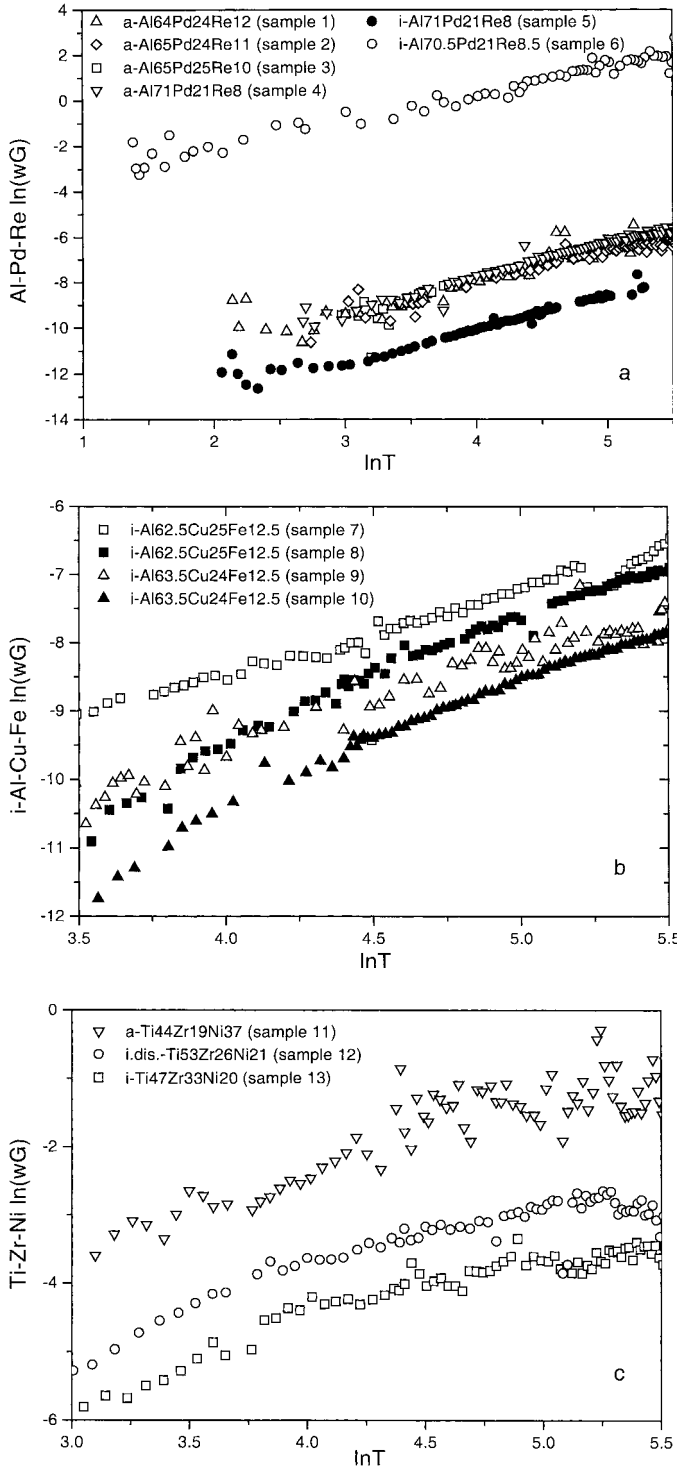


Fig. 2. $\ln(wG)$ vs. $\ln T$ for a) Al-Pd-Re, b) Al-Cu-Fe and c) Ti-Zr-Ni in amorphous (a) and icosahedral (i) states. Bulk sample 6 in a) has different geometrical parameters

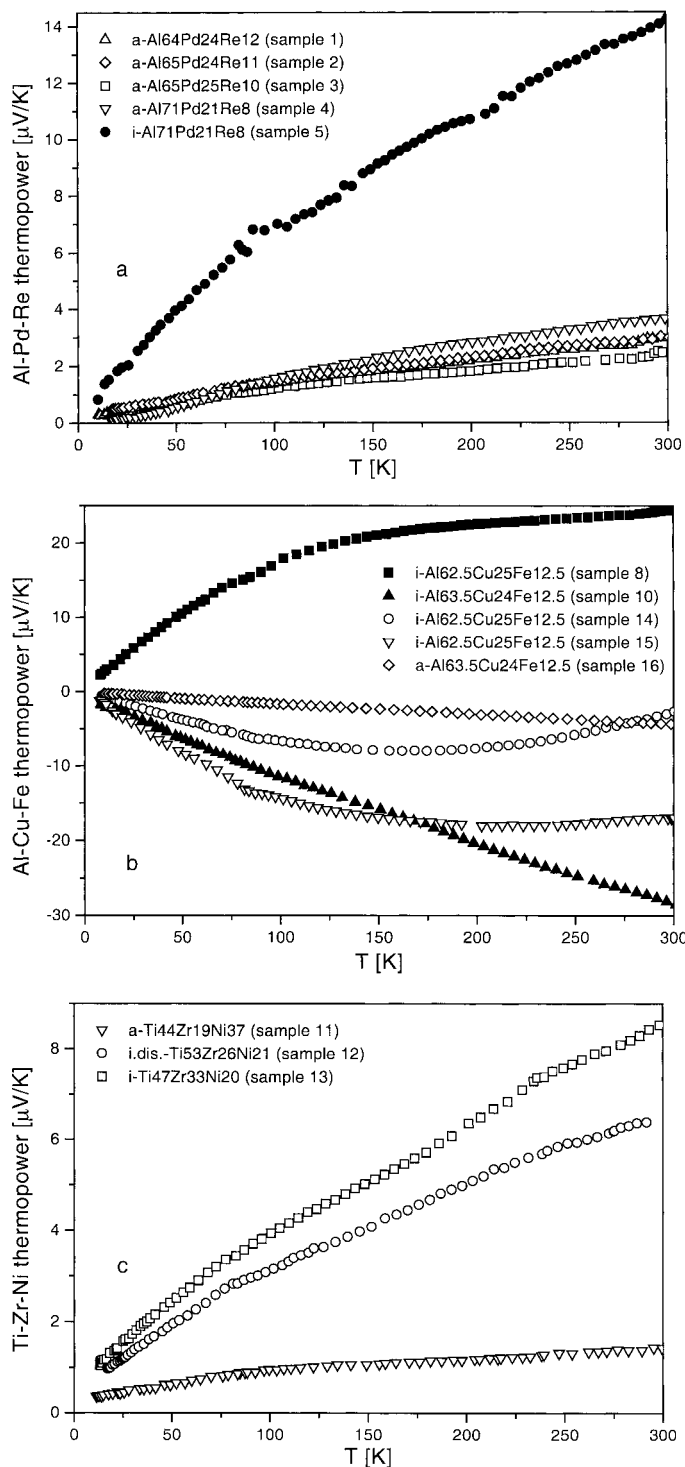


Fig. 3. Thermopower data for a) Al-Pd-Re, b) Al-Cu-Fe, and c) Ti-Zr-Ni. Samples 14, 15 (icosahedral, with the same nominal composition and similar $G(T)$ dependences as that of sample 8), and 16 (amorphous) have been added in b) to illustrate the special sensitivity of $S(T)$ to details in the DOS at E_F . They were prepared under the same conditions as samples 7 to 10 and are not mentioned in Table 1. Sample 16 was annealed only up to about 300 K to preserve its amorphous state

used the $\ln(w\sigma)$ versus $\ln T$ data reduction [8],

$$w = \frac{\partial \ln \sigma(T)}{\partial \ln T},$$

$$\ln(w\sigma) = \ln \zeta C + \zeta \ln T, \quad (3)$$

$$\ln(wG) = \ln \zeta CK + \zeta \ln T,$$

where $G = K\sigma$, the factor K being determined by sample geometry.

For most Al–Pd–Re and Al–Cu–Fe samples, the quasi-linear dependence of $\ln(wG)$ versus $\ln T$ (Fig. 2a to c) allows to derive the T exponent ζ (Table 1). Moreover, from Eq. (2),

$$G(0) = G(T) - KCT^\zeta \quad (4)$$

and average $G(0)$ values can be calculated using KC values derived from the intercept in Eq. (3). Fig. 1a shows the large different behaviour of icosahedral Al–Pd–Re phases of similar composition but different degrees of structural perfection. Bulk sample 6 is close to a perfect icosahedral structure ($G(T)$ tends towards zero with decreasing T), while the icosahedral film (sample 5) is closer to the amorphous samples 1 to 4 ($G(T)$ tends toward a finite value at low T). It should be mentioned that for a “perfect” icosahedral structure, free of any detectable crystalline phases, the room temperature conductivity is about an order of magnitude higher than in disordered structures.

Two of the Al–Cu–Fe icosahedral films (samples 8 and 10, Fig. 2b) show a slight negative curvature of the $\ln(wG)$ versus $\ln T$ dependence, resulting in a higher average ζ (Table 1). A similar effect was noticed for the Ti–Zr–Ni icosahedral ribbons (Fig. 2c), where $\ln(wG)$ could be approximated by two linear regions, at low ($\ln T < 4.25$) and high ($\ln T > 4.25$) temperatures (Table 1). This behaviour underlines the approximate character of Eq. (2) and (3) when used over a wide T range, where changes in the conduction mechanism might take place (see Section 4.1)

Thermopower data S are shown in Fig. 3 as a function of T . Some samples display a quasi-linear dependence, although a negative curvature is seen in most graphs with $S > 0$.

4. Discussion

4.1 Conduction mechanisms

The temperature exponent ζ (Eq. (2)) is very close to $3/2$ in most Al–Pd–Re films, both amorphous and icosahedral (Table 1). This value is in agreement with a semi-metal-like conduction mechanism, extending over the whole temperature range investigated. However, the bulk icosahedral sample 6, with a high degree of structural perfection displays a lower ζ exponent (Table 1), closer to the $\zeta = 1$ value predicted by the hierarchical cluster model [4]. The $G(T)/G(300\text{ K})$ values in Al–Pd–Re samples are rather composition-independent in amorphous and icosahedral films (Fig. 1a, samples 1 to 5). However, in the annealed, well-structured bulk icosahedral phase (sample 6), a decrease of this ratio by a factor larger than 100 is noticed at low T , with an obvious trend towards zero. These observations suggest that the structural disorder present in the Al–Pd–Re icosahedral and amorphous films increases the superposition of valence and conduction bands, thereby enhancing the carrier concentration at low T 's and inducing a semi-metal-like $T^{3/2}$ dependence.

In Al–Cu–Fe icosahedral films with a linear $\ln(wG)$ versus $\ln T$ behaviour (samples 7 and 9 in Fig. 2b), ζ takes lower values (≈ 1.1 , Table 1) over the temperature range 10 to 300 K. This exponent value suggests a rather strong electron localization, in agreement with the variable range hopping mechanism proposed by Janot [4]. Two Al–Cu–Fe films (samples 8 and 10) showed a peculiar conductance behaviour at low temperatures. Below about 24 K, G was found to decrease with increasing T (Fig. 1b), as also reported in [9]. This behaviour also influences the slope of the $\ln(wG)$ dependence at low T (Fig. 2b).

The Ti–Zr–Ni as-quenched ribbons are in different structural states: a well-structured icosahedral phase (sample 13), a slightly disordered one (sample 12) and an amorphous sample 11. They were obtained in this order at increasing quenching speeds of the melt. Ribbon 13 also contained very small amounts of a hexagonal Laves phase. Details about the structure investigations on this system are reported in [6, 7]. The variation of the slope $\ln(wG)$ with $\ln T$ (Fig. 2c) can be approximated by two quasi-linear zones, more evident in the icosahedral phases 12 and 13. The average ζ exponents derived for the two zones are ≈ 1.5 ($20 \text{ K} \leq 70 \text{ K}$) and ≈ 0.6 ($70 \text{ K} \leq T \leq 300 \text{ K}$) (Table 1), suggesting a semi-metal-like behaviour at lower T . In the higher T range, a localization mechanism seems to take over. Using eqn. (1), a rather weak localization factor ($\nu \approx 0.6$ to 1) can be derived for the critical states, in the high- T range. This cross-over of the $\sigma(T)$ dependence from one conduction mechanism to the other might be related to a “depletion” of the electronic states near E_F with increasing T .

In the amorphous Ti–Zr–Ni (sample 11), the high dispersion of the $\ln(wG)$ values (Fig. 2c) prevents definite conclusions. Nevertheless, here also, two T ranges can be distinguished, with ζ values close to those in the icosahedral phases (Table 1). The latter fact suggests a similar short-range order in the amorphous and in the well-structured icosahedral Ti–Zr–Ni ribbons.

The high $G/G(300 \text{ K})$ ratios observed in icosahedral Ti–Zr–Ni samples 12 and 13 at low T , in comparison with the amorphous sample 11 (Fig. 1c), suggest that the Laves phase in sample 13 and probably an additional untraceable secondary phase present in icosahedral sample could alter the real $G(T)$ dependence in this system. We previously observed similar effects in bulk icosahedral $\text{Al}_{70.5}\text{Pd}_{21}\text{Re}_{8.5}$, where a tiny amount of a secondary crystalline phase, barely visible in X-ray diffraction patterns, increased the $G/G(300 \text{ K})$ ratios at low T by a factor of ≈ 100 .

4.2 Thermopower

Thermopower S in icosahedral phases was shown [10] to be very sensitive to the depth of the DOS gap at the Fermi level, as well as to the detailed shape of local conductivity $\sigma(E, T)$ around E_F [11],

$$S(T) = \frac{k_B}{e\sigma} \int_{-\infty}^{E_F} \sigma(E, T) \left(\frac{E_F - E}{k_B T} \right) \left(\frac{\partial f(E, T)}{\partial E} \right) dE,$$

where $f(E, T)$ is the Fermi function and σ is the total conductivity.

Positive thermopower values were measured in icosahedral as well as in amorphous Al–Pd–Re film samples (Fig. 3a). Thermopower follows a quasi-linear T dependence, although curvatures are occasionally noticed, also to be seen in Al–Cu–Fe samples

(Fig. 3b). The S value at 300 K in the icosahedral Al–Pd–Re film (sample 5, Fig. 3a) is a factor of ≈ 5 higher than in amorphous samples (1 to 4), pointing to a better defined and deeper gap at E_F , induced by an increased structural order. A still higher $S(300\text{ K})$ value was reported [12] in a well ordered $\text{Al}_{70.5}\text{Pd}_{21}\text{Re}_{8.5}$ icosahedral phase. Nevertheless, the presence of a DOS gap ($S > 0$) even in the amorphous state supports the similarity of conduction mechanisms in both icosahedral and amorphous states (Section 4.1), suggesting a similar type of short-range order.

In a well-structured icosahedral $\text{Al}_{62.5}\text{Cu}_{25}\text{Fe}_{12.5}$ phase, S values are also positive (Fig. 3b, sample 8). However, other icosahedral films of the same nominal composition and degree of order show negative thermopower (Fig. 3b). Plots of additional samples (not mentioned in Table 1) are inserted in Fig. 3b to illustrate this aspect. These differences point to the special sensitivity of thermopower to details in the DOS around E_F (or to the scattering mechanism of the carriers). Amorphous Al–Cu–Fe alloys of similar composition show S values close to the free-electron $S \cong 0$ (Fig. 3b), as also reported in [10].

Ti–Zr–Ni samples (Fig. 3c) show a quasi-linear T dependence of thermopower, as also reported before [13], with positive S values, suggesting a DOS gap at E_F . The value reached at 300 K strongly depends on the degree of structural order: $8.6\ \mu\text{V/K}$ in the well-structured icosahedral phase (sample 13), $6.5\ \mu\text{V/K}$ in the slightly disordered one (sample 12), reaching $1.4\ \mu\text{V/K}$ for the amorphous ribbon (sample 11) and suggesting again a relationship between the degree of icosahedral order and the depth of the DOS gap. Positive S values show that a Hume-Rothery gap (related to icosahedral short-range order) is present even in amorphous Ti–Zr–Ni samples.

5. Conclusions

Icosahedral, as well as amorphous phases in the systems Al–Pd–Re, Al–Cu–Fe and Ti–Zr–Ni were obtained as thin films or bulk samples.

The temperature dependence of the conductance follows a power law T^ζ for $10\text{ K} \leq T \leq 300\text{ K}$, attributable, for the amorphous and icosahedral Al–Pd–Re films, to a semi-metal behaviour ($\zeta \cong 1.5$). However, a well-structured bulk i-Al–Pd–Re phase shows a lower ζ , indicative of a transition to electron localization in an hierarchy of clusters. The quasi-perfect icosahedral character of this sample is supported by the vanishingly small residual conductance $G(0)$. The same semi-metal-type conduction was found to prevail in Ti–Zr–Ni icosahedral phases at low T 's. At higher temperatures, electron localization in clusters apparently takes over in these samples, with a rather weak localization exponent of the critical wave functions ($\nu \approx 0.6$ to 1). Localization-type conductivity dependence was also found in two of the i-Al–Cu–Fe phases ($\zeta \approx 1.1$) over the whole T range investigated. Anomalous behaviour of $\sigma(T)$ below 24 K was noticed in other two Al–Cu–Fe films, affecting the global value of the ζ exponent.

Positive thermopower data confirm the presence of a deep Hume-Rothery DOS gap at E_F in an icosahedral Al–Pd–Re film. In Ti–Zr–Ni bulk i phases, this gap is less pronounced, presumably because of the impurity crystalline phases present in these alloys. The gap becomes more shallow when disorder increases in Ti–Zr–Ni icosahedral phases, inducing a smaller (but still positive) S . The presence of positive thermopower even in amorphous Al–Pd–Re and Ti–Zr–Ni samples suggests a similar ico-

hedral short-range order in both structures, despite the differences in the long-range ordering of the elemental icosahedral units. In icosahedral Al–Cu–Fe films, positive as well as negative thermopower values were measured for close compositions, suggesting a high sensitivity of S to DOS details around E_F .

We can conclude that, in icosahedral Al–Pd–Re, Al–Cu–Fe and Ti–Zr–Ni phases, two conduction mechanism prevail: semi-metal behaviour and weak localization of electrons in hierarchical atomic clusters.

These mechanisms are manifest in different temperature ranges, depending on the system investigated. The magnitude of the positive thermopower in all these systems can be related to the depth of the DOS gap at E_F , increasing with the degree of icosahedral structural order. Thus, a continuum of structures is revealed, from amorphous to well-structured icosahedral phases, in which the type of short-range order is similar, but the degree of long-distance icosahedral order gradually increases. Thermopower values are directly related to this degree of order, via the depth of the DOS gap at E_F . The conduction mechanism is also influenced, in some systems, by the degree of long-distance icosahedral order. In well-structured icosahedral Al–Cu–Fe and Al–Pd–Re samples, electron localization in hierarchical clusters is manifest, while in amorphous Al–Cu–Fe films a semi-metal behaviour of the conductance takes over.

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