0.1 Electronic transport parameters and spectral fine structure: From approximants to quasicrystals

H. Solbrig and C. V. Landauro
Technische Universität Chemnitz
Institut für Physik
D-09107 Chemnitz
Germany

0.1.1 Introduction

One of the crucial challenges posed by quasicrystals (QCs) is that metallic chemical components can be alloyed to resemble doped semiconductors in view of the low-temperature electronic transport. At certain well-defined stoichiometries, resistivities were found up to several $10^4 \Omega cm$ [1] together with large thermoelectric powers and Hall coefficients that even change their signs [2]. All that cannot be due to thermal excitation from impurity states to ballistic band states, because it is a property of atomically perfect structures. In the quasiperiodic limit, the electrons occupy critical states [3] that reveal multifractal properties [4]. The electronic transport obeys the anomalous Drude formula, $\sigma \propto \tau^{2\beta-1}$ (Sire, Mayou, Bellissard et al. [5]), where the really interesting cases of subdiffusive transport are addressed by $\beta < 0.5$. Defects and excitations of the quasiperiodic structure cause the electrons to leave their states after the scattering time $\tau$. Summarizing, two transport regimes are proposed [6, 7, 8]: If $\tau$ is sufficiently large the non-ballistic propagation of electrons in critical states will be most important. For small $\tau$, however, hopping between critical states will predominate, with the consequence that the spectral distribution of the critical states is most important. Nevertheless, several attempts [9, 10, 8, 11] within the Bloch-Boltzmann concept have demonstrated for approximants that high resistivities are caused by narrow flat bands close to the Fermi energy. The weak point is that the conductivity is extracted from the dispersion of ballistic band states, in obvious contrast to rigorous results for quasiperiodic systems. However, a useful conclusion can be drawn: The origin of the non-metallic behavior may reside on the length scale of the approximant unit cell. This fits well to the results of numerical studies with sequences of approximants to quasiperiodic one-component systems, namely that the typical non-metallic transport regime of certain QCs can hardly be due to quasiperiodicity alone (tight-binding study for the three-dimensional Penrose tiling [12], TB-LMTO study for decagonal aluminum [13]). We conclude that a critical co-operation of at least two chemical components is required.

Pierce et al. [2] reported sufficient evidence for a rapidly varying spectral conductivity in ordered icosahedral phases. This explains why the striking peculiarities of QCs appear only at low temperatures where the thermal energy window, $k_B T$, is narrow enough to resolve electronic spectral features that arise from extended quasiperiodicity. At high temperatures, however, the relationship of QCs with approximants [2, 1] and even with amorphous phases [14] results from equivalent conditions on shorter length scales. There is experimental evidence for spectral fine structures around the Fermi energy down to a few 10 meV [15]. Janot et al. [16] propose to treat QCs as arrays of clusters. Such arrays form virtual bound
electron states [17]. We have shown [18, 19] that several physically significant 100 meV features in the spectral resistivities of the approximants $\alpha$-AlMn(Si) and $i$-AlCuFe (1/1) depend critically on the well-configured networks of the Mn respectively the Fe atoms. This work presents additional evidence.

Complex systems such as QCs exhibit phenomena that may be well handled on the basis of physically reasonable models. The two-band model [20] puts emphasis on the fact that both signs of the Hall coefficient are observed just as common for semiconductors. Since experimental data are available for QCs from energy scales down to a few 10 meV the modeling of spectral properties appears most hopeful. Enderby et al. [21] have demonstrated with the Anderson metal-insulator transition that models of the spectral conductivity provide access to the whole zoo of transport parameters. The link is established by means of the Chester-Thellung Kubo-Greenwood formulas [22]. Models of the state density were proposed [23] that consider spiky features in addition to a wide parabolic pseudogap with square-root wings. We have contributed [24, 25] with a different concept starting from the $ab$-$initio$ calculated spectral conductivities of approximants. The idea is that spectral features close to the Fermi energy which depend on the co-operation of typical atom clusters may persist in the QC where related clusters co-operate on extended length scales. Such spectral information is extracted in terms of a Lorentzian resistivity model of the approximant and subsequently upscaled to the quasicrystal. The latter step employs the experimental thermopower curve of the QC.

After a brief introduction to the theoretical framework we proceed in two steps. A first step deals with spectral information that is accessible by $ab$-$initio$ methods, i.e. for selected (1/1) approximants we will show that there is physically significant fine structure, and we examine where it originates. The second step is devoted to the spectral resistivity modeling of the related QCs.

0.1.2 Transport parameters

Within the Chester-Thellung Kubo-Greenwood (CTKG) formalism, temperature-dependent transport parameters are derived from a given set of spectral conductivities, $\sigma_{\alpha,\beta}(\epsilon)$, which are either calculated by $ab$-$initio$ methods or suitably set up as model conductivities. This has the advantage that the transport concept employed in the spectral conductivities can be checked on the same footing with a great amount of experimental data.

Energy scales

We replace the atomic polyhedra by atomic spheres (ASs, sites $\mathbf{R}_p$) and obtain [26] a physically revealing representation of the partial density of states (DOS) of embedded self-consistent ASs,

$$n_{pI}(\epsilon) = n_{pI}^0(\epsilon) \left( 1 + \text{Re} \frac{1}{2l+1} \sum_m T_{pL.pL} \right),$$

(1)

where $L = (l, m)$ is the angular momentum, and $n_{pI}^0(\epsilon)$ means the partial DOS of the same AS in vacuum. Complex amplitudes,

$$T_{pL.pL} = e^{i\eta_p}\langle p L | (I - PF)^{-1} P | p L \rangle e^{i\eta_p},$$

(2)
account for back-scattering by the environment. $F$ is the diagonal matrix of all AS scattering
amplitudes, $(\exp(i2\eta_{\alpha}(\epsilon)) - 1)/2$, and $\eta_{\alpha}(\epsilon)$ are scattering phase shifts. The propagation
matrix $P$ describes transitions between atomic-site angular-momentum channels via vacuum
waves. The exponentials in Eq. 2 accomplish transitions from AS partial waves that are sup-
posed by $\gamma_{\alpha}^{\alpha}(\epsilon)$ to vacuum waves and, after multiple scattering, vice versa. Propagation-
caused phase gains are thus mixed with local ones which is particularly important for $d$
bands. The $\gamma_{\alpha}^{\alpha}(\epsilon)$ contribute wide $sp$ bands ($\sim$ ryd) and less extended $d$ bands ($\sim$ 0.1
ryd). Spectral fine structures arise from rapid variations of the back-scattering, Eq. 2. For
a rough estimate we confine ourselves to propagation-caused changes of the inward single
back-scattering of $s$ waves from $N$ equally spaced shells of scatterers (shell spacing $d$). This
provides $\langle p00 | (I - PF)^{-1}P | p00 \rangle \propto \exp(i k N d) \sin(k(N + 1)d) / \sin(kd)$. Distinct spectral
features require $\Delta k \approx 1/N d$, and the energy scales are estimated by $\Delta \epsilon \approx 2 \Delta k$. There are
two important cases: (i) Atomic-scale coherence effects close to the Fermi energy, $\epsilon_F$, such
as Hume-Rothery pseudogaps correspond to $N \approx 10, d \approx \pi / k_F \rightarrow \Delta \epsilon \sim 10^{-1}$ ryd. However,
with a transition-metal $d$ resonance around $\epsilon_F$, hybridization acts on the same energy
scale [27]. (ii) In agreement with predictions of the hierarchical model [16], medium-range
coherence effects can be expected in networks of such transition-metals which are considered
by $N \approx 10, d \approx 10 \AA \approx 5 \pi / k_F \rightarrow \Delta \epsilon \sim 10^{-2}$ ryd. This kind of fine structure is the central
issue of our work. There is experimental evidence for such spectral features [15] in addi-
tion to competing ones that are caused by electron-electron interaction. The so-called "spiky
structure" (scale $\sim 10^{-3}$ryd) of calculated DOS curves of low approximants turned out to
disappear if higher approximants are examined with a sufficient $k$-space treatment [28].

**Transport parameters from spectral information**

In the CTKG framework, the kinetic coefficients with $i, j = 1$ or 2,

$$L_{i\alpha}^{ij}(T) = (-1)^{i+j} \int d\epsilon \epsilon_{\alpha\alpha}(\epsilon) (\epsilon - \mu)^{i+j-2} \left( - \frac{\partial f^0(\epsilon, \mu, T)}{\partial \epsilon} \right),$$

play a central role. $f^0(\epsilon, \mu, T)$ is the Fermi-Dirac distribution function, and the chemical
potential will be used in the low-temperature representation [29].

$$\mu(T) \approx \epsilon_F - (k_B T)^2 \frac{\pi^2}{3} \left( \frac{d \ln(\tilde{n}(\epsilon))}{d\epsilon} \right)_{\epsilon = \epsilon_F} \equiv \epsilon_F - \xi T^2.$$

(4)

The kinetic coefficients are thus low-order moments of the spectral conductivities taken from
the thermal energy window centered at $\mu(T)$. Certain applications below deal with only one
transport direction, in such cases the subscripts $\alpha, \beta$ will be omitted. Within this scheme we
obtain the electronic conductivity and its low-temperature Sommerfeld approximation,

$$\sigma(T) = L^{11}(T) \approx \tilde{\sigma}(\epsilon_F) + \frac{\pi^2}{6} \left( \frac{d \ln(\tilde{n}(\epsilon))}{d\epsilon} \right)^2 \tilde{\sigma}(\epsilon)_{\epsilon = \epsilon_F} \left( \frac{d \ln(\tilde{n}(\epsilon))}{d\epsilon} \right)^2 \tilde{\sigma}(\epsilon)_{\epsilon = \epsilon_F}.$$

(5)

The Einstein relation on the energy surface,

$$\tilde{\sigma}(\epsilon) = \frac{e^2}{\sqrt{\pi}} \tilde{n}(\epsilon) \tilde{D}(\epsilon),$$

(6)
leads to the electronic spectral diffusivity, $\bar{D}(\epsilon)$. One obtains the thermoelectric power with its Mott-like approximation,

$$S(T) = \frac{1}{|e|T} \frac{L^2(T)}{\sigma(T)} \approx -\frac{\pi^2 k_B^2 T}{3 |e|} \left( \frac{d \ln(\bar{\sigma}(\epsilon))}{d \epsilon} \right)_{\epsilon=\mu},$$

(7)

the electronic thermal conductivity,

$$K(T) = \frac{1}{|e|^2 T} \frac{C^2(T) - T \sigma(T) S(T)^2}{\sigma(T)},$$

(8)

and the Lorenz number,

$$L(T) = \frac{K(T)}{T \sigma(T)}.$$

(9)

Lorenz numbers close to the Wiedemann-Franz limit, $L_0 = (3/2)(k_B/|e|)^2$, indicate nearly-free electron transport regimes. For a spectral representation of the normal Hall coefficient we start from the Bloch-Boltzmann result (cf. Ziman [30]) and eliminate all $k$-dependent quantities in favor of both spectral diffusivities, $\bar{D}_{\alpha\beta}(\epsilon)$, and energy derivatives of $\bar{\sigma}_{\alpha\beta}(\epsilon)$. Summarizing we arrive at

$$R_H(T) = \frac{1}{\sigma_{xx}(T) \sigma_{zz}(T)} \int d\epsilon \bar{\sigma}_{x,yz}(\epsilon) \left( \frac{\partial f^0(\epsilon, \mu, T)}{\partial \epsilon} \right),$$

(10)

$$\bar{\sigma}_{x,yz}(\epsilon) = |e| \left( \bar{D}_{zz}(\epsilon) \frac{d}{d\epsilon} \bar{\sigma}_{zz}(\epsilon) - \bar{D}_{xx}(\epsilon) \frac{d}{d\epsilon} \bar{\sigma}_{zz}(\epsilon) \right) \approx \frac{Q}{\sigma} \frac{d^2 \bar{\sigma}(\epsilon)}{d\epsilon}.$$

(11)

Note that off-shell information is included due to the energy derivatives (cf. [31]). We confine ourselves to the approximate version in Eq. 11 where $Q$ is a positive constant [25]. This applies to systems such as i-AlCuFe where experiments [32, 2] reveal correlated signs of $\bar{\sigma}_{\alpha\beta}$, Eq. 7, and almost the same electronic diffusivities of several i-AlCuFe phases close to the quasicrystalline stoichiometry (12-13 at.% Fe) [33].

**Methods**

In the *ab-initio* calculations we rely on the atomic-sphere approximation to the linear muffin-tin orbital method (ASA-LMTO [34], ASA-correction included, special $k$-sets [35]). This provides the energy eigenvalues, $\epsilon_i$, the partial-wave decomposed LMTO band states, and the scattering phase-shifts of the self-consistent effective atoms to be applied for the following purposes: (i) We calculate state densities on replacing the discrete levels by Gaussians (half width $\geq 10$ meV). (ii) We calculate the velocity matrix, $\langle i | v_\alpha | j \rangle$, and evaluate the Kubo-Greenwood formula (KGF),

$$\bar{\sigma}_{\alpha\beta}(\epsilon + \hbar \omega) = \frac{\hbar |e|^2}{V} \sum_{ij} \langle i | v_\alpha | j \rangle \langle j | v_\beta | i \rangle \delta(\epsilon - \epsilon_i) \delta(\epsilon + \hbar \omega - \epsilon_j),$$

(12)

as formerly demonstrated [36]. $\omega$ is the frequency of an external field. The limit $\omega \rightarrow 0$ of Eq. 12 provides spectral conductivities, $\bar{\sigma}_{\alpha\beta}(\epsilon)$. Optical conductivities, $\sigma_1(\omega)$, are obtained
on taking an energy integral of Eq. 12 with the weight \((f^0(\epsilon, \mu, T) - f^0(\epsilon + h\omega, \mu, T))/h\omega\). Lorentzian level broadening (variable half widths \(\Gamma\)) simulates thermal transitions. (iii) We calculate the Landauer conductance of an infinite slab of approximant cells by means of a muffin-tin scattered-wave implementation of the Landauer method (MT-SW LM [37]). The resistance scaling with the thickness \(L\) reveals a trend towards a non-metallic transport regime. (iv) We calculate the DOS at the central atom of a cluster where a part of the cluster atoms are omitted. This is accomplished by means of a muffin-tin scattered-wave cluster-recursion method (MT-SW RM [26]). Thus, the chemical origin of certain spectral features can be analyzed.

### 0.1.3 Spectral fine structure on the scale 100 meV

The spectral resistivities of several icosahedral (1/1) approximants reveal pronounced 100 meV peaks close to the self-consistently calculated Fermi energies, \(\epsilon_F\). The top resistivities depend on both the depths of the accompanying DOS pseudogaps and the electronic diffusivities. In such spectral ranges, transport conditions are found that resemble those of related QCs. Defects can shift the actual Fermi energies, \(\epsilon_F\), by a few 100 meV away from the calculated positions (experiments [2], LMTO calculation [18]). We suppose \(\epsilon_F\) of real high-resistivity phases shifted towards such narrow spectral features.

#### Models

For the (1/1) approximant of i-AlCuFe we prefer the hypothetical Cockayne model (CM [38]) which is fully characterized and obviously disposed for high resistivities. The latter fact indicates that essential properties of the Fe-network in the QC must be represented in the unit cell \((a=12.3 \, \text{Å}, 80 \, \text{Al} + 32 \, \text{Cu} + 16 \, \text{Fe})\). Four interpenetrating Bergman clusters bear each 3 Fe atoms (the b-Fe) in the inner icosahedral shell. The remaining 4 Fe atoms (the g-Fe) belong to the glue. They link the triangles of b-Fe to form the iron network without direct Fe-Fe contacts. The Elser-Henley model (EHM [39]) of \(\alpha\)-AlMn(Si) is employed for an (1/1) approximant to the metastable i-AlMnSi. This is a bcc lattice of MacKay icosahedra with additional Al glue (114 Al + 24 Mn + 14 voids). The Mn icosahedra are arranged to form sequences of Mn planes along the sides of the cubic cell (spacing LSL). Icosahedral approximants in both the Al-Cu-Ru and the Al-Pd-Re systems were constructed after prescriptions given by Sugiyama et al. [40].

#### Resistivity peaks and pseudogaps

Within 6 eV around \(\epsilon_F\) spectral properties of the above approximants (columns) are presented in Fig. 1. The panels in lines show a) the resistivities, b) the diffusivities, c) the state densities, and d) the total \(s\text{p}\) weights of the LMTO band states in the unit cell \((s\text{p}\text{d} \text{w} \text{e}g \text{t} \text{e} \text{w} \text{s} \text{t} \text{e} = 1)\). In the sequence of columns, starting left, all \textit{ab-initio} calculations were performed with 14/9/3 types of effective atoms, with 120/120/20 irreducible special \(\text{k}\) points, and with 20/20/15 meV half width of the Gaussians and Lorentzians. In the KGF, Eq. 12, \(f\) orbitals were considered for transition metals, and the energy mesh was about 1 meV. All fine structure around \(\epsilon_F\) may be physically significant. Particularly clear results were obtained with the CM of i-AlCuFe (1/1).
A pronounced pseudogap in the DOS (width $\sim$ 200 meV, Fig. 1c) is accompanied by a 600 $\mu$Ωcm resistivity peak (width $\sim$ 100 meV, Fig. 1a). This narrow DOS pseudogap is centered at $\epsilon_F^c + 230$ meV, the profile is V-shaped but non-symmetric. The lowest DOS occurs at $\epsilon_F^c + 260$ meV. Apart from minor shifts and rescalings, both features prove stable against several modifications ($k$ set, number of different effective atoms). Former LMTO calculations [10, 8] did not reveal such a distinct DOS pseudogap. Two items are to be noted in view Fig. 1: (i) High resistivities (Figs. 1a) are not only due to low state densities (Figs. 1c). Moreover, less diffusive electron states are required (Figs. 1b). This makes the difference to non-approximant Hume-Rothery systems such as Al$_{12}$Fe [41] where diffusivities up to 10 cm$^2$/s occur at $\epsilon_F^c$. (ii) The LMTO band states around $\epsilon_F^c$ have $sp$ weights close to 4/9 (Figs. 1d) which implies 5/9 for the $d$ weights. This equipartition makes them highly disposed for hybridization. States below $\epsilon_F^c$ are rather $d$ like with low diffusivities (Figs. 1d,b) whereas the states above acquire increasing $sp$ weights which promotes the diffusivity. The general conclusion is that even

![Figure 1](image-url)

Figure 1: Spectral resistivity (a), diffusivity (b), state density (c), and the $sp$ weight of LMTO band states around the Fermi energy, Fe, Mn, Ru $d$ resonances indicated by arrows.
(1/1) approximants produce narrow pseudogaps in the DOS close to $\epsilon_F^2$ that are accompanied by resistivity peaks. The top resistivities are well above the level of related amorphous phases due to both low DOS and diffusivity.

**Subdiffusive transport in the narrow resistivity peak**

A finite electron life time, \( \tau \), due to thermal transitions can be simulated in the KGF, Eq. 12, by a Lorentzian half width \( \Gamma \approx \hbar/2\tau \). This invokes the ionic dynamics of the system that may be phonon-like with \( \tau \propto T^{-1} \) at high temperatures. Suppose a subdiffusive regime where \( \beta = 3/8 \) [42, 8]. On such conditions, the anomalous Drude formula provides \( \sigma \propto T^{2\beta-1} \propto T^{1/4} \). Experiments with i-AlPdRe [43], on the contrary, report scalings \( \sigma \propto T^{1-\frac{\beta}{2}} \) up to 700 K.

![Graph showing subdiffusive transport in the narrow resistivity peak](image)

**Figure 2:** i-AlCuFe (1/1): Spectral resistivities calculated from Eq. 12 with increasing Lorentzian half width, \( \Gamma \). a) The inverse top resistivities at the two main peaks in Fig. 1a compared with \( \Gamma^{1/4} \). b) The whole spectral curves calculated with the \( \Gamma \) indicated.

The Bloch-Grüneisen law, \( \tau \propto T^{-5} \), has been proposed [42, 8] to remove the above difficulty at least below a critical Debye temperature (400 ... 500 K [44]). In the present approach, the temperature-dependent conductivity, Eq. 5, is derived from the spectral conductivity in the thermal energy window (center \( \mu(T) \), width \( k_B T \)). Hence, the transport will be subdiffusive provided that \( \hat{\sigma} \propto T^{1-2\beta} \) holds in the thermal window with \( \beta < 1/2 \). We have examined this scaling for i-AlCuFe (1/1) [25, 45]. Note first in Fig. 2b that the two narrow resistivity peaks almost symmetrical to \( \epsilon_F^2 \) have different thermal stabilities. Only the upper peak survives at higher temperatures due to the V-shaped spectral profiles (cf. DOS, Fig. 1c). Figure 2a examines whether the transport can be expected to be subdiffusive if the energy window is put to such a fine structure peak. We compare with the case \( \beta = 3/8 \) [42, 46]. The lines fit the physically significant parts of the scaling curves quite well. Hence, the upper resistivity peak reveals a subdiffusive transport regime up to high temperatures. This promotes the idea that related high-temperature transport properties of a QC and its approximants may arise from actual Fermi energies, \( \epsilon_F \), in such spectral fine structures. Support comes from the optical conductivity, \( \sigma_1(\omega) \). *Ab-initio* calculations for the approximant were performed at \( T = 0 \) K
with the actual Fermi energy shifted to several positions inside the upper resistivity peak and to 1 eV above (Fig. 3). With the former choice of the Fermi energy, the Drude peak at low frequencies (typical in amorphous metals) is clearly missing, in agreement with the experiment for the QC [47]. Note also the shift of the calculated maximum to about 1 eV above the experimental one. In the real QC, the electron states on energy shells separated by $>1$ eV are obviously less correlated.

### 0.1.4 Transition metal network generates spectral fine structure

Quasiperiodic one-component systems cannot reproduce the non-metallic transport properties of high-resistivity QCs [12, 13]. However, two experimental facts reveal the possible origin: (i) Such QCs contain 10...20 at% of a transition metal with a $d$ resonance close to $\epsilon_F$, and a remarkable stoichiometric sensitivity is observed [48, 44]. At such stoichiometries, transition-metal networks can be formed where the atoms are next-nearest neighbors in the QC. (ii) At high temperatures, the transport properties resemble those of the approximants. The origin of the transport anomalies must thus be found on length scales where both phases are equivalent. Hence, such transition-metal networks are to be examined more in detail.

The role of the iron network in the Cockayne model

It has been shown [17] that 12 small Mn icosahedra embedded in a simulated Al matrix produce electronic resonances. One can even go one more step [19]. Figure 4a shows the part of the total DOS at the central b-Fe atom in a 16000-atom Cockayne cluster which is due to scattering paths strictly confined to the Fe network (2000 b/g-Fe cluster, MT-SW RM, 5 meV steps, $\eta_{el}(\epsilon)$ taken from ASA-LMTO with the full approximant). The corresponding LMTO result for the full approximant is shown in Fig. 4b (120 special $k$ points, 10 meV half width).
Figure 4 includes a $\sim$0.2 eV shift of the energy scale which accounts for the common effect of all Al and Cu atoms. Both curves suffer from artifacts. Figure 4a exhibits spurious oscillations in the pseudogap due to the cluster surface whereas Fig. 4b has spurious features throughout the band due to the incomplete $k$ sum. Nevertheless, the pseudogap is caused by extended multiple scattering in the Fe network.

**Figure 4:** DOS at b-Fe atoms in i-AlCuFe (1/1): a) calculated from scattering paths with the 2000 Fe atoms in a 16000-atom Cockayne cluster (MT-SW RM, 5 meV steps), b) the full approximant (ASA-LMTO, $\Gamma = 10$ meV).

**Critical manganese network in the Elser-Henley model**

We have examined [19, 18] whether the anomalous transport properties of the EHM survive serious distortions of the co-operation between rigid MacKay icosahedra such as a mutual rotation. For proof we built slabs of about two approximant cells thickness ($L = 25.9 \, \text{Å}, 300$ atoms, $\eta_{\text{Mk}}(\epsilon)$ taken from ASA-LMTO, plane-wave amplitude transmission matrix $\tilde{t}(\epsilon, k_{\perp}, L)$). For computational efficiency, voids were not considered as scatterers. Once a new atom was added we have calculated the spectral conductance per cell cross section, $\tilde{G} = (2e^2/h) \, \text{Tr}(\tilde{t}^2 \tilde{t})$, for a $27 \times 27$ net of $k_{\perp}$ throughout a quadrant of the lateral Brillouin zone (MT-SW LM). The electron energy was chosen slightly above $\epsilon_{\text{F}}$. Figure 5 presents two columns of resistance contour plots, on the left the perfect EHM, and on the right after rotating the MacKay’s about their centers by a few degrees which destroys the LSL stacking of Mn planes in the EHM [18]. After rotation the Al glue has been relaxed. The unit resistance corresponds to a homogeneous wire (same cross section, same length, resistivity 200 $\mu$Omega cm). We conclude: (i) The resistance of the EHM exhibits a non-Ohmic length scaling with a pronounced $k_{\perp}$ dependence. (ii) After rotation the system resembles common amorphous metals where Ohm’s law holds in the considered length segment, and the influence of $k_{\perp}$ is weak. The message of the study is that the MacKay’s in the EHM are only the means that configure the Mn network. Cluster-orientation order is thus essential.
Figure 5: α-AlMn(Si): Contour plots of the Landauer resistance of up to 300 atoms arranged according to the Elser-Henley model (left), and after random rotation of the MacKay icosahedra (right). The unit resistance corresponds to a resistivity of 200 μΩcm. Note the Ohmic scaling after rotation. The energy is fixed slightly above $E_f$.

Non-isotropic transport

Approximants with cubic unit cells can generate non-isotropic transport profiles due to special distributions of the scattering power in the cells. This is shown by Fig. 5. A related study with i-AlCuFe (1/1) reveals even more a pronounced influence of $k_z$. Three perfect CM cells (383 atoms, only Al, Cu, Fe) are joined to model a crystal slab (thickness $L \approx 36.32$ Å). The energy of this 3-component study corresponds approximately to 76 meV below $E_f$ of the 14-component study (Fig. 1). We obtain again contour plots of the Landauer resistance. However, contrary to the EHM (Fig. 5, left column) the parts of the Brillouin zone with large resistances do not change. Adding atom by atom guides monotonously to the final state shown in Fig. 6a. The unit resistance, $R \approx 5000$ Ω, corresponds again to a homogeneous material (200 μΩcm). Hence, around the gamma point, the slab resembles amorphous metals. However, close to
This modeling intends to include only those features in the electronic transport parameters and spectral fine structure: From approximants to quasicrystals. It is proved for QCs [6, 43] as well as for thin-film transient phases [49, 14]. Below 100 K, a gap opens with up to 48 resistance units. This interpretation is supported by L-resolved information up to \( L = 45.8 \, \text{Å} \) (480 atoms, Figs. 6b,c). In Fig. 6c we show the 32 (at \( \mathbf{k}_{\perp}^{\text{app}} \)) respectively 37 (at \( \Gamma \)) eigenvalues of the Hermitian current matrix, \( \mathbf{f}_{\Gamma} \), after joining 10, 100 ... atoms to the slab. At \( \mathbf{k}_{\perp}^{\text{app}} \), no current-carrying channels are available beyond 100 atoms, and the resistance rises exponentially (Fig. 6b). At \( \Gamma \), on the contrary, the transport regime beyond two approximant cells corresponds to a crystal slab in the vacuum. Despite of such extremes, the BZ average stays Ohmic-like (Fig. 6b).

![Figure 6](image.png)

**Figure 6:** A slab of i-AlCaFe (1/1), thickness \( L \), resistance \( \mathbf{R} \), energy slightly below \( \epsilon_{F}^{\text{p}} \): a) \( \mathbf{R}(\mathbf{k}_{\perp}) \) at \( L = 36.9 \, \text{Å} \) (383 atoms), \( \mathbf{R}_{\perp} = 5000 \, \Omega \sim \) amorphous. b) \( \mathbf{R}(L) \) at \( \mathbf{k}_{\perp}^{\text{app}} = (0, 0)/(\pi/a), \mathbf{k}_{\perp}^{\text{app}} = (0.6, 1.0)/(\pi/a) \), BZ average (av), 480 atoms at the most. c) The 37 (at \( \mathbf{k}_{\perp}^{\text{app}}, \text{solid} \), respectively 32 (at \( \mathbf{k}_{\perp}^{\text{app}}, \text{dashes} \)) eigenvalues of the current matrix, \( \mathbf{f}_{\Gamma} \), after joining 10/100(480 solid/200 dashes) atoms to the slab.

Cell relaxation, the average slope of the curve corresponds to a resistivity of 690 \( \mu \Omega \cdot \text{cm} \). With the KGF (isotropic k-sampling, \( T > 0 \) simulated) resistivities up to 600 \( \mu \Omega \cdot \text{cm} \) were obtained (Fig. 1a). We conclude that even two unit cells of the iron network along the transport direction suffice to generate vastly fluctuating propagation conditions for electrons that correspond to beam sets with different lateral symmetries.

### 0.1.5 Spectral resistivity models of icosahedral phases

This modeling intends to include only those features in the \textit{ab-initio} calculated spectral resistivities of approximants that cause high resistivities. Such transport models do not attempt to be correct in spectral ranges which never belong to the thermal energy window. We believe that the generic properties of icosahedral high-resistivity QCs arise from the special cooperation of the clusters [16], and that even low approximants should exhibit corresponding spectral signatures to be extracted and then upscaled to the appearance in the QCs.

#### Inverse Matthiessen rule

Suppose, the inverse Matthiessen rule (IMR) has been observed in a group of phases. This means that the conductivities, \( \sigma(T) = \sigma_{\text{e}}(\epsilon_{F}) + \Delta \sigma(T) \), of the group members have a common positive \( \Delta \sigma(T) \) that rises monotonously \( \propto T^{1.5} \) up to high temperatures. The IMR is proved for QCs [6, 43] as well as for thin-film transient phases [49, 14]. Below 100 K
where the terminated expansion holds in Eq. 5, a parabolic $\Delta \sigma(T)$ can be expected. This parabola will be universal throughout the group if the second derivatives with respect to the number of states, $[(d/(\tilde{n} \, d\epsilon)) \, 2 \tilde{\sigma} (\epsilon)]_{\epsilon = \epsilon_F}$, scale as $\tilde{n}(\epsilon_F)^{-2}$ among the group members. For an estimate we adopt rigid-band arguments where the above demand is fulfilled by $\tilde{\sigma} (\epsilon) = c_1(1 + c_2(\epsilon - \epsilon_1)^2)$ together with a constant state density ($c_1, c_2, \epsilon_1$ constants). The above analysis probes only the immediate environment of the Fermi energy, much too less for reproducing the IMR-typical scaling up to $\sim 1000$ K. Nevertheless, if the profile starts parabolic, the profiles of the spectral resistivity and the state density close to $\epsilon_F$ may be supposed Lorentzian-like, respectively flat. This puts demands on the spectral diffusivity (cf. Einstein relation, Eq. 6).

**Lorentzian resistivity models**

Lorentzians can thus be considered as reasonable building blocks of transport models. They are characterized by their heights, $1/(\pi \gamma)$, and positions $\delta$ with reference to $\epsilon_F^\circ$. The resistivity model of i-AlCuFe (1/1) requires two Lorentzians,

$$\tilde{\rho}_L(\epsilon) = A \left( \frac{\gamma_1 / \pi}{(\epsilon - (\epsilon_F^\circ + \delta_1))^2 + \gamma_1^2} + \frac{\gamma_2 / \pi}{(\epsilon - (\epsilon_F^\circ + \delta_2))^2 + \gamma_2^2} \right),$$

the first one for the wide peak in Fig. 1a that is common with amorphous phases [45], and the second one for the narrow peak above $\epsilon_F^\circ$. The actual Fermi energy will be set to the spectral range of the latter Lorentzian. The parameters $A$, $\gamma$, $\delta$, and $\gamma_1$ are obtained by fitting to

<table>
<thead>
<tr>
<th>Phase, ref. experiment</th>
<th>$p_{4K}$ $\mu\Omega\text{cm}$</th>
<th>$A$ $\mu\Omega\text{cm}$</th>
<th>$\delta_1$ eV</th>
<th>$\gamma_1$ eV</th>
<th>$\alpha$ eV</th>
<th>$\delta_2$ eV</th>
<th>$\gamma_2$ meV</th>
</tr>
</thead>
<tbody>
<tr>
<td>i-AlCuFe (1/1)</td>
<td>610</td>
<td>1.6</td>
<td>580</td>
<td>-0.2</td>
<td>0.1</td>
<td>0.23</td>
<td>44</td>
</tr>
<tr>
<td>i-AlCuFe film [50]</td>
<td>2333</td>
<td>7.8</td>
<td>1047</td>
<td>-0.2</td>
<td>1.35</td>
<td>0.32</td>
<td>0.23</td>
</tr>
<tr>
<td>i-Al$<em>{63}$Cu$</em>{25}$Fe$_{12}$ [51]</td>
<td>4957</td>
<td>11</td>
<td>1400</td>
<td>-0.2</td>
<td>1</td>
<td>0.45</td>
<td>0.23</td>
</tr>
<tr>
<td>i-Al$<em>{60}$Cu$</em>{25.5}$Fe$_{12.5}$ [51]</td>
<td>7241</td>
<td>31</td>
<td>1047</td>
<td>-0.2</td>
<td>1.35</td>
<td>0.98</td>
<td>0.23</td>
</tr>
<tr>
<td>i-Al$<em>{63.5}$Cu$</em>{25}$Fe$_{12.5}$ [44]</td>
<td>8078</td>
<td>34</td>
<td>1047</td>
<td>-0.2</td>
<td>1.35</td>
<td>1</td>
<td>0.23</td>
</tr>
</tbody>
</table>

**$ab-initio$ results** for the approximant (Table 1, 1-st line). Common amorphous metals are properly described by one wide Lorentzian [45]. Close to quasicrystalline stoichiometries, however, on annealing at high temperatures, sequences of transient phases were formed that acquire successively transport properties of QCs [50]. Such thin-film phases require an additional narrow Lorentzian (Table 1, 2-nd line). Our upscaling to poly-quasicrystalline icosahe- dral Al-Cu-Fe phases (Table 1, lines 3,4) considers that the thermopower, $S^{zzp}(T)$. In the present work, we employ results published by Bilušić et al. [51]. Recently, the data reported by Pierce et al. [44] were used to model the i-Al$_{60.25}$Cu$_{25}$Fe$_{12.5}$ bulk-QC [25, 45] (Table 1, line 5). The following three steps are performed:
1. $\delta_1$ and $\delta_2$ are fixed at the approximant values.

2. For a starting value of $\xi$ in the chemical potential, $\mu(T)$, Eq. 4, we suppose constant diffusivity. This provides $(d(\ln(\bar{m})/de)_e = (d(\ln(\bar{a})/de)_e$ which allows to apply the Mott formula, Eq. 7: $\xi \approx -|\epsilon|/2) (S^{exp}(T)/T)_{T \to 0}$.

3. $A, \alpha, \gamma_1,$ and $\gamma_2$ are fitted as to fulfill two demands: $\bar{\rho}(\epsilon_F) = \rho_{\text{exp}}^{\text{exp}}$, and minimum $\chi^2$ for the approximation of $S^{exp}(T)$ up to 300 K. The fitting results in Table 1 account thus for the average performance of the QCs in this wide temperature range.

Anomalous temperature curves of transport parameters must occur once the real Fermi energy crosses a predominating narrow resistivity peak. We characterize this preeminence by the ratio of the peak heights, $x \equiv \alpha(\gamma_1/\gamma_2)$. Table 1 demonstrates that $x$ rises with increasing $\rho_{\text{exp}}$, i.e. if quasiperiodicity is improved.

The present parametrization scheme acts on the level of spectral quantities where arbitrary transport mechanisms can be included. Two-band models of quasicrystals [20] employ terms such as particles and holes which suppose sharp planes in $k$-space. Recently, both modeling procedures have been applied to thin-film transient phases [50].

**Transport parameters of the Al-Cu-Fe quasicrystal**

Figure 7 presents temperature-dependent transport parameters of the poly-quasicrystalline icosahedral phases as calculated with the model parameters shown in Table 1. We compare with available experimental results. Our conclusions are:

(i) Simple spectral resistivity models (Eq. 13) with only two Lorentzians reproduce the experimental results at least up to 300 K. At high temperatures where the thermal energy window samples more extended spectral information (cf. Fig. 1a) additional Lorentzians may be required (e.g. i-AlCuRu [45, 52]).

(ii) The optical conductivity (Fig. 7c, $\epsilon_F$ within 15 meV off $\epsilon_F^{\text{exp}} + \delta_2$, $T = T^{\text{exp}} = 295$ K [47]) is calculated according to the Lorentzian model on replacing $\bar{\sigma}(\epsilon, \epsilon + \hbar \omega)$ (Eq. 12) in the energy integral by $1.8 (\bar{\rho}_L(\epsilon) \times \hbar \omega)^{-1/2}$. Within this approximation, no comparison is performed between states that are separated by $\hbar \omega$. The obvious break-down of the approximation for $\hbar \omega > 1.5$ eV (Fig. 7c) is a consequence of this simplification. The ab-initio result for the approximant (Fig. 3) agree much better with the experiment for the QC, because the elements of the velocity matrix in Eq. 12 do really compare the wave patterns of states on different energy shells. Obviously, the composition of electron states changes drastically on scales of $\sim 2$ eV (cf. Figs. 1d).

(iii) We employ the simplified form of $\bar{\sigma}_{y_{\text{f}}}(\epsilon)$ in Eq. 11 with $Q = 3 \times 10^{-5}$ Am$^2$. This has the consequence that zeros of $\bar{S}(T)$ and $R_H(T)$ will ever occur at closely related temperatures, such as 373 K and 357 K, respectively, in the Figs. 8b,d.

(iv) Measurements of thermal conductivities provide only the sum of ionic and the electronic contributions. Hence, the electronic thermal conductivity is commonly estimated from the electronic conductivity by means of Eq. 9 where the Wiedemann-Franz limit, $L_0$, of the Lorenz number is supposed. However, we have shown [25] that even the Lorenz
Figure 7: Poly-quasicrystalline icosahedral Al-Cu-Fe phases (i-Al\textsubscript{62}Cu\textsubscript{25.5}Fe\textsubscript{12.5} solid, i-Al\textsubscript{63}Cu\textsubscript{24.5}Fe\textsubscript{12} dashes), transport parameters derived from Lorentzian models (Table 1), a) conductivity, b) thermopower, c) optical conductivity, d) Hall coefficient, e) electronic thermoconductivity, and f) Lorenz number. Experimental results (•) and (○) after [51], for i-Al\textsubscript{63}Cu\textsubscript{24.5}Fe\textsubscript{12}(▲) after [47], (♀) after [48].

number of i-AlCuFe (1/1) deviates markedly from $L_0$. The spectral model of the QC predicts enhanced temperature variation of the Lorenz number (Fig. 7f), and strongly increasing electronic thermal conductivity (Fig. 7e). We find $L(300K)/L_0 \approx 2$ and $K(300K) \approx 0.5$ W/m/K for both poly-quasicrystalline phases. The experimental result for the total thermal conductivity of the i-AlCuFe bulk-QC is $\sim 1.3$ W/m/K [53].

Lorenz number

Suppose, an analytical expression is available for $\tilde{\sigma}(\epsilon)$. In that case, one can employ a power-law expansion and integrate term by term. Lorentzian resistivity models such as Eq. 13 can be useful in this respect provided that three conditions are fulfilled up to the intended temperature limit: (i) The chemical potential (center of the thermal energy window) must be known. This requires detailed DOS information as can be inferred from Eq. 4. (ii) The model must account for the real system in the whole thermal energy window. (iii) The analytic evaluation must consider sufficiently high powers of the temperature. By such analytical means, on the level of the available spectral information, Maciá [59] and Landau [60] have dealt with deviations of the Lorenz number, Eq. 9, from the Wiedemann-Franz limit. It turned out that a partly $T^2$-confined analytical study [59] provides the Lorenz number almost temperature-independent close to the Wiedemann-Franz value. Note that the "true" results for given input data can be obtained by numerical integration (cf. Fig. 7f) which reveals Lorenz numbers close to $L_0$ only well below 50 K. However, if subsequent terms are consequently included [60] the validity of
the analytical expression can be extended to higher temperatures.

**Icosahedral Al-Pd-Re phases**

Huge resistivities up to $2 \times 10^7 \mu\Omega\text{cm}$ at 0.45 K [56] qualify icosahedral Al-Pd-Re QCs as candidates for a metal-insulator transition. However, the experimental results are not conclusive. On the one hand, variable-range hopping has been reported [57] with $\sigma(T \to 0) = 0$ whereas other data [58] support rather a finite residual conductivity. Unfortunately, no recognized (1/1) approximants are known as yet. Hence, *ab-initio* calculations employ the structure models of systems with related diffraction patterns (Krajič et al. [54]: i-AlPdMn (1/1); Tamura et al. [55]: almost the EHM). The present work comments on two issues: (i) Low DOS in pronounced pseudogaps can be balanced by large diffusivity. The spectral resistivity remains normal. (ii) Lorentzian resistivity models of the Al-Pd-Re QC break down at very low temperatures. We employ two models, a first model is derived from the EHM on replacing the 24 Mn atoms by Re atoms. The resulting icosahedral phase, $\text{Al}_{114}\text{Re}_{24}$, with 17.4 at% Re is far from the bulk-QCs (about 7 at% Re). A second model, $\text{Al}_{80}\text{Pd}_{15}\text{Re}_{18}$, with 14.6 at% Re is derived from the i-AlPdMn (1/1) approximant [40]. Figure 8 (left column) confirms the first above statement. High resistivity may be expected throughout the deep DOS pseudogap below $\varepsilon_F^P$ (Fig. 8c). However, the states are highly diffusive (Fig. 8b) due to large $sp$ contents (Fig. 8d).
that keeps the resistivity rather low. The right column in Fig. 8 belongs to the second above model but the curves resemble those of Fig. 1, left column. We take advantage of this fact and start the fitting for the i-Al-Pd-Re QCs with the Lorentzian model parameters of the i-AlCuFe QC. The narrow Lorentzian and the chemical potential (parameters $\gamma_2, \alpha, \epsilon_F, \xi$) are chosen as to reproduce the measured conductivities versus temperature [49]. The fitting results (Fig. 8e) are quite satisfactory except for 7.5 at.\% Re below 100 K. Such Re contents are close to the quasicrystalline Re abundance. The sequence of experimental points indicates an insulating state in the limit $T \to 0$ K. This requires a real gap in the spectral conductivity which is out of the range of Lorentzian resistivity models.

0.1.6 Summary and conclusions

This theoretical work deals with the origin of the anomalous electronic transport in a group of icosahedral high-resistivity phases. Members of this group are quasicrystals as bulk, polyquasicrystalline or thin-film phases, crystalline approximants, and annealed amorphous thin-film phases. Magnetic systems are excluded. We employ the well-established linear-response formulas where quantum-mechanical transport information enters in terms of spectral conductivities. Hence, results of ab-initio calculations and model conductivities are both suitable inputs. The considered phases include 10 . . . 20 at.\% of a transition-metal with an atomic resonance close to the Fermi energy. The stoichiometries prove quite sensitive which indicates that networks are formed with typical length scales of $\sim 10$ Å. The icosahedral atom clusters configure the networks provided they have the right positions and orientations. Even unit cells of small approximants bear seeds of active transition-metal networks. Medium-range coherence effects in such undistorted networks give rise to spectral features on energy scales $\sim 100$ meV. The present work demonstrates that the observed transport anomalies can be derived from this kind of spectral fine structure.

We report ab-initio results for spectral electronic transport parameters ((1/1) approximants to i-AlCuFe, i-AlMn(Si), i-AlCuRu, i-AlPdRe) and show that certain spectral features close to the Fermi energy depend critically on the configurations of the transition metal networks. This kind of spectral structure is supposed to survive in the quasicrystals, however with reduced widths, due to the more extended networks. We present spectral resistivity models of the approximants that extract physically significant spectral features in terms of Lorentzians. In the subsequent upscalings to models for the corresponding quasicrystals we rely mainly on experimentally determined thermopowers of the quasicrystals. Our results support the concept that extended quasiperiodicity alone does not produce the observed transport anomalies of quasicrystals.

Acknowledgements We thank Prof. P. Häussler and his group as well as Dr. E. S. Zijlstra for many exciting discussions, and to the Deutsche Forschungsgemeinschaft we owe thanks for financial support (projects SO 288/2-1 and SO 288/2-2).
Bibliography

Bibliography


[60] C. V. Landauro, to be published.