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Electronic transport in AlMn(Si) and AlCuFe quasicrystals: Break-down of the semiclassical model

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The semi-classical Bloch-Boltzmann theory is at the heart of our understanding of conduction in solids, ranging from metals to semiconductors. Physical systems that are beyond the range of applicability of this theory are thus of fundamental interest. It appears that in quasicrystals and related complex metallic alloys, a new type of break-down of this theory operates. This phenomenon is related to the specific propagation of electrons. We develop a theory of quantum transport that applies to a normal ballistic law but also to these specific diffusion laws. As we show phenomenological models based on this theory describe correctly the anomalous conductivity in quasicrystals. Ab-initio calculations performed on approximants confirm also the validity of this anomalous quantum diffusion scheme. This provides us with an ab-initio model of transport in approximants such as α-AlMnSi and AlCuFe 1/1 cubic approximant.

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1 Introduction

Since the early 1990's experimental investigations have indicated that the conduction properties of several stable quasicrystals (AlCuFe, AlPdMn) are at the opposite of those of good crystals [1–3]. Within a decade a series of new quasiperiodic phases and approximants were discovered and intensively studied. These investigations taught us that indeed electrons' and phonons' properties could be deeply affected by this new type of order. There is now strong evidence that these non standard properties result from a new type of break-down of the semi-classical Bloch-Boltzmann theory of conduction.

Since the discovery of Shechtman et al. [4] our view of the role of quasiperiodic order has evolved. For electronic or phonon properties of most known alloys it appears that the medium range order, on one or a few nanometers, is the real length scale that determines properties. This observation has lead the scientific community to adopt a larger point of view and consider quasicrystals as an example of a larger class. This new class of Complex Metallic Alloys contains quasicrystals, approximants and alloys with large and complex unit cells with possibly hundreds of atoms in the unit cell.

In this paper we shall concentrate on "the way electrons propagate" in actual quasicrystal or in a complex metallic alloys. The main objective is to show that the non standard conduction properties of some quasicrystals and related complex metallic alloys result from purely quantum effects and cannot be interpreted through the semi-classical theory of transport.

In the Bloch-Boltzmann model the charge carriers are viewed as classical particles with velocity V and charge e. Their propagation is ballistic between two scattering events, separated by a characteristic time τ, and they are scattered by static defects and/or phonons. This semi-classical description is valid if the size $L_{\rm WP}$ of the wave-packet is smaller than the distance of traveling between two scattering events $V\tau$, i.e. $V\tau > L_{\rm WP}$. But in a small velocity regime (SVR) such that $V\tau < L_{\rm WP}$, the semi-classical Block-Bolzmann model breaks down [5]. The SVR differs from another well known regime were the Bloch-Boltzmann model fails i.e. the regime with quantum interferences (weak or strong localization in disordered systems).

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We develop a theory of quantum transport that applies to a normal ballistic law but also to these specific diffusion laws [5,6]. This new formalism is combined with ab-initio band structure calculations for several approximant phases (α-AlMnSi, 1/1 AlCuFeSi) that share similar conduction properties with AlCuFe and AlPdMn icosahedral quasicrystals. As a result, we show that SVR explains the unconventional transport properties in quasicrystals and related phases.

2 Experimental evidence of quantum diffusion in quasicrystals and related phases

2.1 *Low density of states*

Experimentally a low density of states (DOS) at the Fermi energy E_{F} is usually measured in quasicrystals and their crystalline approximants. For instance, a density of states at E_{F} reduced by the order of 1/3 from its free electrons value is measured in i-AlCuLi and R-AlLiCu approximant [1]. The presence of the pseudogap in these phases is confirmed by NMR experiments [7] and X-ray measurements [8].

For icosahedral phases containing transition metal (TM) elements, specific heat measurement indicate a DOS at E_{F} the order of 1/3 of the free electron value for i-AlCuFe and 1/10 for i-AlCuRu and i-AlPdRe [1, 2]. From X-ray spectroscopy the pseudogap in the DOS is confirmed for many icosahedral quasicrystals in the systems: AlMn (metastable), AlMnSi, AlCuFe, AlCuFeCr, AlPdMn, AlCuRu, AlPdRe (see Ref. [9] and Refs. therein). The pseudogap has been also measured in many approximants of quasicrystals. For instance R-AlCuFe [2,7], 1/1 AlCuFeSi [10] α-AlMnSi [2], 1/1 AlCuRuSi [11,12], 1/1 AlReSi [13] have a DOS at E_{F} reduced by a similar factor as in i-AlCuTM and i-AlPdMn.

2.2 *Conductivity: close to metal-insulator transition*

The first quasiperiodic alloys AlMn were metastable and they contained many structural defects. As a consequence they had conduction properties similar to those of amorphous metals with resistivities in the range 100–500 $\mu\Omega$cm [2]. In 1986 the first stable icosahedral phase was discovered in AlLiCu. This phase was still defective. Although its resistivity was higher (800 $\mu\Omega$cm) it was still comparable to that of amorphous metals. The real breakthrough came with the discovery of the stable AlCuFe icosahedral phase, having a high structural order. The resistivity of these well ordered systems were very high, of the order of 10 000 $\mu\Omega$cm, which gave a considerable interest in their conduction properties. Within a few years several important electronic characteristics of these phases were experimentally demonstrated. The conductivity presented a set of characteristics that were either that of semi-conductors or that of normal metals.

The density of states in AlCuFe is smaller than in Al, about one third of that of pure Al, but still largely metallic. Quasicrystals of high structural quality reveal unusual transport properties [1–3,14]. For instance, one of the main features is the low conductivity $\sigma_{4K} = 100 - 200\ \Omega\mathrm{cm}^{-1}$ for icosahedral AlPdMn and AlCuFe. In particular weak-localization effects were observed that are typical of amorphous metals. Yet the conductivity was increasing with the number of defects just as in semi-conductors.

Another remarkable experimental result is the linear energy dependence of the optical conductivity of AlCuFe and the absence of Drude peak [15,16].

In 1993 another breakthrough was the discovery of AlPdRe which had resistivities in the range of $10^6\ \mu\Omega$cm [17–23], although the DOS still has a metallic character. This material displays a strong decrease of the conductivity when the temperature is reduced and the conductivity value can fall below $1\,(\Omega\mathrm{cm})^{-1}$ at 4 K. Although the behavior depends strongly on the composition and the preparation of the sample, many authors [17–23] reported that AlPdRe quasicrystal are very close to the metal-insulator transition. Three successive regimes are revealed [22] as the temperature is increased to room temperature: a low temperature variable range hopping-like behavior, followed by a Thouless regime and a high temperature critical regime.

It was also experimentally shown that transition metal (TM) elements play an important role on the unusual transport properties of quasicrystals and related phases [24–28].

Experimental measurements show that approximant phases like α-AlMnSi [2], 1/1 AlCuFeSi [10], R-

AlCuFe [2], 1/1 AlReSi [13, 29] etc., have transport properties similar to those of quasicrystals AlPdMn and AlCuFe. This suggests that the local atomic order on the length scale of the unit cell, *i.e.* $10 - 30$ Å, determines their transport properties. As atomic medium-range order of quasicrystals and approximants are similar, it should also be important in the understanding of transport properties of quasicrystals. This remark is confirmed by the fact that AlTM crystals with a small unit cell (typically less than 50 atoms in a unit cell) do not exhibit such unusual transport properties. In the following, crystals with small unit cell that do not exhibit transport properties similar to quasicrystals are called "simple crystals".

Finally it should be noted that in quasicrystals and approximants, the electron/phonons coupling is small and polarons [30] are not expected.

2.3 *Inverse Mathiessen rule*

The resistivity, $\rho = 1/\sigma$, for crystals with a small unit cell, increases temperature T. Generally it follows the Mathiessen rule:

$$\rho(T) = \rho_0 + \Delta\rho(T). \tag{1}$$

On the opposit, the resistivity of some quasicrystals and approximants (AlPdMn, AlCuFe) decreases when temperature increases , and their conductivity follows approximatively the so-called *"inverse Mathiessen rule"* [2, 31]:

$$\sigma(T) = \sigma_0 + \Delta\sigma(T). \tag{2}$$

Besides, after annealing sample, with a strong reduction of the structural defects, the resistivity of quasicrystals and approximants increases. The relation between the particular transport properties of these phases and their structure is still debated. For AlPdMn quasicrystals, J.J. Préjean and F. Hippert [32, 33] found that local defects might be related with the occurrence of Mn atoms with localized magnetic moment (see also F. Hippert and J.J .Préjean in this issue). Thus, magnetic properties, transport properties and structural quality are intimately linked for those complex phases.

3 Main characteristics of electronic structure

3.1 *Calculated density of states*

Electronic structure determinations have been performed in the frame-work of density functional theory (DFT) within the local density approximation (LDA) by using the self-consistent Tight-Binding (TB) Linear Muffin Tin Orbital (LMTO) method in the Atomic Sphere Approximation (ASA) [34].

The LMTO DOS of an α-AlMn idealized approximant has been first calculated by T. Fujiwara [37, 38]. This original work shows the presence of a Hume-Rothery pseudogap near the Fermi energy E_{F} in agreement with experimental results [1, 2]. Other approximants such as 1/1-AlCuFe(Si) exhibit also a pseudogap near E_{F} (see Refs. [11, 42] and Refs. in there)

The role of the transition metal (TM, TM = Ti, V, Cr, Mn, Fe, Co, Ni) element in the pseudogap formation has been shown from ab-initio calculations [41,42]. Indeed the formation of the pseudogap results from a strong sp–d coupling associated to an ordered sub-lattice of TM atoms. Just as for Hume-Rothery phases, a description of the band energy can be made in terms of pair interactions. It was shown that a medium-range TM–TM interaction mediated by sp(Al)–d(TM) hybridization plays a determinant role in the occurrence of the pseudogap [35–47]. It is thus essential to take into account the chemical nature of elements to analyze the electronic properties of approximants. The electronic structures of simpler crystals such as Al_6Mn, $\omega - Al_7Cu_2Fe$, $Al_{13}Fe_4$, $Al_{12}Mn$, present [42] also a pseudogap near E_{F} which is less pronounced than in complex approximant phases.

3.2 *Electron localisation by atomic clusters*

As for the local atomic order, one of the characteristics of the quasicrystals and approximants, is the occurrence of atomic clusters on a scale of 10–30 Å [48]. Nevertheless the clusters are not well defined because some of them overlap, and in addition there are a lot of so-called glue atoms. The role of clusters has been much debated in particular by C. Janot [49] and in Ref. [50]. It is realistic to consider a model of clusters that are not isolated but are embedded in metallic medium.

As shown in Refs. [50, 51], the variation $\Delta n_{\text{cluster}}(E)$ of the DOS due to a TM cluster exhibits strong deviations from the Virtual Bound States (1 TM atom in metallic medium). Indeed several peaks and shoulders appear. The width δE of the most narrow peaks ($\delta E \simeq 10 - 100\,\text{meV}$) are comparable to the fine peaks of the calculated DOS in the approximants. Each peak indicates a resonance due to the scattering by the cluster. These peaks correspond to states "localized" by the cluster. They are not eigenstate, they have finite lifetime of the order of $\hbar/\delta E$, where δE is the width of the peak. Therefore, the stronger the effect of the localization by cluster is, the narrower is the peak. A large lifetime is the proof of a localization, but in real space these states have a quite large extension on length scale of the cluster (~ 50 atoms).

This effect is a multiple scattering effect, and it is not due to an overlap between d-orbitals because TM atoms are not first neighbors (TM – TM first neighbors distance is $\sim 4.8\,\text{Å}$). We have also shown that these resonances are very sensitive to the geometry of the TM cluster. For instance, they disappear quickly when the radius of the TM icosahedron increases, and they are strongly reduce by vacancy. Therefore transport properties should be very sensitive to the atomic positions of TM atoms and to the chemical composition.

4 Calculated transport properties

4.1 *Atomic structure model for approximants*

To illustrate the quantum diffusion in approximants of quasicrystals we consider two phases: the α-AlMnSi approximant and a model for AlCuFeSi 1/1 cubic approximant.

For the α-AlMnSi phase, we use the experimental atomic structure [52] with the Si positions proposed by E. S. Zijlstra and S. K. Bose [53] for the composition α-$Al_{69.6}Si_{13.0}Mn_{17.4}$. This phase contains 138 atoms in a cubic unit cell: 96 Al atoms, 18 Si atoms, and 24 Mn atoms.

V. Simonet *et al.* [55] refined experimentally the atomic structure and the chemical decoration of Al–Cu–Fe–Si 1/1 cubic approximants. The authors give a revised description of the structure of α'-$Al_{71.7}Si_7Cu_{3.8}Fe_{17.5}$ phases and α-$Al_{55}Si_7Cu_{22.5}Fe_{12.5}$ phase. α'-phase has a chemical decoration similar to that of α-Al–Mn–Si, whereas the structure and the composition of the α-phase is different. It is characterized by several Wyckoff sites with mixed occupancy between Al/Cu, Al/Fe and Cu/Fe. As an example, we used this structure to calculate the LMTO DOS for phase with the composition $Al_{78}Cu_{48}Fe_{13}$ in a cubic unit cell.

In Fig. 1, the total DOS $n(E)$ of these phases are presented. A pseudogap near E_{F} is clearly seen. Following the Hume-Rothery condition, it is expected that the most realistic value of E_{F} corresponds to the minimum of the pseudogap. As shown previously for AlCuFe model approximant [56], the positions of Fe atoms have strong effects on the DOS near the E_{F}, and thus on the pseudogap and the stability. A detailed analysis [54] of a modified Cockayne model after a structural relaxation confirms the effect of the TM positions on the stability. Results presented here for 1/1 AlCuFe give thus a good qualitative example of the quantum diffusion in approximants, but a more detailed studies of the composition effect are still necessary to obtain quantitative results in AlCuFe(Si) approximants.

4.2 *Ab-initio calculations of the quantum diffusion*

We now present calculations of quantum diffusion in perfect crystalline systems. In literature, several calculations have already been done from ab-initio studies (see for instance Refs. [58, 60–62]). They give indication of non-ballistic diffusion [58–62, 71]. In our approach of quantum diffusion, the main quantities

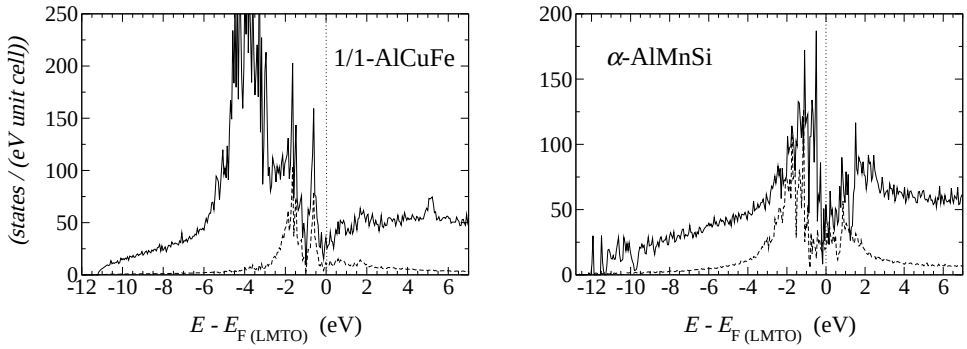

Figure 1. Ab-initio LMTO DOS in α-$Al_{69.6}Si_{13.0}Mn_{17.4}$ and $Al_{78}Cu_{48}Fe_{13}$ 1/1-cubic approximant: (line) total DOS and (dashed line) local TM DOS (TM = Mn or Fe).

are the *velocity correlation function*:

$$C(E,t) = \Big\langle V_x(t)V_x(0) + V_x(0)V_x(t)\Big\rangle_E = 2\,\mathrm{Re}\Big\langle V_x(t)V_x(0)\Big\rangle_E, \tag{3}$$

where V_x is the velocity operator, and the *square spreading* $\Delta X^2(E,t)$ of electronic states with energy E at time t [63]. These two quantities are simply related by the relation:

$$\frac{\mathrm{d}}{\mathrm{d}t}\Delta X^2(E,t) = \int_0^t C(E,t')\mathrm{d}t'. \tag{4}$$

In crystals, these quantities can be decomposed in a ballistic contribution (Boltzmann term) and a non-ballistic contributions (non-Bolzmann term):

$$C(E,t) = 2\ V_{\mathrm{B}}(E)^2 + C_{\mathrm{NB}}(E,t) \quad \text{and} \quad \Delta X^2(E,t) = V_{\mathrm{B}}(E)^2t^2 + \Delta X^2_{\mathrm{NB}}(E,t), \tag{5}$$

where V_{B} is the Boltzmann velocity at energy E. The ballistic terms:

$$C_{\mathrm{B}} = 2V_{\mathrm{B}}(E)^2 \ \text{ and } \ \Delta X_{\mathrm{B}} = V_{\mathrm{B}}(E)^2t^2 \ \text{ with } \ V_{\mathrm{B}}(E)^2 = \langle|\langle n\vec{k}|V_x|n\vec{k}\rangle|^2\rangle_{E_n=E}, \tag{6}$$

are due to intraband contributions; and the non-ballistic terms $C_{\mathrm{NB}}(E,t)$, $\Delta X^2_{\mathrm{NB}}(E,t)$ are due to the interband contributions:

$$\Delta X^2_{\mathrm{NB}}(E_{\mathrm{F}},t) = 2\hbar^2\left\langle \sum_{m\,(m\neq n)} \frac{1-\cos\Big((E_n-E_m)\frac{t}{\hbar}\Big)}{(E_n-E_m)^2}\Big|\langle n\vec{k}|V_x|m\vec{k}\rangle\Big|^2\right\rangle_{E_n=E_{\mathrm{F}}}. \tag{7}$$

In equations (6) and (7), $|n\vec{k}\rangle$ is an eigenstate with energy E_n. $\Delta X^2_{\mathrm{NB}}(E)$ is the average spreading of the state within a unit cell. Thus a relation exists between $\Delta X^2_{\mathrm{NB}}(E)$ and the length L_c of the unit cell in the chosen direction namely [6]

$$\Delta X^2_{\mathrm{NB}}(E,t) \leq \left(\frac{L_c}{2}\right)^2. \tag{8}$$

From self-consistent LMTO eigenstates, we compute the velocity correlation function $C(E,t)$ and $\Delta X(E,t)$ for crystals (approximant and simple crystals). In equations (3) (7), the average $\langle\ \rangle_E$ on states with the same energy E is obtained by taking the eigenstates for each $\vec{k}$ vector with an energy $E_n(\vec{k})$ such as $E-\Delta E/2 < E_n(\vec{k}) < E+\Delta E/2$. ΔE is the energy resolution of the calculation. The calculated

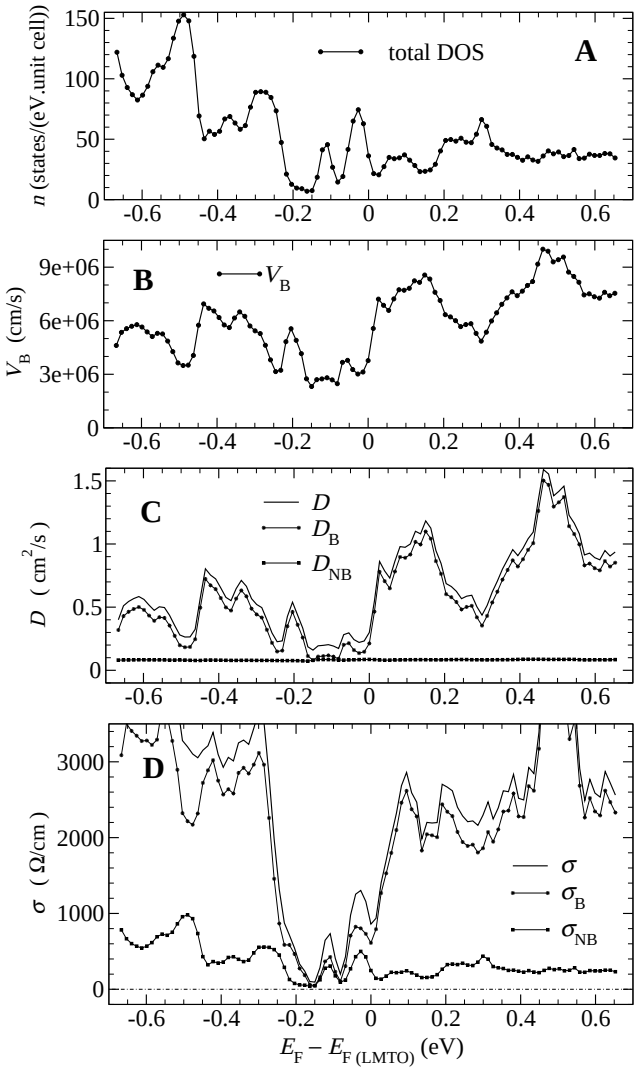

Figure 2. (**A**) LMTO total DOS n, (**B**) Bolztmann velocity V_B, (**C**) diffusivity $D = D_B + D_{NB}$, and (**D**) conductivity $\sigma = \sigma_B + \sigma_{NB}$, in the cubic approximant α-$Al_{69.6}Si_{13.0}Mn_{17.4}$. Points are the calculated values and lines are guides for the eyes. D and σ are calculated for $\tau = 1.5 \times 10^{-14}$ s.

$C(E,t)$ is sensitive to the number N_k of $\vec{k}$ vectors in the first Brillouin zone when N_k is too small. Therefore N_k is increased until $C(E,t)$ does not depend significantly on N_k. For 1/1-AlCuFe and α-AlMnSi, $\Delta E = 0.0272$ eV and $N_k = 32^3$.

4.3 *Results*

The Boltzmann velocity (intra-band velocity) V_B in α-AlSiMn versus the Fermi energy E_F, is shown on figure 2.B. Similar results are obtains in 1/1 AlCuFe. These values for approximants are also similar to the original work of T. Fujiwara et al. [38,56,57]. V_B in approximants varies very rapidly with a small variation of E_F, which shows the crucial effect of the chemical composition on transport properties. The minimum value of V_B is about 2.7×10^6 cm.s^{-1}, it corresponds to minimum in the DOS $n(E)$ (figure 2.A). In simple crystals Al (f.c.c.) and cubic $Al_{12}Mn$: $V = 9 \times 10^7$ and 4×10^7 $cm.s^{-1}$, respectively [64]. The reduction of V_F in the approximant phases with respect to simple crystal phases shows the importance of a quasiperiodic medium-range order (up to distances equal to 12–20 Å). This leads to a very small Boltzmann conductivity in approximants.

The velocity correlation function $C(E_F,t) = C_B + C_{NB}$ for the α-AlSiMn is shown in figure 3. In the case of Al and other simple crystal, $C(E_F,t)$ is almost always positive, and the Boltzmann value is reached rapidly

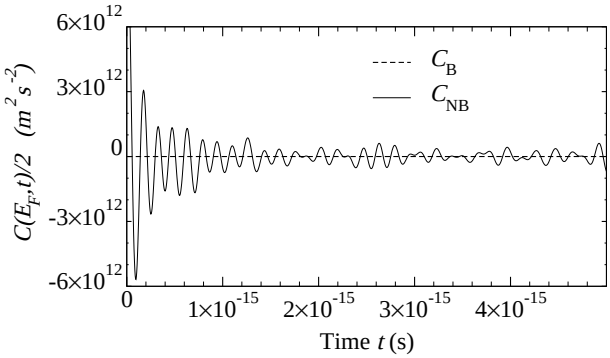

Figure 3. Velocity correlation function $C(E_{\rm F},t)$ in α-$Al_{69.6}Si_{13.0}Mn_{17.4}$ versus large time t. Dashed lines are the corresponding Boltzmann velocity correlation function $C_{\rm B}(E_{\rm F},t) = 2v_{\rm F}^2$.

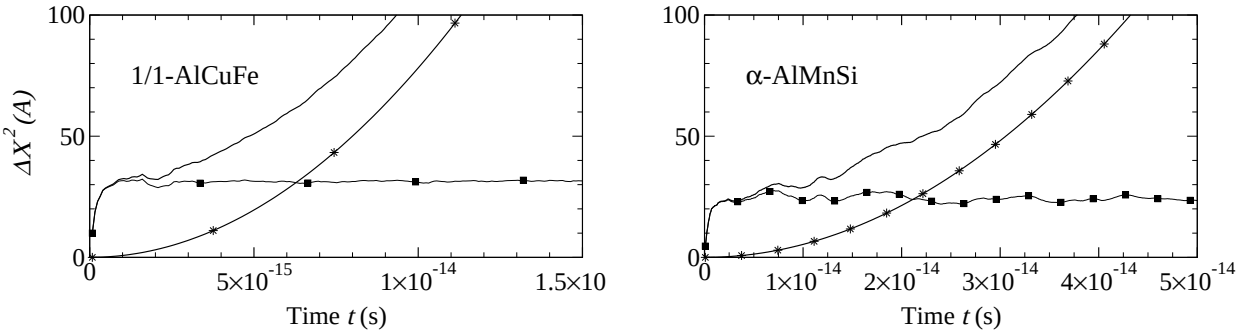

Figure 4. Square spreading ΔX^2 of electrons states with Fermi energy $E_{\rm F}$ versus time t, in 1/1 AlCuFe phases and α-$Al_{69.6}Si_{13.0}Mn_{17.4}$: (simple line) total ΔX^2, (line with stars) Bolzmann term $\Delta X_{\rm B}^2$ and (line with square) non-Bolzmann term $\Delta X_{\rm NB}^2$.

when t increases [64]. But for many t values the velocity correlation functions $C(E_{\rm F},t)$ of approximants are negative. This means that at these times the phenomenon of *backscattering* occurs [6,64,65]. The transport properties depend on the average value of $C(E_{\rm F},t)$ on a time scale equals to the scattering time τ [63,70]. Therefore, in simple crystals, the backscattering (negative value of $C(E_{\rm F},t)$) should have a negligible effect on the transport properties, whereas this effect must be determinant for approximants.

The phenomenon of backscattering is associated to unusual quantum diffusion. It is illustrated on the plot of the average spreading of states ΔX^2 versus time t (figure 4). The non-Boltzmann contribution, $\Delta X_{\rm NB}^2$, increases very rapidly and saturates to a maximum value of the order of the square size of the unit cell. In approximants, at small time t, $\Delta X_{\rm B}^2$ is smaller than in simple phases due to a very small velocity $V_{\rm B}$.

Thus approximants are a non-conventional metal at these time scale i.e. when the scattering time is $\tau < \tau^*$ where τ^*, the limit of two regimes (see next section), is around 1.5×10^{-14} s and 6×10^{-15} s, in α-AlMnSi and 1/1 AlCuFe, respectively. At realistic scattering times scale for approximants, typically $\sim 10^{-14}$ [31], both terms $\Delta X_{\rm B}^2$ and $\Delta X_{\rm NB}^2$ have the same magnitude ($\tau \lesssim \tau^*$); whereas in normal crystals, the $\Delta X_{\rm NB}^2(t)$ term is negligible with respect to the Boltzmann term $\Delta X_{\rm B}^2(t)$ because $\tau \gg \tau^*$.

5 Static conductivity of approximants in relaxation time approximation

For finite temperature, the effect of the Fermi-Dirac distribution on transport properties was studied in the literature [66–69]. But, theses analyzes could not explain the unconventional conduction of quasicrystals and related alloys (very high resistivity at low temperature, and conductivity that increases strongly when defects or temperature increases). In the following, the Fermi-Dirac distribution function is taken equal to its zero temperature value. This is valid provided that the electronic properties vary smoothly on the thermal energy scale $k_{\rm B}T$. However, the effect of defects and temperature on the conductivity is taken

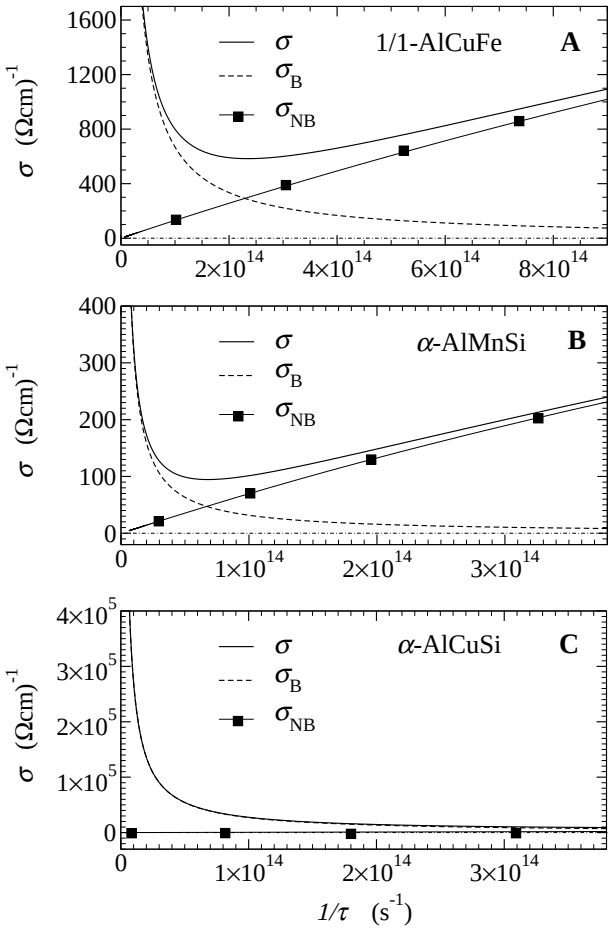

Figure 5. Ab-initio dc-conductivity σ ($\sigma = \sigma_{\rm B} + \sigma_{\rm NB}$) versus inverse scattering time $1/\tau$, in (**A**) 1/1 approximant AlCuFe, (**B**) approximant α-$Al_{69.6}Si_{13.0}Mn_{17.4}$, and (**C**) hypothetical approximant α-$Al_{69.6}Si_{13.0}Cu_{17.4}$.

into account via the Relaxation Time Approximation (RTA). A scattering time τ is defined as the average time between two collisions of an electron with static impurities and/or phonons. τ includes both elastic and inelastic scatterings, it decreases when temperature or static defects increase.

Within the RTA, the velocity correction function $C'(E,t)$ with disorder are related to $C(E,t)$ without disorder through [63]:

$$C'(E,t) = C(E,t)\mathrm{e}^{-|t|/\tau}, \tag{9}$$

and the dc-diffusivity at energy E is given by

$$D(E) = \frac{1}{2}\int_0^{+\infty} \mathrm{e}^{-t/\tau} C(E,t)\mathrm{d}t = D_{\rm B}(E) + D_{\rm NB}(E), \tag{10}$$

where Boltzmann diffusivity is $D_{\rm B}(E) = V_B^2(E)\tau$, and the non-Boltzmann term is

$$D_{\rm NB}(E) = \frac{1}{2}\frac{1}{\tau^2}\int_0^{+\infty} \mathrm{e}^{-t/\tau}\Delta X_{\rm NB}^2(E,t)\mathrm{d}t. \tag{11}$$

As figure 2.C shows, $D_{\rm NB}$ is almost independent on E, whereas the $D_{\rm B}$ values depend strongly on E, as $V_{\rm B}$ value depends on E. The dc-conductivity is

$$\sigma(E_{\rm F}) = \mathrm{e}^2 n(E_{\rm F})D(E_{\rm F}) = \sigma_{\rm B}(E_{\rm F}) + \sigma_{\rm NB}(E_{\rm F}) \tag{12}$$

where e is the charge of electron. The Boltzmann term is given by the Einstein relation, $\sigma_{\rm B}(E_{\rm F}) = {\rm e}^2 n(E_{\rm F}) V_{\rm B}^2 \tau$. It is proportional to scattering time τ and it is small in approximants. The non-Boltzmann term $\sigma_{\rm NB}(E_{\rm F})$ is calculated from $\Delta X_{\rm NB}$ via equation (11). As $X_{\rm NB}$ is almost constant for significant t values (figure 4), one obtains that $\sigma_{\rm NB}(E_{\rm F})$ is almost proportional to $1/\tau$. Therefore :

$$\sigma \;=\; e^2 n V_{\rm B}\tau \;+\; e^2 n \frac{L^2(\tau)}{\tau} \quad \text{with} \quad L(\tau) \simeq L, \tag{13}$$

where L is bound by the size L_c of the unit cell along which σ is calculated (equation(8)). Roughly speaking, L is the spreading of electron states in each cell. In simple crystals, L is small, but in approximants it is larger. As an electronic localisation by cluster exist in approximants (Sec. 3.2), L should be close to the size of cluster. A large value of L is thus a consequence of a quasiperiodic local order. The minimum value of $\sigma(\tau)$ is obtains for $\tau = \tau^* = L/(V_B\sqrt{2})$.

The predicted static conductivity (dc-conductivity) of the α-AlMnSi and 1/1 AlCuFe approximants assuming the value of the Fermi energy at the minimum of the pseudogap, are shown figure 5 versus the inverse scattering time. Two regimes appear clearly:

- A metallic regime (Boltzmann regime), for $\tau > \tau^*$, where σ is almost proportional to τ, and then σ decreases with disorder (static disorder or temperature) as for simple crystals (Mathiessen rule).
- An "insulating like" regime (non Boltzmann regime), for $\tau < \tau^*$, where σ is almost proportional to $1/\tau$, and then σ increases with disorder as observed experimentally for approximants and quasicrystals (inverse Mathiessen rule). It should be noted that in this cases the system is always metallic (no gap in the DOS), but its conductivity is "insulating like".

For α-AlSiMn, realistic τ values [31] correspond to the "insulating like" regime. Therefore, σ increases when defects or temperature increases. σ varies from 100 $(\Omega\,{\rm cm})^{-1}$ for $\tau = 1.5\times10^{-14}$ s, to $\sim$ 2000 $(\Omega\,{\rm cm})^{-1}$ for $\tau = 10^{-15}$ s. This is consistent with experimental results in α-AlMnSi: $\sigma(4\ K) \simeq 200\ (\Omega\,{\rm cm})^{-1}$ and $\sigma(900\ K) \simeq 2000\ (\Omega\,{\rm cm})^{-1}$ and with standard estimates for the scattering time in these systems [2].

Within the relaxation time approximation used here, the optical conductivity $\sigma(\omega)$ can also be calculated as the sum of two terms [5, 6]. The Boltzmann contribution gives rise to the so-called Drude peak and the non Boltzmann conductivity gives rise to a nearly frequency independent contribution. The absence of Drude peak in quasicrystals and approximant is thus explained by the insulating like regime for realistic τ values.

To evaluate the effect of TM elements on the conductivity, we have considered an hypothetical α-$Al_{69.6}Si_{13.0}Cu_{17.4}$ constructed by putting Cu atoms in place of Mn atoms in the actual α-$Al_{69.6}Si_{13.0}Mn_{17.4}$ structure. Cu atoms have almost the same number of sp electrons as Mn atoms, but their d DOS is very small at $E_{\rm F}$. Therefore in α-$Al_{69.6}Si_{13.0}Cu_{17.4}$, the effect of sp(Al)-d(TM) hybridization on electronic states with energy near $E_{\rm F}$ is very small. As a result, the pseudogap disappears in total DOS [41, 42], and the dc-conductivity is now metallic as shown on figure 5.C.

Equation (13) allows also to understand transport in quasicrystals (non periodic phases). Indeed in quasicrystals $V_{\rm B}$ should be very small, and L_c is equal to infinity. But a finite value of L is possible depending on the electron localisations by the quasiperiodic structure. Therefore in quasicrystals, the non Boltzmann term dominates and an "insulating like" regime is expected.

6 Conclusion

In this paper we calculated quantum diffusion and electronic conduction properties in two 1/1 approximants. We found deviations from the standard ballistic propagation in good agreement with experimental measurements. The anomalous diffusion mode is related to a tendency to localization and to a phenomenon of backscattering which is well known in disordered systems. The phenomenon of backscattering is the fact

that an impulse of electric field creates a current density which is opposite to the electric field at large time. Backscattering is associated with an increase of conductivity with frequency and disorder. The physics of phonons in quasicrystals could also be affected by the anomalous diffusion phenomenon. In particular it has been argued that the heat conductivity could be sensitive to this effect [72].

The concepts developed here open also a new insight in the physics of correlated systems. Indeed recent studies of some heavy fermions or polaronic systems [73–76], where charge carriers are also slow, show that their conduction properties present a deep analogy with those described here. In particular a transition from a metallic like regime at low temperature where scattering is weak to an insulating like regime at higher temperature with a stronger scattering is observed.

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