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Quasicrystals / Quasicristaux

Anomalous electronic transport in quasicrystals and related complex metallic alloys

Transport électronique anormal dans les quasicristaux et les alliages métalliques complexes reliés

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A B S T R A C T

We analyse the transport properties in approximants of quasicrystals α-AlMnSi, 1/1-AlCuFe and for the complex metallic phase λ-AlMn. These phases present strong analogies in their local atomic structures and are related to existing quasicrystalline phases. Experimentally, they present unusual transport properties with low conductivities and a mix of metallic-like and insulating-like characteristics. We compute the band structure and the quantum diffusion in the perfect structure without disorder and introduce simple approximations that allow us to treat the effect of disorder. Our results demonstrate that the standard Bloch–Boltzmann theory is not applicable to these intermetallic phases. Indeed their dispersion relations are flat, indicating small band velocities, and corrections to quantum diffusion, which are not taken into account in the semi-classical Bloch–Boltzmann scheme, become dominant. We call this regime the small velocity regime. A simple relaxation time approximation to treat the effect of disorder allows us to reproduce the main experimental facts on conductivity qualitatively and even quantitatively.

R É S U M É

Nous analysons les propriétés de transport électronique dans les approximants de quasicristaux α-AlMnSi, 1/1-AlCuFe et pour la phase complexe reliée λ-AlMn. Ces phases présentent de fortes analogies au niveau de leurs structures atomiques locales et sont reliées à des phases quasicrystallines existantes. Expérimentallement, elles présentent des propriétés de transport inhabituelles, avec une faible conductivité et un mélange de propriétés de type métallique et de type isolant. Nous calculons la structure de bande et la diffusion quantique de la structure parfaite et introduisons une approximation simple, qui permet de traiter l'effet du désordre. Nos résultats démontrent que la théorie standard de Bloch–Boltzmann n'est pas applicable à ces systèmes intermétalliques. En effet, leurs relations de dispersion sont plates, indiquant une faible vitesse de bande, tandis que les corrections à la diffusion quantique, qui ne sont pas prises en compte par la théorie semi-classique, deviennent dominantes. Nous appelons ce régime le régime de faible vitesse. Une simple approximation du temps de relaxation pour traiter l'effet du désordre permet

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de reproduire les principaux résultats expérimentaux sur la conductivité qualitativement et même quantitativement.

1. Introduction

Immediately after the discovery by Shechtman et al. [1] of quasiperiodic intermetallics, one major question was raised about the physical properties of phases with this new type of order. In particular, one expected that the electronic and thermal properties could be deeply affected [2–5]. Indeed, the description of electrons or phonons in periodic phases rests on the Bloch theorem, which cannot be applied to a quasiperiodic structure. Within a decade, a series of new quasiperiodic phases and approximants were discovered and intensively studied. These investigations learned us that indeed the electrons and the phonons properties could be deeply affected by this new type of order.

The first quasiperiodic alloys were metastable and contained many structural defects. As a consequence, they had conduction properties similar to those of amorphous metals, with resistivities in the range 100–500 μΩ cm. The real breakthrough came with the discovery of the stable AlCuFe icosahedral phase, having a high structural order. The resistivities of these very well-ordered systems were very high, of the order of 10 000μΩ cm [6,7], which provoked a considerable interest in their conduction properties. Within a few years, several important electronic characteristics of these phases were experimentally demonstrated. The density of states in AlCuFe was smaller than in Al, about one third of that of pure Al, but still largely metallic. The conductivity presented a set of characteristics that were either those of semi-conductors or those of normal metals. In particular, weak-localization effects were observed, which are typical of amorphous metals. Yet the conductivity was increasing with the number of defects just as in semi-conductors. Optical measurements showed that the Drude peak, characteristic of normal metals, was absent. In 1993, another breakthrough was the discovery of AlPdRe, which had resistivities in the range of 10^6 μΩ cm [8–10]. This system gave the possibility of studying a metal–insulator transition in a quasiperiodic phase. There are still many questions concerning electronic transport in AlPdRe phases.

Since the discovery, the view of the role of quasiperiodic order has evolved. On the one hand, the long-range quasiperiodic order can induce electronic states neither localized nor extended, called *"critical states"* (see Ref. [11] and references therein). On the other hand, 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 led the scientific community to adopt a larger point of view and to consider quasicrystals as an example of a larger class. This 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 article, we study "how electrons propagate" in aluminum-based quasicrystals, approximants, or complex metallic alloys with structure related to quasiperiodicity. 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. This is of great importance, since the semi-classical Bloch–Boltzmann theory is at the heart of our understanding of conduction in solids, ranging from metals to semi-conductors.

This new type of quantum transport is related to the specific propagation mode of electrons in these systems. Indeed in quasicrystals and related complex phases, the quantum diffusion law deviates from the standard ballistic law characteristic of perfect crystals in two possible ways. In a perfect quasicrystal, the large-time diffusion law is a power law instead of a ballistic one in perfect crystals. In a complex crystal, the diffusion law is always ballistic at large times, but it can deviate strongly from the ballistic law at sufficiently small times. It is this specific character that provides a basis for the interpretation of the strange conduction properties of AlCuFe, AlPdMn, and probably also for those of AlPdRe.

This paper is organized as follows. In Section 2, the formalism of the linear response for conductivity (Kubo formalism) is presented in terms of the quantum diffusion. The numerical method to calculate numerically quantum transport in actual phases is described briefly. Then we present in Section 3 the results for two approximant phases α-AlMnSi, 1/1-AlCuFe and for the complex metallic phase λ-AlMn. These results show that the Boltzmann approach is no more valid in these systems. This is because electron velocity is small (flat bands) and wave packets have large spatial extension. We call this regime of transport the small velocity regime. In Section 4 we propose a simple phase diagram, at zero temperature, for the Anderson metal–insulator transition in phases within the small velocity regime. As we show, the small velocity regime deeply influences the occurrence of the Anderson transition in the presence of static disorder. In standard systems the Anderson transition always occurs when the disorder increases, whereas here the behavior is more complex. In the conclusion (Section 5), we briefly summarize our main findings and discuss some open questions as well as the connection to other systems.

2. Formalism for quantum diffusion calculation

2.1. Quantum diffusion and conductivity

The present study relies upon the evaluation of the Kubo–Greenwood conductivity using the Einstein relation between the conductivity and the quantum diffusion [12–19]. Central quantities are the velocity correlation function of states of energy E at time t,

$$C(E,t) = \left\langle \hat{V}_x(t)\hat{V}_x(0) + \hat{V}_x(0)\hat{V}_x(t)\right\rangle_E = 2\,\mathrm{Re}\left\langle \hat{V}_x(t)\hat{V}_x(0)\right\rangle_E \tag{1}$$

and the average square spreading (quantum diffusion) of states of energy E at time t along the x direction,

$$X^2(E,t) = \left\langle \left(\hat{X}(t) - \hat{X}(0)\right)^2\right\rangle_E \tag{2}$$

In Eqs. (1) and (2), $\langle \ldots \rangle_E$ is the average on states with energy E, $\mathrm{Re}\,A$ is the real part of A, $\hat{V}_x(t)$ and $\hat{X}(t)$ are the Heisenberg representation of the velocity operator $\hat{V}_x$ and the position operator $\hat{X}$ along x direction at time t,

$$\hat{V}_x = \frac{1}{i\hbar}[\hat{X}, \hat{H}] \tag{3}$$

$C(E,t)$ is related to quantum diffusion by the relation [17],

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

From the Kubo–Greenwood formula, the conductivity is given by the Einstein relation,

$$\sigma(E_\mathrm{F}) = e^2 n(E_\mathrm{F}) D(E_\mathrm{F}) \tag{5}$$

where e is the electron charge, E_F the Fermi energy, n the density of states and D the diffusivity related to the square spreading by the relation [17,18],

$$D(E_\mathrm{F}) = \frac{1}{2}\lim_{t\to\infty}\frac{\mathrm{d}}{\mathrm{d}t}X^2(E_\mathrm{F},t) \tag{6}$$

2.2. Conductivity in perfect periodic systems

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

$$C(E,t) = 2V_\mathrm{B}(E)^2 + C_\mathrm{NB}(E,t) \tag{7}$$

and after Eq. (4):

$$X^2(E,t) = V_\mathrm{B}(E)^2 t^2 + X^2_\mathrm{NB}(E,t) \tag{8}$$

where $V_\mathrm{B}(E)$ is the Boltzmann velocity at energy E,

$$V_\mathrm{B}(E)^2 = \left\langle \left|\langle n\vec{k}|\hat{V}_x|n\vec{k}\rangle\right|^2\right\rangle_{E_n=E} \tag{9}$$

$V_\mathrm{B}(E)$ is also the average band velocity at the energy E in x direction, since the band velocity is given by:

$$\frac{1}{\hbar}\frac{\partial E_n(\vec{k})}{\partial k_x} = \langle n\vec{k}|\hat{V}_x|n\vec{k}\rangle \tag{10}$$

where E_n is the energy of the eigenstate $|n\vec{k}\rangle$ at wave vector $\vec{k}$. In (7) and (8), the ballistic terms $C_\mathrm{B} = 2V_\mathrm{B}(E)^2$ and $X_\mathrm{B} = V_\mathrm{B}(E)^2 t^2$ are due to intra-band contributions. And the non-ballistic terms $C_\mathrm{NB}(E,t)$, $X^2_\mathrm{NB}(E,t)$ are due to the inter-band contributions:

$$X^2_\mathrm{NB}(E_\mathrm{F},t) = 2\hbar^2\left\langle \sum_{m(m\neq n)} \frac{1-\cos((E_n-E_m)\frac{t}{\hbar})}{(E_n-E_m)^2}\left|\langle n\vec{k}|\hat{V}_x|m\vec{k}\rangle\right|^2\right\rangle_{E_n=E_\mathrm{F}} \tag{11}$$

$X^2_\mathrm{NB}(E,t)$ is the average spreading of the state for large time t it oscillates (see next section). From its maximum value the length $L_\mathrm{wp}(E)$ is defined:

$$X^2_{NB}(E,t) \leqslant L_{wp}(E) \tag{12}$$

$L_{wp}(E)$ represents the average expansion of wave packet eigenstates at energy E. Therefore a small $L_{wp}(E)$ value is expected for confined states by atomic clusters [20–22]. In the Boltzmann theory for electronic transport, the non-Boltzmann contributions are neglected. This is a reasonable assumption for rather simple metallic phases, but non-Boltzmann terms are essential to understand complex metallic alloys such as quasicrystals and related phases.

In practice, from self-consistent LMTO eigenstates or tight-binding eigenstates, we compute the velocity correlation function $C(E,t)$ and $X(E,t)$ for crystals. In Eqs. (1), (2), (9), and (11), the average is obtained by taking the eigenstates for each $\vec{k}$ vector with and energy $E_n(\vec{k})$ such as:

$$E - \frac{1}{2}\delta E < E_n(\vec{k}) < E + \frac{1}{2}\delta E \tag{13}$$

δE is the energy resolution of the calculation. N_k is the number of $\vec{k}$ vectors in the first Brillouin zone that we use for numerical calculations. When N_k is too small, the calculated quantities are sensitive to the number N_k of $\vec{k}$ vectors in the first Brillouin zone. Therefore N_k is increased until results do not depend significantly on N_k. We use $\delta E = 0.01$ eV; $N_k = 32^3$ for 1/1-AlCuFe and α-AlMnSi, and $N_k = 8 \times 8 \times 16$ for λ-AlMn.

2.3. Conductivity in system with defects

The effect of the elastic scattering (static defects) and/or the inelastic scattering (electron–phonon, electron–electron) can be treated in a phenomenological way in the scheme of the relaxation time approximation (RTA) [17,18]. We introduce a scattering time τ, beyond which the propagation becomes diffusive due to the destruction of coherence through scattering by defects. Following previous works [17,18,23,24], we assume that the velocity correlation function $C_s(E,t)$ of the system with scatterers (defects) is given by:

$$C_s(E,t) \simeq C(E,t)e^{-|t|/\tau} \tag{14}$$

where $C(E,t)$ is the velocity correlation of the system without defects. The propagation given by this formalism is unaffected by scattering at short times ($t < \tau$) and diffusive at long times ($t > \tau$) as it must be. Using the $t = 0$ conditions, $X^2(E,t=0) = 0$ and $\frac{d}{dt}X^2(E,t=0) = 0$, and performing two integrations by part, we obtain from Eqs. (4), (5), (6) and (14), [18]:

$$\sigma(E_F,\tau) = e^2 n(E_F) D(E_F,\tau) \tag{15}$$

$$D(E_F,\tau) = \frac{L^2(E_F,\tau)}{2\tau} \tag{16}$$

$$L^2(E_F,\tau) = \frac{1}{\tau}\int_0^{\infty} X^2(E_F,t)e^{-t/\tau}\,dt \tag{17}$$

where $L(E_F,\tau)$ the mean-free path and $D(E_F,\tau)$ the diffusivity. $X^2(E,t)$ is calculated for the system without defect (Section 2.2). The above equations treat the scattering in a way that is equivalent to the standard approximation in mesoscopic physics. Indeed, in the presence of scattering, it is usually assumed that $L(E_F) \simeq \sqrt{X^2(E_F,\tau)}$, thus the conductivity is given by the Einstein formula, with a diffusivity $D(E_F,\tau) \simeq X^2(E_F,\tau)/(2\tau)$ [25], which is essentially equivalent to the above equations.

In periodic systems, the dc-diffusivity at energy E is given by

$$D(E) = \frac{1}{2}\int_0^{+\infty} e^{-t/\tau} C(E,t)\,dt = D_B(E) + D_{NB}(E) \tag{18}$$

where Boltzmann diffusivity is $D_B(E) = V_B^2(E)\tau$, and the non-Boltzmann term is:

$$D_{NB}(E) = \frac{1}{2}\frac{1}{\tau^2}\int_0^{+\infty} e^{-t/\tau} X^2_{NB}(E,t)\,dt \tag{19}$$

3. Ab initio transport properties in approximants and complex metallic alloys

3.1. Atomic structures

To present the quantum diffusion in approximants of quasicrystals and complex metallic alloys related to quasiperiodicity, we consider three phases: the α-AlMnSi approximant, a model for AlCuFeSi 1/1 cubic approximant and the complex metallic

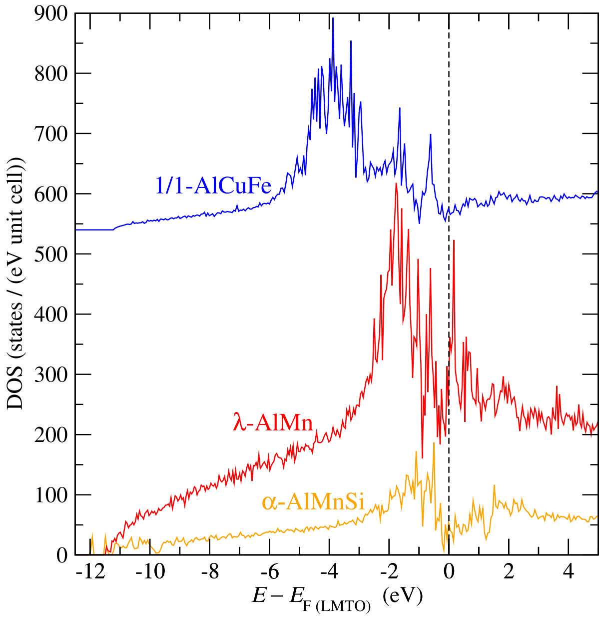

Fig. 1. (Colour online.) LMTO density of states (DOS), $n(E)$, in 1/1-$Al_{56.1}Cu_{34.5}Fe_{9.4}$, α-$Al_{69.6}Mn_{17.4}Si_{13.0}$ and λ-$Al_{4.6}Mn$.

phase λ-AlMn. Results for λ-AlMn are new and are compared to previous results for α-AlMnSi and 1/1 AlCuFeSi that have already been presented in Refs. [23,26].

For the α-AlMnSi phase, we use the experimental atomic structure [27] with the Si positions proposed by Ref. [28] 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. [29] 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 are 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 ab initio electronic structure for phase with the composition 1/1-$Al_{56.1}Cu_{34.5}Fe_{9.4}$, i.e. $Al_{78}Cu_{48}Fe_{13}$ in a cubic unit cell.

The complex λ-$Al_{4.6}$Mn phase [30] crystallizes in a large hexagonal structure $P6_3/mmc$ with a unit cell containing about 590 atoms. The structure of λ-$Al_{4.6}$Mn phase is closely related to that of hexagonal μ-$Al_{4.12}$Mn [31]. These phases are not quasicrystal approximants, but their local environment is related strongly to the local and medium-range order induced by quasiperiodicity [30,32]. We calculated the electronic structure of the λ phase from LMTO by using an atomic structure with minor modifications [33] from the experimental structure to avoid mixed occupied sites. The same modification has been done to study μ-$Al_{4.12}$Mn [33]. The structure used to calculate the electronic properties has the composition $Al_{483}Mn_{104}$ in a cubic unit cell.

3.2. Density of states

In the framework of the density functional approximation, the ab initio electronic structure of the studied phases is computed by using the LMTO method [34,35]. In Figs. 1 and 2a, the non-magnetic total density of states (DOS), $n(E)$, of the studied phases is presented. A pseudogap near E_F is clearly seen, its weight is about 200 meV or more. Following the Hume–Rothery condition, the stabilization is obtained when the Fermi sphere matches a pseudo-Brillouin zone (also called Jones zone) (see Refs. [36,37] and references therein). This condition is reached for Fermi level E_F in proximity of the minimum of the pseudogap. It is well know that this pseudogap is due to the diffraction by Bragg planes of the pseudo-Brillouin zone, but this mechanism is strongly increased by the sp–d hybridization between Al, Si sp states and transition metal d orbitals [38–50,37]. It must be noted that the diffraction by Bragg planes, leading to a pseudogap in the DOS, can be understood in terms of oscillating pair potential interactions in the real space due to Friedel oscillations of the charge density [51,52].

As shown first by T. Fujiwara [53,54], the DOS is also characterized by the presence of fine peaks, called *"spiky peaks"*. Their width is about 10–100 meV. In approximants, they are a consequence of flat bands, $E_n(\vec{k})$, in the reciprocal space and they show a new kind of confinement of electrons by the local and medium-range atomic order. Indeed numerical calculations have shown that atomic clusters, with typical size equal to 20 Å or more, can confine electrons by forming *"cluster virtual bound states"* [21,22,52]. The existence or not of spiky peaks in the DOS of actual approximants and quasicrystals

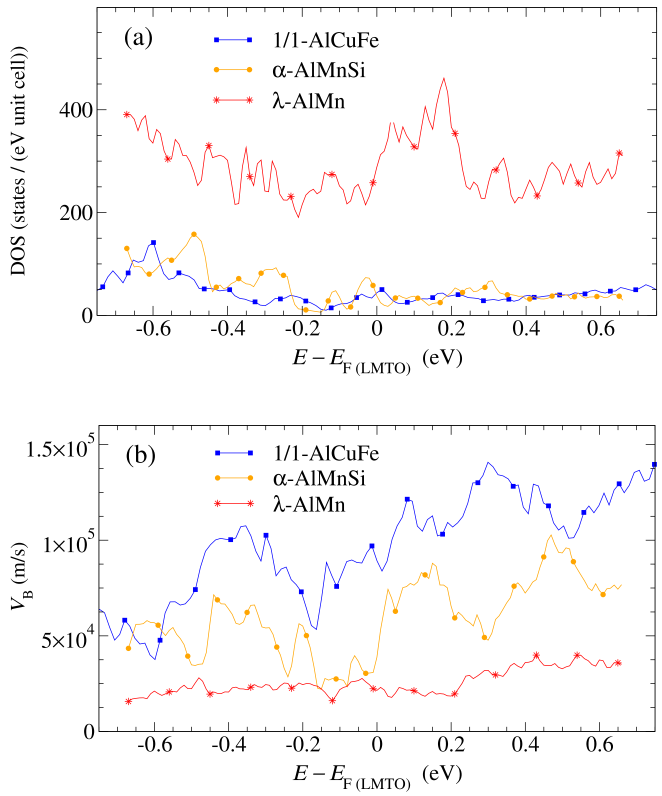

Fig. 2. (Colour online.) LMTO (a) DOS and (b) Boltzmann velocity in 1/1-$Al_{56.1}Cu_{34.5}Fe_{9.4}$, α-$Al_{69.6}Mn_{17.4}Si_{13.0}$ and λ-$Al_{4.6}Mn$, around $E_{F(LMTO)}$.

has been much debated experimentally and theoretically (see Ref. cited in [52]). More recently, low-temperature scanning tunneling spectroscopy [55–58] confirmed the presence of fine peaks in the DOS of surfaces of μ-AlMn phases, icosahedral AlPdMn, and decagonal AlNiCo.

The Boltzmann velocity (intra-band velocity) V_B calculated from Eq. (9) is shown in Fig. 2b. These results are similar to the original work of T. Fujiwara et al. [54,59,60] for approximants. V_B in small approximants 1/1-AlCuFe and α-AlMnSi varies very rapidly with a small variation of E, which shows the crucial effect of the chemical composition on transport properties. The minimum value of $V_B(E)$ is about 2×10^6 cm s^{-1}, whereas in simple crystals Al (f.c.c.) and cubic $Al_{12}Mn$: $V_B = 9 \times 10^7$ and 4×10^7 cm s^{-1}, respectively [61]. For λ-AlMn, the reduction for V_B with respect to usual intermetallic alloys is even stronger.

3.3. Mean square spreading

The mean square spreading is the sum of a quadratic term (Boltzmann term) and a non-Boltzmann term (8). Fig. 3 presents the typical behavior of the non-Boltzmann term X_{NB}, versus energy E and time t. As expected from Eq. (11), for large t values $X_{NB}(t)$ oscillates. For some energies, the amplitude of the oscillations is large, but for other energies this amplitude is small. These last energies correspond approximatively to a local minimum of the DOS. Therefore, they correspond to realistic values of the Fermi energy E_F. For these energies, at large t, $X_{NB}(t)$ is almost constant and one can define $L_{wp}(E)$ by,

$$L_{wp}(E) \simeq \sqrt{X^2_{NB}(E,t)} \quad \text{for large } t \tag{20}$$

$L_{wp}(E)$ is the spatial extension of the wave packet at energy E. From ab initio calculations, its values vary from ~ 50 Å to large values in λ-AlMn (Fig. 3). In α-AlMnSi [23] and 1/1-AlCuFe [26], the minimum value of $L_{wp}(E)$ is about 20 Å, which corresponds to the size of smallest atomic clusters in these phases (Mackay clusters or Bergman clusters) [62]. At these energies, one can then assume that:

$$X^2(E,t) \simeq V_B(E)^2 t^2 + L^2_{wp}(E) \tag{21}$$

From ab initio calculations, this behavior is obtained for energy E_F, corresponding the local minimum in the DOS as expected from stabilization mechanism.

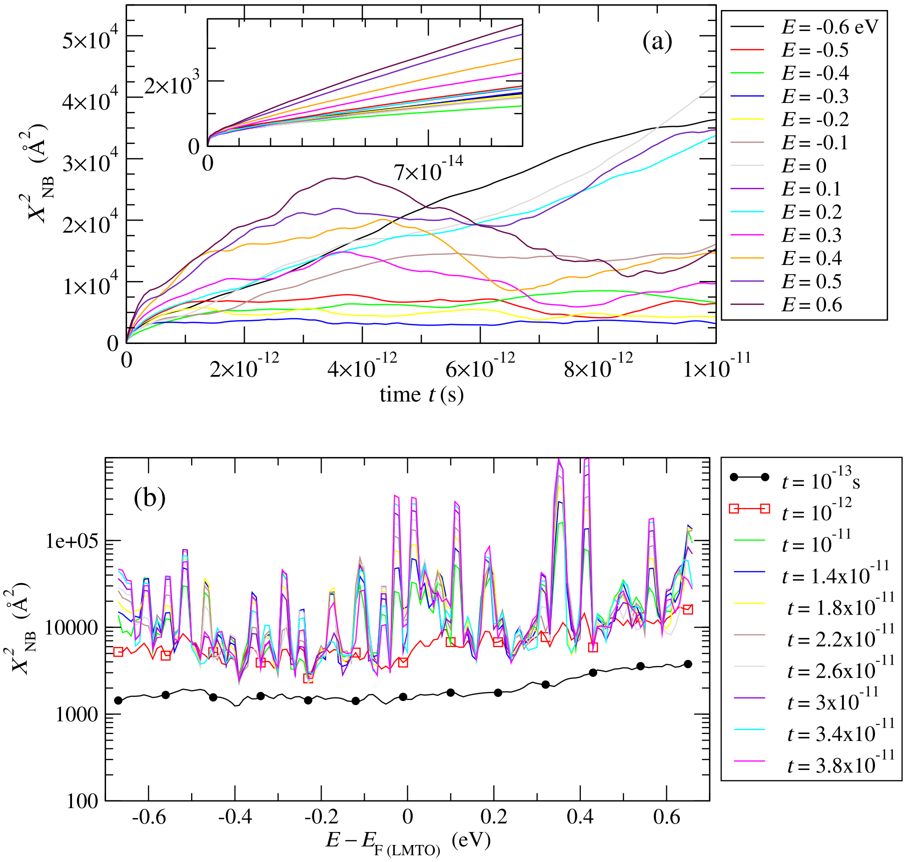

Fig. 3. (Colour online.) LMTO non-Boltzmann average square spreading X^2_{NB} in λ-$Al_{4.6}Mn$. (a) X^2_{NB} versus time t for various energy values, (b) X^2_{NB} versus energy E for various time values.

3.4. Conductivity in the small velocity regime

The semi-classical theory of transport in crystal is based on the concept of a charge carrier wave packet propagating at a velocity V_B. Moreover, in real materials, defects induce scattering events of the wave packet (elastic or inelastic scattering) separated by an average time τ. The validity of the wave packet concept requires that the extension L_{wp} of the wave packet is smaller that the traveling distance $V_B\tau$ between two scattering events. In phases with a small Boltzmann velocity and enough large extension of the wave packet, this condition in no more valid and:

$$L_{wp} > V_B\tau \tag{22}$$

Thus, when (22) is satisfied the semi-classical (Boltzmann) approach for transport is no more valid, and a new diffusion regime, called *"small velocity regime"* (SVR), is reached [23].

For realistic values of the scattering time, $\tau \simeq 10^{-14}$ s or $\tau \simeq 10^{-13}$ s, in quasicrystals and approximants [7], our ab initio calculation shows that the SVR is reached for many energies. Results for α-AlMnSi and 1/1-AlCuFe are presented in Refs. [23,26]. The diffusivity and conductivity in λ-AlMn are shown in Figs. 4 and 5.

When (21) is satisfied for realistic Fermi energy values, one obtains simple equations for the diffusivity [23]:

$$D(E_F) = V_B^2(E_F)\tau + \frac{1}{2}\frac{L^2_{wp}(E_F)}{\tau} \tag{23}$$

and the conductivity,

$$\sigma(E_F) = e^2 n(E_F)V_B^2(E_F)\tau + \frac{1}{2}e^2 n(E_F)\frac{L^2_{wp}(E_F)}{\tau} \tag{24}$$

where the first terms are the Boltzmann terms and the second terms the non-Boltzmann terms. This two terms are shown in Figs. 4 and 5 for the λ phase. Fig. 6 compares the conductivity in approximants and complex phases with those in simple phases that have a standard metallic behavior. From Eq. (23), it is clear that the Boltzmann (non-Boltzmann) term increases (decreases) when τ increases. The minimum of diffusivity (conductivity) is thus obtained when:

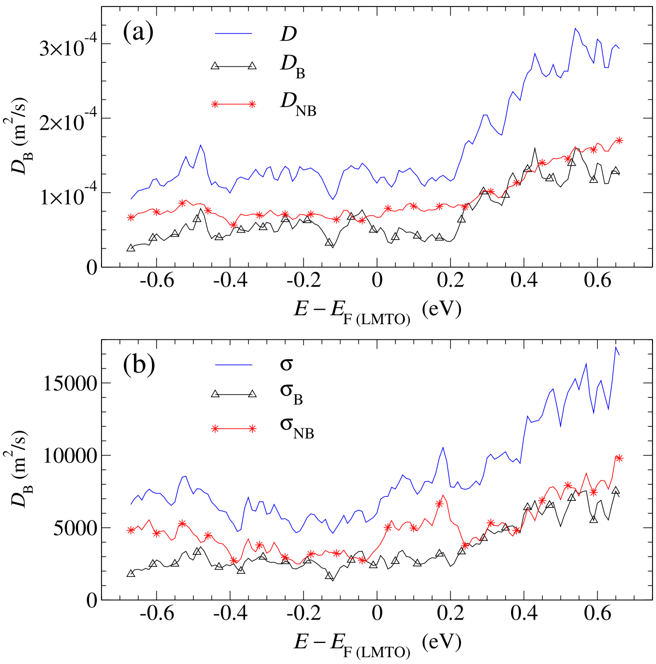

Fig. 4. (Colour online.) Electronic (a) diffusivity and (b) conductivity in λ-$Al_{4.6}Mn$ calculated from ab initio LMTO method for scattering time $\tau = 10^{-13}$ s.

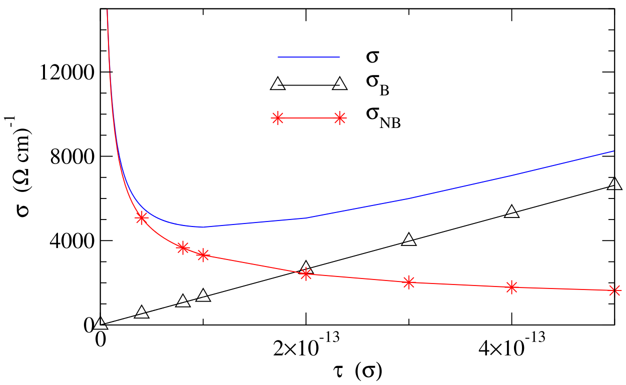

Fig. 5. (Colour online.) LMTO conductivity versus scattering time τ in λ-$Al_{4.6}Mn$ at energy $E = -0.12$ eV.

$$\tau = \tau^* \quad \text{with } \tau^* = \frac{L(E_F)}{\sqrt{2}V_B(E_F)} \tag{25}$$

For a scattering time, $\tau > \tau^*$, the Boltzmann term dominates and the diffusivity (conductivity) increases as τ increases. As τ decreases when defects and/or temperature increase, the behavior is thus *metallic-like*: σ decreases when defects and/or temperature increase. But, for $\tau < \tau^*$, the conductivity increases when defects and/or temperature increase and the behavior is *insulating-like*. From ab initio calculations in realistic phases, τ^* is around a few 10^{-14} or $\sim 10^{-13}$ s. These scattering time values correspond to scattering time estimates in quasicrystals and approximants from transport measurements at low temperature (4 K) [2,9,7]. Therefore, when temperature increases from low temperature, the behavior of these complex phases is insulating, like it has been found experimentally. From Eq. (24), when the Boltzmann term is negligible, $\tau \ll \tau^*$, the conductivity follows the *inverse Mathiessen rule* found experimentally [9,7]:

$$\sigma(T) = \sigma_{4K} + \Delta\sigma(T) \tag{26}$$

In α-AlMnSi, the minimum value of the conductivity obtained from ab initio calculation, $\sigma(E_F, \tau^*)$, is about 200 $(\Omega\,\mathrm{cm})^{-1}$, which is in good agreement with measurements [9]. This value is very low with respect to standard metallic alloys (Fig. 6), as expected in Al-based quasicrystals. In the complex metallic alloys λ-AlMn, the minimum value of $\sigma(E_F, \tau^*)$ is not so low, but the insulating-like regime is obtained for a larger range of τ values, as illustrated in Fig. 6. This shows that the small velocity regime can be observed in a great number of complex metallic alloys, even if their conductivity is

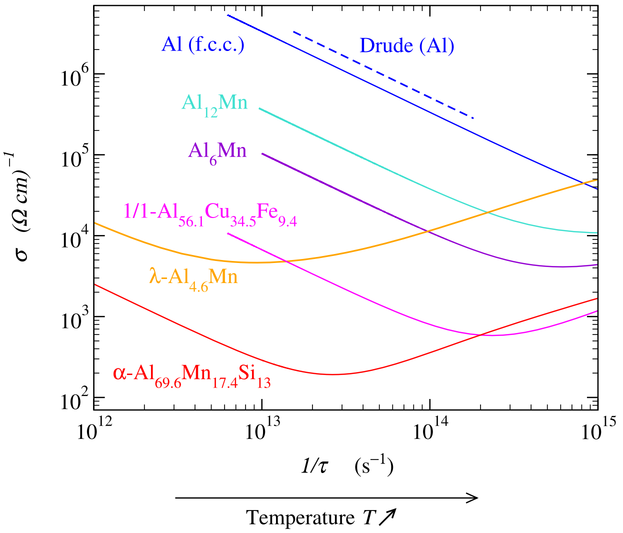

Fig. 6. (Colour online.) LMTO conductivity $\sigma(E_m)$ versus inverse scattering time $1/\tau$ in log–log scale. For each phase, E_m is the energy near to E_F for which $\sigma(E)$ reaches a minimum value.

not very low. Indeed, Dolinšek et al. [63,64] (see also review [65] and references therein) were able to analyse experimental transport properties of several complex metallic phases by using the small velocity regime model.

It must be noted that the quick variation of the DOS with energy implies also that the DOS will be modified by disorder. This also can contribute to the variation of the conductivity. Indeed the discussion here focuses on the variation of the diffusivity, but a variation of the DOS also contributes to a variation of the conductivity. Yet we believe that the variation of the diffusivity is an important ingredient, as indicated by the numerical values obtained in this model. In addition, as explained in Ref. [23], the small velocity regime also explains the absence of a Drude peak in the low-frequency optical conductivity that is observed experimentally.

4. Metal–insulator transition

Let us discuss now the nature of the phase at zero temperature as a function of the static disorder [25]. We recall here that we consider only non-interacting electrons in a three-dimensional system. For standard metals, it is well known that static disorder can induce a transition from a metallic to an insulating state when disorder increases. This is the Anderson transition. Here we discuss the role of static disorder for the case where the electrons propagate in an unusual way with a non-Boltzmann contribution to diffusion that cannot be ignored. As we show, this may strongly modify the occurrence of the insulating state. We discuss the metal–insulator phase diagram at zero temperature according to the scaling theory of localization. According to this theory, a central quantity is the conductance g of a cube with a size equal to the elastic mean-free path $X(E_F,\tau)$,

$$g \simeq e^2 n(E_F) D(E_F,\tau) X(E_F,\tau) \tag{27}$$

where $n(E_F)$ is the density of states at the Fermi energy and $D(E_F,\tau)$ is the diffusivity computed in the relaxation time approximation. The typical propagation length $X(E_F,\tau)$ on a time scale τ, i.e. the mean-free path, is such that:

$$X^2(E_F,\tau) = X_{NB}^2 + V^2\tau^2 \tag{28}$$

Let us introduce g_0, which is characteristic of the *perfect crystal* and is defined by:

$$g_0 = e^2 n(E_F) X_{NB}^2 V \tag{29}$$

Let us introduce an adimensional value $\tilde{\tau}$ of the scattering time τ defined by:

$$\tilde{\tau} = \frac{V\tau}{X_{NB}} = \frac{\tau}{\sqrt{2}\tau^*} \tag{30}$$

Let us define also the function $f(x)$,

$$f(x) = \left(\frac{1}{2x} + x\right)\sqrt{(1+x^2)} \tag{31}$$

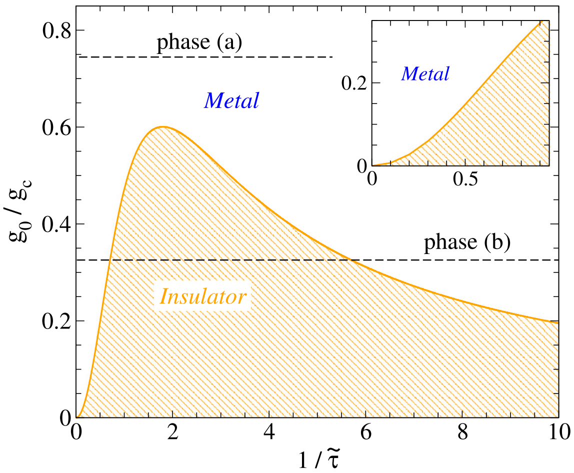

Fig. 7. (Colour online.) Metal–insulator phase diagram as a function of the two parameters g_0/g_c and $1/\tilde{\tau} = \sqrt{2}\tau/\tau^*$. The insert represents the limit of a normal metal, i.e. for fixed τ and V the limit of a small X_{NB}. After (29) and (30), this limit is in the region of the phase diagram at small g_0/g_c and small $1/\tilde{\tau}$.

then one has:

$$g = g_0 f(\tilde{\tau}) \tag{32}$$

After the scaling theory [25], a three-dimensional system is insulating (metallic, respectively) if $g < g_c$ (resp. $g > g_c$), where g_c is the value of the universal critical conductance in the scaling theory. Using $g = g_0 f(\tilde{\tau})$, it is equivalent to say that the system is insulating if $g_0/g_c < 1/f(\tilde{\tau})$ and metallic if $g_0/g_c > 1/f(\tilde{\tau})$. We emphasize that g_0/g_c is characteristic of the perfect crystal, whereas $1/\tilde{\tau}$ measures the scattering rate $1/\tau$ in units of V/X_{NB}. Fig. 7 illustrates this phase diagram.

A first remarkable property of this phase diagram is that if $g_0 > Rg_c$ with $R = 2/(\Phi)^{5/2}$, where Φ is the Golden Mean ($R \simeq 0.6$); then the system is always metallic whatever the value of the scattering rate (phase (a) in Fig. 7). This is not the case for normal metals that always become insulating at sufficiently small scattering times τ (i.e. at sufficiently large disorder). Note that for a system like AlMnSi, $g_0/g_c \simeq 2$, and therefore this phase should always be metallic, independently of the amount of disorder.

If $g_0 < Rg_c$, the system is metallic at large and small scattering rates and insulator in an intermediate zone (phase (b) in Fig. 7). This means that if the system is in the large $1/\tilde{\tau}$ metallic region, it will become insulating by *decreasing* $1/\tilde{\tau}$, that is by *decreasing* disorder! This is just the opposite of the standard conditions for the occurrence of the Anderson localization transition. This anomalous behavior occurs because in that regime quantum diffusion is dominated by the non-Boltzmann term and not by the ballistic term. The other insulator–metal transition is normal in the sense that the metallic state is obtained by decreasing disorder.

Note that the case of a normal metal corresponds to the limit $X_{NB} \to 0$. In that case, one uses the asymptotic form of the function $f(\tilde{\tau})$ for large $\tilde{\tau}$, namely $f(\tilde{\tau}) \simeq \tilde{\tau}^2$. One then recovers the standard criterion for free-like electrons.

5. Conclusion

To summarize, this article shows that approximant phases α-AlMnSi, 1/1-AlCuFe and the complex phase λ-AlMn present unusual band structure and Bloch states. This can explain their anomalous transport properties when compared to standard metallic phases. In particular, the analysis of the quantum diffusion in these phases shows that it is badly reproduced by the standard semi-classical theory. As we find, the square of the quantum diffusion length is the sum of two terms that depend on time. One term is the ballistic contribution and the other term is the non-Boltzmann contribution. Depending on the scattering time, one term or the other can dominate the conductivity. If the ballistic term dominates, this corresponds to a standard metallic behavior. If the non-Boltzmann term dominates (small velocity regime), this induces an insulating-like behavior that is in good agreement qualitatively and even quantitatively with experimental results. As we discussed also, the occurrence of an Anderson transition is also deeply affected by the anomalous quantum diffusion and the possible existence of a small velocity regime.

We note also that a small velocity regime can be found in other systems that present flat electronic bands. This is the case in the recently studied rotated bilayers of graphene [66–68]. Indeed these systems have large unit cells, and it has been shown that the electronic coupling between the two layers tends to decrease the Fermi velocity and even cancel it at some specific small angles.

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References

[1] D. Shechtman, J. Blech, D. Gratias, J.W. Cahn, Phys. Rev. Lett. 53 (1984) 1951.
[2] S.J. Poon, Adv. Phys. 41 (1992) 303.
[3] C. Berger, E. Belin, D. Mayou, Ann. Chim. Mater. (Paris) 18 (1993) 485.
[4] C. Berger, in: F. Hippert, D. Gratias (Eds.), Lectures on Quasicrystals, Les Éditions de Physique, Les Ulis, 1994, p. 463.
[5] T. Grenet, in: E. Belin-Ferré, C. Berger, M. Quiquandon, A. Sadoc (Eds.), Quasicrystals: Current Topics, World Scientific, Singapore, 2000, p. 455.
[6] T. Klein, C. Berger, D. Mayou, F. Cyrot-Lackmann, Phys. Rev. Lett. 66 (1991) 2907.
[7] D. Mayou, C. Berger, F. Cyrot-Lackmann, T. Klein, P. Lanco, Phys. Rev. Lett. 70 (1993) 3915.
[8] P.S. Pierce, S.J. Poon, Q. Guo, Science 261 (1993) 737;
F.S. Pierce, S.J. Poon, B.D. Biggs, Phys. Rev. Lett. 70 (1993) 3919.
[9] C. Berger, T. Grenet, P. Lindqvist, P. Lanco, J.G. Grieco, G. Fourcaudot, F. Cyrot-Lackmann, Solid State Commun. 87 (1993) 977.
[10] H. Akiyama, Y. Honda, T. Hashimoto, K. Edagawa, S. Takeuchi, Jpn. J. Appl. Phys. 32 (1993) L1003.
[11] C. Sire, in: F. Hippert, D. Gratias (Eds.), Lectures on Quasicrystals, Les Éditions de Physique, Les Ulis, 1994, p. 505.
[12] D. Mayou, Europhys. Lett. 6 (1988) 549.
[13] D. Mayou, S.N. Khanna, J. Phys. I Paris 5 (1995) 1199.
[14] S. Roche, D. Mayou, Phys. Rev. Lett. 79 (1997) 2518.
[15] S. Roche, D. Mayou, Phys. Rev. B 60 (1999) 322.
[16] F. Triozon, J. Vidal, R. Mosseri, D. Mayou, Phys. Rev. B 65 (2002) 220202.
[17] D. Mayou, Phys. Rev. Lett. 85 (2000) 1290.
[18] D. Mayou, G. Trambly de Laissardière, in: T. Fujiwara, Y. Ishii (Eds.), Quasicrystals, in: Handbook of Metal Physics, Elsevier Science, Oxford, 2008, p. 209.
[19] P. Darancet, V. Olevano, D. Mayou, Phys. Rev. B 81 (2010) 155422.
[20] C. Janot, M. de Boissieu, Phys. Rev. Lett. 72 (1994) 1674.
[21] G. Trambly de Laissardière, D. Mayou, Phys. Rev. B 55 (1997) 2890.
[22] G. Trambly de Laissardière, S. Roche, D. Mayou, Mater. Sci. Eng. A 226–228 (1997) 986.
[23] G. Trambly de Laissardière, J.-P. Julien, D. Mayou, Phys. Rev. Lett. 97 (2006) 026601.
[24] S. Ciuchi, S. Fratini, D. Mayou, Phys. Rev. B 83 (2011), 081202(R).
[25] P.A. Lee, T.V. Ramakrishnan, Rev. Mod. Phys. 57 (1985) 287.
[26] G. Trambly de Laissardière, J.-P. Julien, D. Mayou, Philos. Mag. 88 (2008) 2131.
[27] K. Sugiyama, N. Kaji, K. Hiraga, Acta Crystallogr. C 54 (1998) 445.
[28] E.S. Zijlstra, S.K. Bose, Phys. Rev. B 67 (2003) 224204.
[29] V. Simonet, F. Hippert, R.A. Brand, Y. Calvayrac, J. Rodriguez-Carvajal, A. Sadoc, Phys. Rev. B 72 (2005) 024214.
[30] G. Kreiner, H.F. Franzen, J. Alloys Compds. 261 (1997) 83.
[31] C.B. Shoemaker, D. Keszler, D. Shoemaker, Acta Crystallogr. B45 (1989) 13.
[32] G. Kreiner, H.F. Franzen, J. Alloys Compds. 221 (1995) 15.
[33] D. Nguyen-Manh, G. Trambly de Laissardière, J. Magn. Magn. Mater. 262 (2003) 496.
[34] O.K. Andersen, Phys. Rev. B 12 (1975) 3060.
[35] G. Krier, O. Jepsen, A. Burkhart, O.K. Andersen, in: The TB-LMTO program, Stuttgart, 1995.
[36] U. Mizutani, in: Hume-Rothery Rules for Structurally Complex Alloy Phases, Taylor & Francis, 2010.
[37] G. Trambly de Laissardière, D. Nguyen Manh, D. Mayou, Prog. Mater. Sci. 50 (2005) 679.
[38] J. Friedel, F. Dénoyer, C. R. Acad. Sci. Paris, Ser. II 305 (1987) 171.
[39] D. Nguyen-Manh, et al., J. Phys. F, Met. Phys. 17 (1987) 999.
[40] Z. Dankhazi, et al., J. Phys. Condens. Matter 5 (1993) 3339.
[41] E. Belin, D. Mayou, Phys. Scr. T 49 (1993) 356.
[42] D. Mayou, F. Cyrot-Lackmann, G. Trambly de Laissardière, T. Klein, J. Non-Cryst. Solids 153–154 (1993) 412.
[43] G. Trambly de Laissardière, D. Mayou, D. Nguyen Manh, Europhys. Lett. 21 (1993) 25;
G. Trambly de Laissardière, D. Mayou, D. Nguyen Manh, J. Non-Cryst. Solids 153–154 (1993) 430.
[44] G. Trambly de Laissardière, D. Nguyen Manh, L. Magaud, J.-P. Julien, F. Cyrot-Lackmann, D. Mayou, Phys. Rev. B 52 (1995) 7920.
[45] G. Trambly de Laissardière, et al., Phys. Rev. B 51 (1995) 14035.
[46] M. Krajčí, et al., Phys. Rev. B 51 (1995) 17355.
[47] V. Simonet, F. Hippert, M. Audier, G. Trambly de Laissardière, Phys. Rev. B 58 (1998) R8865.
[48] F. Hippert, V. Simonet, G. Trambly de Laissardière, M. Audier, Y. Calvayrac, J. Phys. Condens. Matter 11 (1999) 10419.
[49] G. Trambly de Laissardière, G. Mayou, Phys. Rev. Lett. 85 (2000) 3273.
[50] G. Trambly de Laissardière, Phys. Rev. B 68 (2003) 045117.
[51] G. Trambly de Laissardière, D. Nguyen Manh, D. Mayou, J. Non-Cryst. Solids 334–335 (2004) 347.
[52] G. Trambly de Laissardière, Z. Kristallogr. 224 (2009) 123.
[53] T. Fujiwara, Phys. Rev. B 40 (1989) 942.
[54] T. Fujiwara, S. Yamamoto, G. Trambly de Laissardière, Phys. Rev. Lett. 71 (1993) 4166.
[55] R. Widmer, et al., Philos. Mag. 86 (2006) 781.
[56] R. Widmer, P. Gröning, M. Feuerbacher, O. Gröning, Phys. Rev. B 79 (2009) 104202.
[57] R. Mader, et al., New J. Phys. 12 (2010) 073043.
[58] R. Mader, et al., Phys. Rev. B 87 (2013) 075425.
[59] G. Trambly de Laissardière, T. Fujiwara, Phys. Rev. B 50 (1994) 5999.
[60] G. Trambly de Laissardière, T. Fujiwara, Phys. Rev. B 50 (1994) 9843;
G. Trambly de Laissardière, T. Fujiwara, Mater. Sci. Eng. A 181–182 (1994) 722.
[61] G. Trambly de Laissardière, J.-P. Julien, D. Mayou, Philos. Mag. 86 (2006) 663.
[62] D. Gratias, F. Puyraimond, M. Quiquandon, A. Katz, Phys. Rev. B 63 (2000) 24202.

[63] J. Dolinšek, et al., Phys. Rev. B 76 (2007) 174207.
[64] J. Dolinšek, et al., Phys. Rev. B 79 (2009) 184201.
[65] J. Dolinšek, Chem. Soc. Rev. 41 (2012) 6730–6744.
[66] G. Trambly de Laissardière, D. Mayou, L. Magaud, Nano Lett. 10 (2010) 804–808.
[67] G. Trambly de Laissardière, D. Mayou, L. Magaud, Phys. Rev. B 86 (2012) 125413.
[68] I. Brihuega, et al., Phys. Rev. Lett. 109 (2012) 196802.