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Fermi surfaces and electronic transport properties of quasicrystalline approximants

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Abstract

We present *ab initio* calculations of the Fermi surfaces and of the electronic transport properties of the 1/1 and 2/1 approximants to icosahedral AlPdRe and AlPdMn quasicrystals. Our investigations are based on realistic structural models produced by a cut-and-projection method, a self-consistent tight-binding linearized muffin-tin orbital (TB-LMTO) Hamiltonian and Bloch–Boltzmann as well as Kubo–Greenwood theories for the electronic transport properties. Our results are analysed in the light of the current discussions of the character of electronic eigenstates in quasicrystals in general and of the very exotic transport properties of icosahedral AlPdRe in particular.

1. Introduction

Quasicrystals are highly ordered intermetallic alloys with diffraction patterns displaying rotational symmetries that are incompatible with translational invariance. Hence Bloch's theorem for the electronic eigenstates of conventional crystals does not hold. In addition, the electronic and magnetic properties of quasicrystals are highly unusual—sometimes outright disconcerting, in view of the well known properties of metallic alloys [1]. In particular, the electrical and thermal conductivities have been found to be very low, close to and in a few cases even beyond the limit of the minimum metallic conductivity. In addition, the highly resistive quasicrystals show a negative temperature coefficient of the electrical resistivity, and the residual resistivity of quasicrystals is known to increase with increasing quasicrystalline perfection—again in striking contrast with the behaviour of conventional metallic alloys. On the other hand it is known that quasicrystals share many of their unusual properties with certain families of crystalline intermetallic compounds known as quasicrystalline approximants. The structures of these approximants approach quasiperiodic order in a hierarchic sequence determined by the series of the Fibonacci numbers 1/1, 2/1, 3/2, 5/3, ... As the Fibonacci numbers approach the golden mean $\tau = (1 + \sqrt{5})/2$, the length scale of the unit cell goes to infinity and the concentration of local deviations from perfect quasicrystalline symmetry vanishes. Such a hierarchy of approximant phases establishes a natural scaling sequence from which the physical properties of quasicrystals may be deduced.

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Calculations of the electronic spectra of quasicrystals have made extensive use of the concept of quasicrystalline approximants [1–5]. However, when discussing the electronic properties of quasicrystalline approximants, one has to be very careful to distinguish between the results obtained at different energy scales. At a level of resolution of a few tenths of an eV (i.e. comparable to that of most spectroscopic experiments), no significant differences between the total electronic density of states of low- and higher-order approximants and of quasicrystals have been reported. This includes in particular the existence of a pseudo-gap with a width of $\sim$0.5 eV at the Fermi energy, attributed to a Hume-Rothery mechanism (possibly enhanced by d-orbital resonance) and supposed to be an important factor for quasicrystalline stability. At a level of resolution of a few meV the situation is less clear, however. Calculations for the lowest-order approximants produced a density of states consisting of a series of very sharp spikes with a width of 0.001 eV or even less. Attempts to assess the existence of the predicted spikiness of the DOS by high-resolution photoelectron spectroscopy on real quasicrystals failed [1], but it must be admitted that the experimentally observed spectrum might be smoothed by averaging over a rather wide spatial area. Computationally, it is equally difficult to decide whether the spikiness predicted for the low-order approximants should survive in the quasiperiodic limit. A very fine k-point mesh has to be used if convergence of the spectra at the level of 0.01 eV is to be achieved [6].

For understanding the anomalous transport properties, the knowledge of the electronic states in the immediate vicinity of the Fermi level is important. At this point it is important to emphasize an essential difference between the electronic transport in crystalline and quasicrystalline alloys. In crystalline systems, the relation between the Fermi velocity $v_F = (1/\hbar)\partial E_n(k)/\partial k$ determined by the dispersion of the electronic eigenstates and the elastic scattering time τ_{el} set by the concentration of crystalline defects or impurities is such that a quasiclassical treatment of transport is justified in most cases and details of the band structure may be neglected. In quasicrystalline approximants, on the other hand, both band dispersion and the energy spacing between neighbouring bands become very small such that tunnelling between different bands is possible. For a given elastic scattering time τ_{el} the limit set by the Heisenberg uncertainty principle defines an energy window $\Delta E \sim \hbar/\tau_{el}$ around the Fermi level containing the bands involved in the tunnelling transitions.

These considerations establish a connection between the transport properties and the topology of the Fermi surface. For quasicrystalline approximants, like for any periodic systems, Fermi surfaces are well defined and easily calculated. In the hierarchy of higher-order approximants, however, the energy bands are folded down and the Fermi surface is reduced to infinitesimally small electron and hole pockets. Therefore, it was very surprising when de Haas–van Alphen experiments on icosahedral Al–Pd–Mn [7] reported the observation of periodic $1/H$ oscillations which, in a semiclassical treatment of electron dynamics in the applied external field, could be explained only in terms of fairly large extremal cross sections between the Fermi surface and a plane normal to the direction of the applied magnetic field. An alternative explanation of these experimental observations would be that a magnetic breakdown occurs due to tunnelling of electrons between different bands—evidently this interpretation is closely related to the non-classical description of electronic transport properties. So far, investigations of the Fermi surfaces of quasicrystalline approximants have been published only by Roche and Fujiwara [8]. The results for 1/1 approximants show Fermi surfaces consisting of many electron and hole pockets and open orbits—this feature has been described as being characteristic for quasicrystalline approximants.

Investigations of the electronic transport properties of quasicrystals published so far have been based either on quasiclassical Bloch–Boltzmann theory [9, 10] or on different quantum mechanical approaches. However, the quasiclassical treatment has been criticized

on the grounds that the propagation of electrons in quasiperiodic systems can be considered neither as ballistic as in periodic systems nor as diffusive as in highly disordered systems [11, 12]. Attempts to go beyond the quasiclassical treatment have been based on a variety of different approaches such as Landauer–Büttiker theory [13] or the Kubo–Greenwood formalism [11, 14–16]. However, with the notable exception of the work of Fujiwara *et al* [11] on decagonal Al–Cu–Co, these investigations deal with simple model systems such as one-band tight-binding Hamiltonians on Penrose lattices—in many cases even at reduced dimensions. Even the work on decagonal Al–Cu–Co approximants is restricted to the analysis of the diffusivity of a few selected eigenstates in the vicinity of the Fermi level. In the present paper we report on *ab initio* calculations of the Fermi surfaces and of the electronic conductivity of 1/1 and 2/1 approximants of icosahedral Al–Pd–Re and partially also Al–Pd–Mn alloys. These alloys have been selected for our study because previous electronic structure calculations [4] have achieved detailed agreement with photoemission and soft-x-ray spectroscopy and because of the outstanding electronic transport properties of Al–Pd–Re, placing this icosahedral alloy very close to a metal–insulator transition [1, 17, 18].

2. Methodology

The electronic structure calculations have been performed using the self-consistent tight-binding linear muffin-tin orbital (TB-LMTO) method [19]; the conductivity has been calculated both in a semiclassical Bloch–Boltzmann approximation and using quantum mechanical Kubo–Greenwood theory. Within Bloch–Boltzmann theory the conductivity σ_{xx} along the x-direction can be expressed as

$$\sigma_{xx} = \frac{e^2}{\Omega_0}\tau_{el}\sum_{n,\vec{k}} v_{nx}(\vec{k})^2\left(-\frac{\partial f}{\partial E_n(\vec{k})}\right) \tag{1}$$

where τ_{el} is the relaxation time, Ω_0 the volume per atom and f the Fermi–Dirac function. The band velocities are calculated in terms of the gradients of the dispersion relations of the electronic eigenstates as

$$v_{nx}(\vec{k}) = \frac{1}{\hbar}\frac{\partial E_n(\vec{k})}{\partial k_x}. \tag{2}$$

At zero-temperature the conductivity σ may be considered as a function of the position of the Fermi energy, $\sigma = \sigma(E_F)$.

Within Kubo–Greenwood theory [16] the conductivity is given by

$$\sigma_{xx} = \frac{2e^2}{\Omega}\int \mathrm{d}E\left(-\frac{\partial f}{\partial E}\right)\sum_{n,\vec{k}}\delta(E - E_n(\vec{k}))D^{xx}_{n\vec{k}}(E) \tag{3}$$

with

$$D^{xx}_{n\vec{k}}(E) = -\hbar\lim_{\epsilon\to 0+}\mathrm{Im}\langle n,\vec{k}|\hat{v}_x\frac{1}{E - \hat{H} + \mathrm{i}\epsilon}\hat{v}_x|n,\vec{k}\rangle \tag{4}$$

where $\hat{H}$ is the TB-LMTO Hamiltonian and

$$\hat{v}_x = \frac{1}{\mathrm{i}\hbar}[\hat{x}, \hat{H}]$$

is the velocity operator. Ω is volume of the unit cell. $D^{xx}_{n\vec{k}}(E)$ represents the energy-dependent diffusivity of an eigenstate belonging to band n and having wavenumber $\vec{k}$; a sum over all bands and $\vec{k}$-points defines the energy-dependent conductivity $\sigma_{xx}(E)$ along the x-direction.

For the calculation of the conductivity, the $\vec{k}$-integration has to be performed only over planes perpendicular to the direction of the current, with changed boundary conditions in the lateral directions. The calculations of the spectra are of course performed with periodic boundary conditions in all three directions. Our calculations have been performed for a dense $\vec{k}$-space grid so that full convergence of the calculated spectra, Fermi surfaces and electronic diffusivities could be achieved, i.e. the results remain unchanged if an even finer grid is adopted. The effect of a finite ϵ in the calculation of the conductivity is to simulate an inverse inelastic scattering time ($\tau = 1/(2\epsilon)$) which mimics an actual scattering process. For a finite system the conductivity tends to zero for small ϵ due to the discreteness of the spectrum; at large ϵ the conductivity is insensitive to the topology of the lattice due to the strong smearing and one recovers a classical behaviour. At intermediate ϵ we find that σ is almost stationary as a function of ϵ and these values have been chosen for the results presented below.

3. Electronic spectrum

Our investigations have been performed for the stable face-centred icosahedral Al–Pd–Mn and Al–Pd–Re alloys, using structural models based on projections from six-dimensional space, using triacontahedral atomic surfaces (for details see Krajčí *et al* [4]). Here we mention only that the exact stoichiometry depends quite strongly on the order of the approximant. For the 1/1 phase the composition is $Al_{68.8}Pd_{15.6}Mn_{15.6}$; for the 2/1 phase $Al_{68.8}Pd_{25.0}Mn_{6.2}$, the quasiperiodic limit of $Al_{70.8}Pd_{20.6}Mn_{8.6}$ is achieved approximately from the 3/2 approximant onward only. The 1/1, 2/1 and 3/2 approximants to the icosahedral phase contain 128, 544 and 2292 atoms in the periodic cell, of space-group symmetry $P2_13$, respectively. Previously reported calculations of the electronic density of states [17] were based on a fine mesh of 176 $\vec{k}$-points in the irreducible part of the Brillouin zone for the 1/1 approximant and only the Γ point for the 3/2 approximant. At this level of resolution, the electronic density of states is characterized at all energies by spiky peaks with a width of a few 0.01 eV. This fine structure is superposed to the broader structures of the d bands of Pd and Mn(Re) and the parabolic s, p band of Al, modulated by the most intense Bragg reflections. For the 1/1 approximant we find even a true electronic gap of $\sim$0.1 eV just below the Fermi level and a very deep pseudo-gap about 1 eV above E_F (see figure 1(a)). In the 2/1 and 3/2 approximants, some of the fine structure of the DOS survives (see figure 1(b)), but no gaps could be found. The existence of gaps or pseudo-gaps depends in a very sensitive way on details of the structure and chemical order—the gap closes even if a single Re atom is replaced by Al (such a replacement would place the Fermi level into the gap if a rigid band picture were to apply). Evidently this indicates a strong interaction between all local orbitals and a strong spatial coherence of the eigenstates [17]. This is also confirmed by an analysis of the localization properties: around the Fermi level, the participation ratio of all eigenstates fluctuates around 0.5; it does not show any significant variation in the vicinity of the gaps or pseudo-gaps. In the sequence of the approximants, a small decrease of the participation ratio averaged over a small energy interval is observed—this could be compatible with a very weak power-law localization of the eigenstates, but cannot be considered as a conclusive characterization of the transport regime.

It is clear that a true gap in the electronic spectrum at the Fermi level means zero low-temperature electronic conductivity. Existence of such a narrow gap in the electronic spectrum of real quasicrystals would substantially contribute to explaining the observed anomalous transport properties of quasicrystals. However, we have found a true gap in the electronic spectrum only of the 1/1 approximant but not in the spectrum of larger approximants. The observed high sensitivity of the gap to details of the local atomic arrangement indicates a possibility that a slightly different structural model of the 2/1 or higher approximant could also

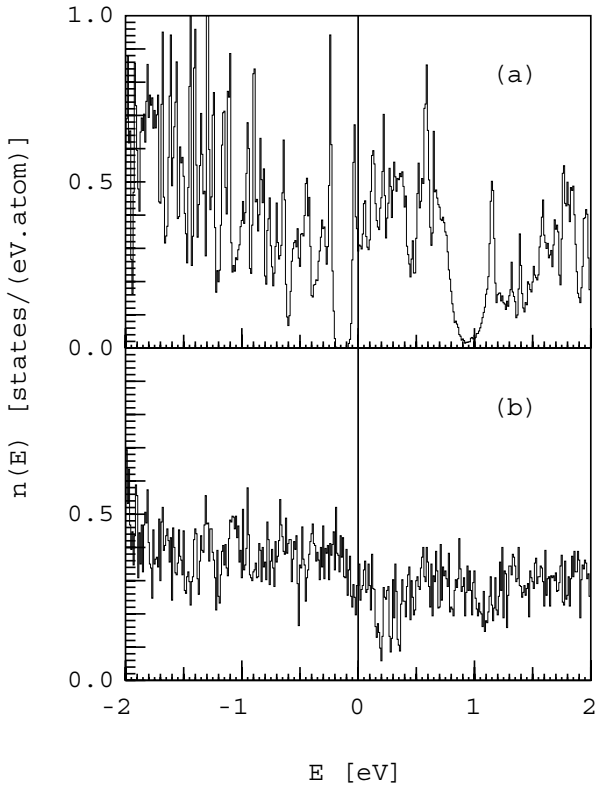

Figure 1. Electronic densities of states of the 1/1 and 2/1 approximants to icosahedral AlPdRe, calculated using grids of 1376 and 45 $\vec{k}$-points in the irreducible part of the Brillouin zone, respectively. (a) 1/1 and (b) 2/1 approximants.

have a narrow gap in the spectrum. We have examined several variants of structural model of the 2/1 approximant differing in the chemical occupation of selected atomic sites. As regards creation of a gap in the spectrum, none of these attempts was successful. However, as we have not examined different topological variants of the 2/1 approximant and also because we did not exhaust all possible chemical variations of the approximant, we cannot exclude the possibility that a narrow gap in the electronic spectrum could exist for different models of the 2/1 or higher approximants.

For the purpose of a determination of the Fermi surfaces and of the quasiclassical calculation of the transport properties, the calculations have been extended to 1376 $\vec{k}$-points for the 1/1 approximants, and to 45 $\vec{k}$-points for the 2/1 approximants. The Kubo–Greenwood calculations could be performed only for 100 and 16 $\vec{k}$-points in the plane perpendicular to the direction of the current, respectively. A first conclusion to be drawn on the basis of these results (and which was not evident from the previous results based on much coarser $\vec{k}$-space grids) is that at a fixed energy resolution, the DOS of the 2/1 approximant is decidedly smoother than that of the 1/1 approximant. To extend this conclusion to a higher level of resolution and to higher-order approximants would demand a very large computational effort, but we tend to agree with the conclusions drawn by Zijlstra and Janssen [6] on the basis of their analysis of quasiperiodic model Hamiltonians that at a fixed level of resolution, the spikiness of the DOS is reduced on approaching the quasiperiodic limit.

The dispersion relations along Γ–X, calculated in an interval of ±0.5 eV around the Fermi level, are shown in figure 2 for approximants to i-AlPdRe. For the 1/1 approximant, this energy window contains about 20 eigenstates and we estimate a Fermi velocity of $v_F \sim 0.5 \times 10^7$ cm s^{-1}; only two bands intersect the Fermi level. A true gap of about 0.1 eV is found just below the Fermi level. For the 2/1 approximant, the same energy window contains about 80 eigenstates and the average Fermi velocity is nearly one order of magnitude lower. Due to the reduced dispersion, the number of bands crossing the Fermi level remains small. It is evident, however, that a very good energy resolution must be achieved for a reliable determination of the Fermi surface.

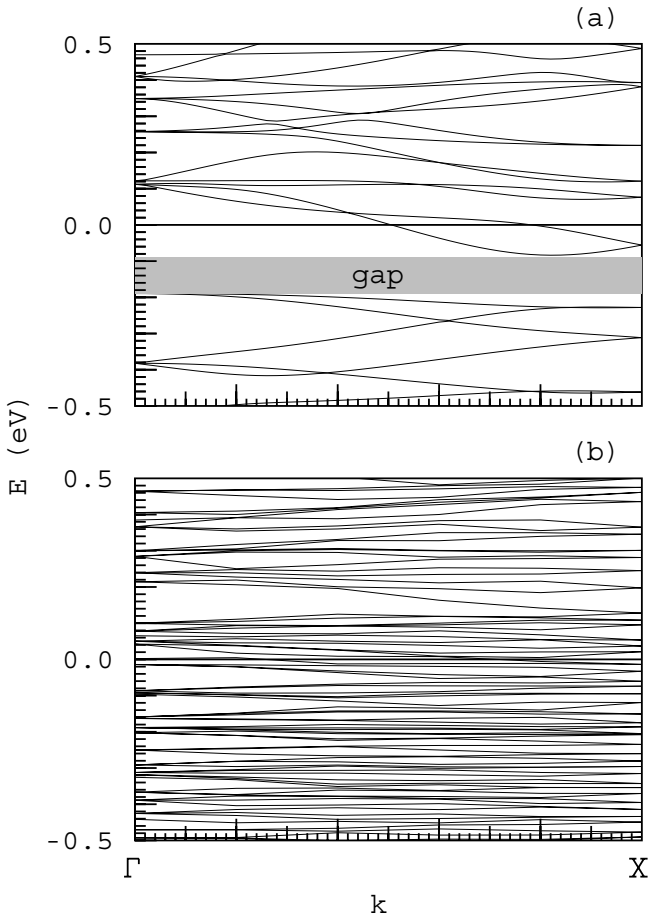

Figure 2. Dispersion relations of electronic eigenstates along Γ–X as calculated for the 1/1 (a) and 2/1 (b) approximant of icosahedral AlPdRe.

4. Fermi surfaces

The Fermi surfaces calculated for the 1/1 approximants of AlPdMn and AlPdRe are shown in figures 3(a) and 3(b) in the form of a series of cuts perpendicular to the k_z-axis. For both icosahedral alloys, the Fermi surface consists of two hole surfaces centred around the Γ points and smaller electron pockets around the R point. The two homologous alloys AlPdRe and

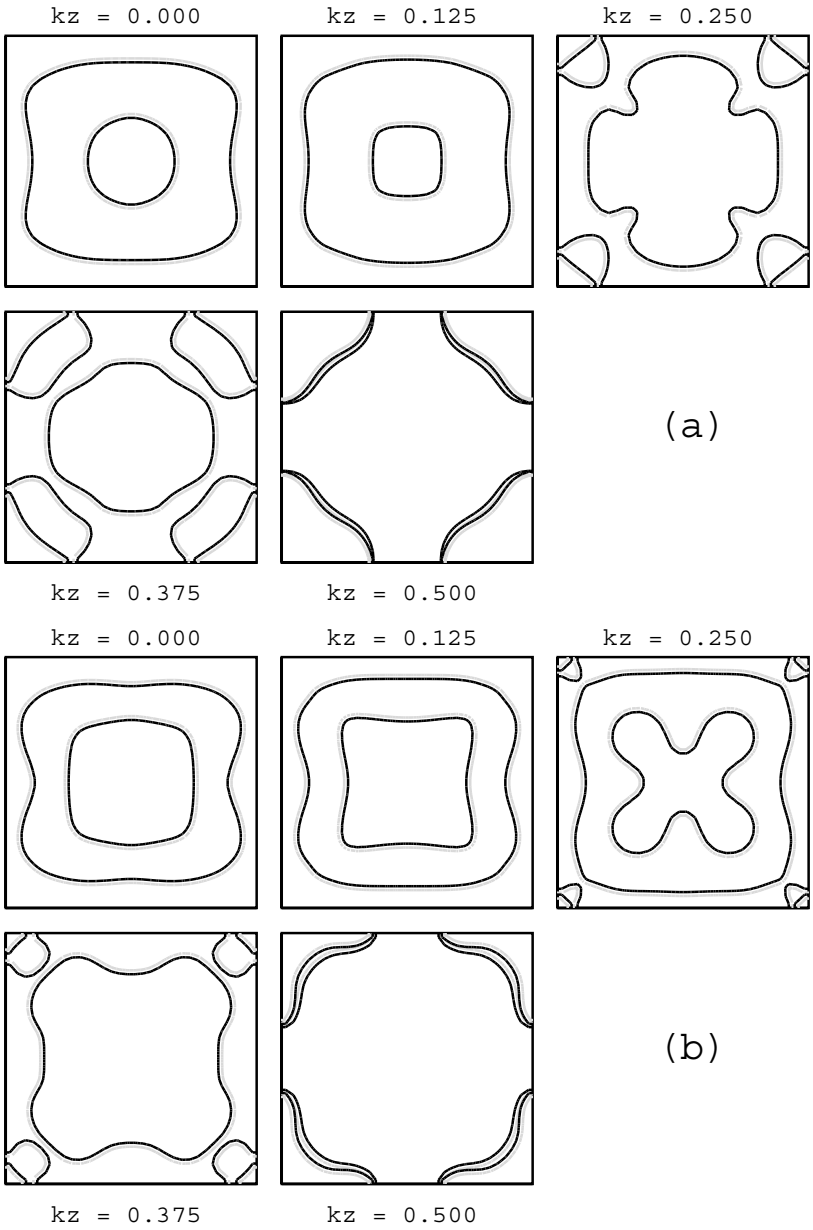

Figure 3. Fermi surfaces of the 1/1 approximants of icosahedral AlPdMn (a) and AlPdRe (b), displayed as cuts perpendicular to the k_z-axis. The occupied region of the Brillouin zone lies at the side of the light-grey contours—i.e. the surfaces centred around Γ are hole surfaces, and those centred at the corners of the Brillouin zone are hole surfaces.

AlPdMn differ only slightly in the shape and diameter of the different pockets. The Fermi surfaces calculated for the 2/1 approximant of AlPdRe are shown in figure 4. We find the same set of hole surfaces centred around Γ, electron pockets around the M and L points and two hole pockets around the R point. This similarity is rather surprising in view of the rather different compositions (and hence different Fermi energies) of the two approximants. On the other hand

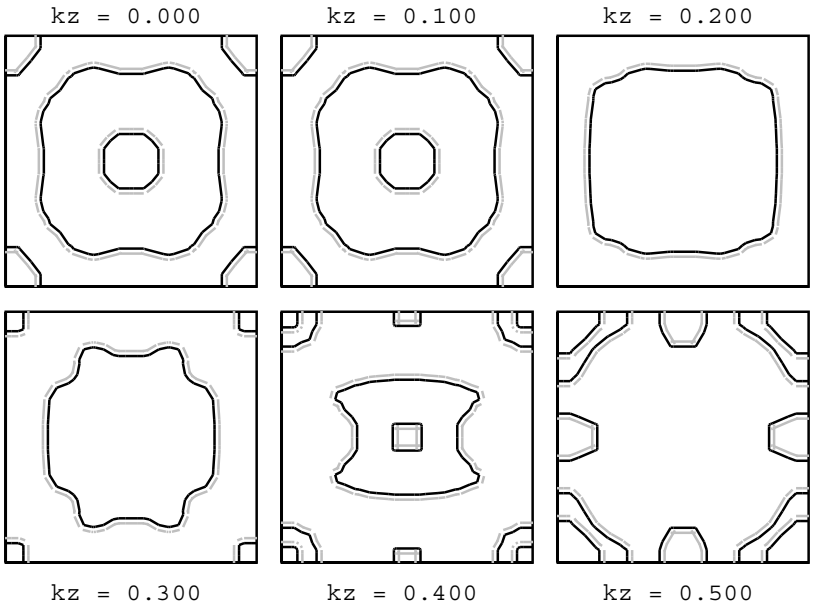

Figure 4. The Fermi surface of the 2/1 approximant of icosahedral AlPdRe, displayed as cuts perpendicular to the k_z-axis. Compare with figure 3.

this suggests that the general character of the Fermi surface will not vary dramatically with band filling.

Fermi surfaces for 1/1 approximants of icosahedral AlCuFe, AlCuFeSi and AlMgZn have been published by Roche and Fujiwara [8]. That the Fermi surface of icosahedral AlMgZn with many electron and hole pockets and open orbits should be very different from the results presented here is not surprising, since the eigenstates around the Fermi level consist of free-electron-like bands with a large dispersion. The Fermi surface reported for 1/1 AlCuFe is not too different from that found for our 1/1 approximants, with a small number of closed electron and hole pockets, but in addition some open orbits. In all cases it is important to emphasize that there are points on the Fermi surface where tunnelling can lead to a coupling between the different closed sheets ('magnetic breakdown'). At the scale set by the diameter of the respective Brillouin zone, there is no qualitative difference between the Fermi surfaces of the 1/1 and 2/1 approximants of AlPdRe—the number of closed shells remains about the same. In terms of absolute units, however, the distance between closed units is reduced and magnetic breakdown induced by tunnelling becomes even more likely. This is also relevant for transport processes because it shows that inter-band transitions will become more likely in the higher-order approximants. For icosahedral AlCuFe and AlCuFeSi Fujiwara and Roche have suggested that the existence of open Fermi surface orbits (which do not exist in the crystalline ω-AlCuFe phase) is a characteristic feature of quasicrystallinity. This is not confirmed by the present results.

5. Electronic conductivity

The energy-dependent conductivity of the 1/1 and 2/1 approximants to icosahedral AlPdRe, calculated in the quasiclassical Bloch–Boltzmann approximation and assuming a relaxation time of $\tau_{el} \sim 10^{-15}$ s is shown in figure 5 (the choice of the relaxation time merely scales the

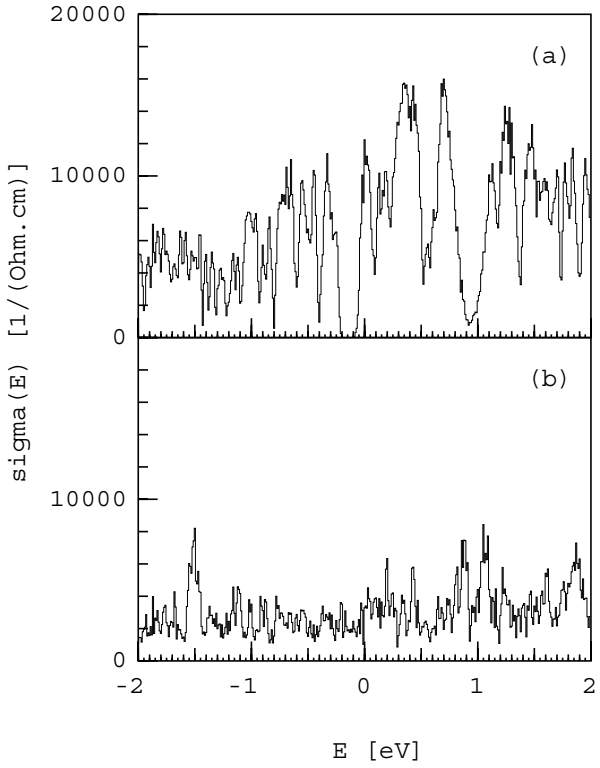

Figure 5. Energy-dependent Bloch–Boltzmann conductivity calculated for the 1/1 (a) and 2/1 (b) approximants of icosahedral AlPdRe. See the text.

conductivity). The energy-dependent electronic conductivity of the 1/1 approximant shows a strong structure that is similar but not identical to the density of states. In particular, we find a conductivity gap just below the Fermi level and a series of deep conductivity minima—not all of them are associated with pseudo-gaps in the electronic DOS (cf. figure 1(a)). However, we can also identify several energy intervals of enhanced conductivity, indicating higher band velocities arising from stronger dispersion of the electronic eigenstates. Around the Fermi level, the characteristic energy scale of the structures seen in the conductivity is a few 0.1 eV; at higher binding energy where the d-electron DOS is dominant and the band velocities are even lower we find more fine structure in $\sigma(E)$ at a scale of a few 0.01 eV. In this energy range, the average conductivity level is also significantly lower than around the Fermi energy. Off course, this fine structure is rather sensitive to the $\vec{k}$-point sampling, but a comparison of the results obtained with 176 and 1376 points in the irreducible part of the Brillouin zone demonstrates that an adequate level of convergence has been achieved.

The Boltzmann conductivity of the 2/1 approximant is considerably reduced compared to that of the 1/1 approximant, as a consequence of the decreasing dispersion of the eigenstates. The strong structures in the conductivity of the 2/1 approximant have largely vanished—this parallels the smoothing of the electronic DOS mentioned above. The fine structure found for the 1/1 approximant in the region of a high d-band DOS only now extends over the entire energy range considered here. Although it has to be admitted that with 45 $\vec{k}$-points only, convergence is comparable only to that achieved with the 176-$\vec{k}$-point set for the 1/1 approximant, we do not expect that a more extended Brillouin-zone sampling would alter the general picture.

The energy-dependent Kubo–Greenwood conductivity calculated for the 1/1 and 2/1 approximants of icosahedral AlPdRe is shown in figure 6. In evaluating the conductivity according to the Kubo–Greenwood equations (3), (4), a small imaginary value ϵ has to be added to the energy. For an infinitely extended system the limit $\epsilon \to 0$ has to be taken; for a finite system the smallest possible value of ϵ is limited by the average level spacing of the system. ϵ also remains finite if a temperature-induced or structural randomness exists in the system. We analysed for both approximants the variation of the conductivity as a function of ϵ. Our results of a decreasing σ in the limits of both small and large ϵ and a stationary behaviour over a wide range of intermediate values agree with the findings of Choy [14] for a tight-binding model on a Penrose lattice, but disagree with the results of Fujiwara *et al* [11] who found for selected eigenstates of decagonal Al–Cu–Co that the diffusivity continues to increase with increasing ϵ. For decagonal Al–Cu–Co, Fujiwara *et al* [11] have performed a scaling analysis of the electronic diffusivity $D(E)$ of selected eigenstates as a function of ϵ and argued that a power-law dependence of the diffusivity on the smallest admissible value of ϵ for a given system size leads to an understanding of the observed anomalous transport properties. It is not our aim to perform a similar investigation for AlPdRe (and since our calculations are restricted to the two lowest-order approximants, this would also hardly be possible); our aim is rather to improve our understanding of the relationship between electronic structure and transport. For the results shown here we have used a value of $\epsilon = 0.01$ eV for both approximants. Reducing ϵ for the 2/1 approximant to 0.0025 eV (i.e. downscaling ϵ proportionally to the increasing size of the model) changes only small details in $\sigma(E)$.

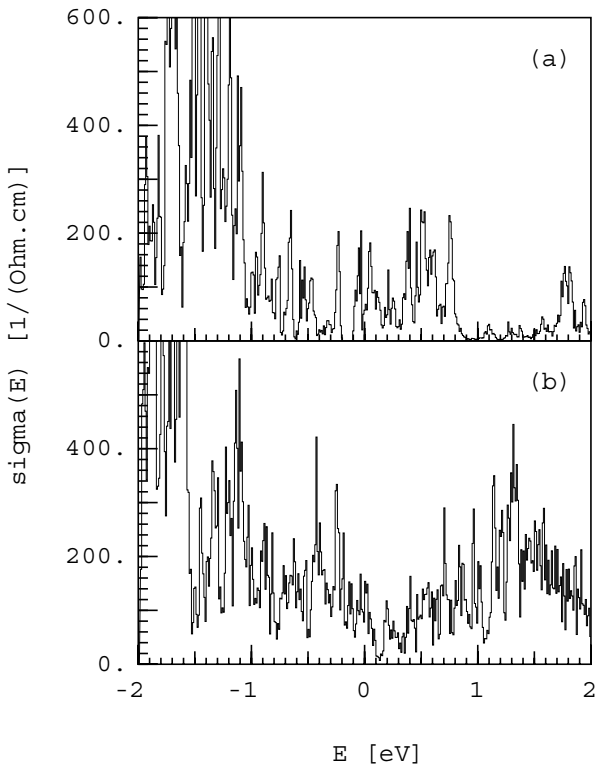

Figure 6. Energy-dependent Kubo–Greenwood conductivity calculated for the 1/2 (a) and 2/1 (b) approximants of icosahedral AlPdRe. See the text.

The results for the 1/1 approximant illustrate the characteristic differences between the quasiclassical and the quantum approach:

(i) The Kubo–Greenwood conductivity shows strong structures in the energy dependence which are not present in the density of states. At the Fermi level for example we calculate an almost vanishing conductivity, although both the DOS and the Boltzmann conductivity are very close to a local maximum.
(ii) There is also a striking difference in the region of 1 to 2 eV below E_F where the d-band DOS strongly increases, but the quasiclassical conductivity is reduced due to the weak dispersion of the d bands. The Kubo–Greenwood conductivity on the other hand is increased compared to that around E_F, due to a stronger inter-band coupling.
(iii) In the region between 1 and 2 eV above the Fermi level, the Kubo–Greenwood calculation predicts almost non-metallic behaviour over a wide energy range, whereas the quasiclassical approach had predicted a high conductivity in spite of a relatively low DOS, due to the higher band velocities.

Passing to the 2/1 approximant we find—similarly to the Boltzmann approach—that the structure in $\sigma(E)$ is reduced on a larger energy scale, although the fine structure is increased. The first effect mostly reflects the change in the band structure—which is also due to the higher Re content of the 2/1 approximant. A striking difference is that the wide range of extremely low conductivities in the region of 1 to 2 eV above E_F has disappeared. On a finer energy scale the structure in $\sigma(E)$ becomes even more pronounced, at least in certain energy ranges. An almost nonmetallic behaviour is found about 0.1 eV above the Fermi level, although the DOS is quite substantial here (cf. figure 1). The details of this fine structure depend of course to some degree on the choice of the $\vec{k}$-space grid and of the energy smearing. The 16-$\vec{k}$-point grid in the plane perpendicular to the current used here represents the limit of what can be achieved with a reasonable computational effort. At a fixed value of the smearing parameter ϵ, the Kubo–Greenwood conductivity averaged over finite energy intervals shows an overall increase rather than the decrease expected on the basis of scaling arguments (and as seen in the Bloch–Boltzmann calculations).

In the literature there has been a lot of discussion of whether icosahedral Al–Pd–Re undergoes a metal–insulator transition at very low temperature. Experimental results scatter widely, samples with the lowest $\sigma(4.2\,\mathrm{K})$ showing also the strongest variation with temperature. For different samples, resistivity ratios $R = \rho(4.2\,\mathrm{K})/\rho(300\,\mathrm{K})$ varying between $R \sim 4$ and $R \sim 200$ have been reported [18, 20]. For the temperature dependence various power laws, $\sigma(T) \propto T^{\beta}$, with β varying between 1/2 and $\sim$1.33 have been proposed, assuming that $\sigma(0)$ remains finite. For samples with an extrapolated zero conductivity at $T = 0\,\mathrm{K}$, the temperature dependence has been analysed assuming variable-range hopping behaviour [21].

It is clear that our results cannot lead to a quantitative interpretation of the experimental data. However, a few observations are useful:

(i) Both electronic spectrum and conductivity depend very critically on the exact composition, structure and band filling. Whereas the structure in the density of states appears to be smoothed in the higher-order approximants at any level of resolution achievable in spectroscopic experiments, the fine structure in the energy-dependent conductivity seems to persist.
(ii) The quantum mechanical treatment of the conductivity within Kubo–Greenwood theory can lead to enhanced as well as reduced conductivities compared to a semiclassical Bloch–Boltzmann approach where the conductivity is roughly proportional to the density of states. For the 1/1 approximant of Al–Pd–Re for example, the conductivity at E_F is very small,

although we calculate a substantial density of states. The fine structure of $\sigma(E)$ also explains the observed sensitivity of the transport properties to composition and structural perfection.

(iii) We should be very careful in analysing the variation of the conductivity in the hierarchy of the approximants. At the Fermi level of the two approximants, $\sigma(E_F)$ increases on going from the 1/1 to the 2/1 approximant. However, whether this is merely the result of the change in the stoichiometry or whether this represents the influence of increasing lattice periodicity (and hence increasing quasicrystallinity) remains an unanswered question.

(iv) The existence of the narrow gap near the Fermi level of the 1/1 approximant is an interesting fact that deserves further investigation.

6. Conclusions

We have presented calculations of the Fermi surfaces and of the quasiclassical Bloch–Boltzmann and quantum mechanical Kubo–Greenwood conductivities of 1/1 and 2/1 approximants of icosahedral Al–Pd–Re. Due to the very weak dispersion of the predominantly d-like states near the Fermi level, the Fermi surfaces of both approximants are comparatively simple and each consist of a small number of closed electron and hole surfaces. This is in striking contrast to the complex multiply connected Fermi surfaces of quasicrystals with a more s-like character of the highest occupied eigenstates [8]. We also note the absence of open orbits which, according to the suggestion of Roche and Fujiwara [8], should constitute a characteristic property of quasicrystals. Extrapolating to the higher-order approximants or the quasiperiodic limit, this would lead to a reduced Brillouin zone and Fermi surfaces shrinking to mere points—this is clearly not the proper way of looking at Fermi surfaces. In the absence of periodicity, the proper thing is to use at an extended zone scheme, generalized as proposed by Niizeki [22]. Niizeki showed that Brillouin zones are readily defined in the periodic six-dimensional hyperspace. A projection onto physical three-dimensional wavenumber space leads to sets of Brillouin-zone centres and special points which are dense everywhere, but with intensities that are strongly modulated by interference effects. The intensities of the special points are reflected in the spectral functions of the electronic eigenstates [2]. The most intense peaks of the spectral functions follow quasiperiodic dispersion relations. As an extension of this concept, we could imagine the construction of a dense network of 'Fermi surfaces' of varying intensities—the most intense of these surfaces could eventually be observed in a de Haas–van Alphen experiment. However, it will be difficult to calculate the spectral functions of large approximants with the required high resolution in energy.

The Bloch–Boltzmann conductivities show an energy dependence following quite closely the electronic DOS; the variation of the quasiclassical conductivities in the sequence of approximants is dominated by the decrease of the band velocities, which is in itself a trivial result of the downfolding of the eigenstates into the smaller Brillouin zones of the higher-order approximants. Extrapolated to the quasiperiodic limit this would lead, in an equally trivial way, to a vanishing conductivity of the quasicrystal—but this is merely a result of the neglect of inter-band transitions.

The Kubo–Greenwood conductivities are instructive in several respects:

(i) The differences in the energy dependencies of the electronic density of states and the electronic diffusivity demonstrate very clearly the importance of inter-band transitions and of quantum effects in electronic transport. We believe that this is the first application of Kubo–Greenwood theory to a realistic icosahedral quasicrystal.

(ii) These results explain the extreme sensitivity of the electronic transport properties of icosahedral Al–Pd–Re to even minimal variations in stoichiometry and structural perfection. In particular we find that nearly insulating behaviour can coexist—at least in a very narrow energy interval and hence only at very low temperature—with a non-vanishing 'metallic' density of states. This explains the strong correlation between the limiting low-temperature conductivity and the resistance ratio.

(iii) Over a wide range, the dependence of the conductivity on the 'smearing parameter' ϵ shows stationary behaviour. With ϵ in this range, we find an overall increase of the conductivity on going from the 1/1 to the 2/1 approximant—as expected for finite periodic systems. We did not attempt to find the 'smallest acceptable' value of ϵ—for such a scaling analysis our data are clearly insufficient.

(iv) As a more technical remark: this difficulty arises not only from the size of the approximants, but also from the need to sample the Brillouin zone on a rather fine $\vec{k}$-point mesh, even for very large cells. Our experience clearly tells against the often-used practice of restricting calculations on larger approximants to the Γ point only. This is acceptable for producing an electronic spectrum with a level of resolution comparable to experiment, but not for resolving the inherent fine structure of the spectrum or for obtaining a converged result for electronic transport properties. Together with the recent analysis of Zijlstra and Janssen [6] our work demonstrates the limitations inherent to a purely numerical analysis of other electronic properties of quasicrystals.

Finally we have to admit that many questions remain unsolved. The most important one probably concerns the variation of a conductivity increasing with the dimension of the approximants. If our result of a conductivity increasing with the order of the approximant had general validity, this would put the scaling analysis of the transport properties [11, 23, 24] into serious doubt. Evidently the challenge is to calculate the Kubo–Greenwood conductivities for a series of approximants which (i) represent realistic three-dimensional models, (ii) use a full s, p, d basis set representative for metallic systems and (iii) allow one to study the variation of spectrum and transport properties through a minimum of four generations of approximants. We are now performing such a study for 'quasi-fcc' Al, and the preliminary results seem to confirm the conjectures made here. These results will be reported soon.

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