

## Metal-insulator transition in approximants to icosahedral Al-Pd-Re

M. Krajčí

*Institut für Theoretische Physik and Center for Computational Materials Science, Technische Universität Wien,  
Wiedner Hauptstraße 8-10/136, A-1040 Wien, Austria  
and Institute of Physics, Slovak Academy of Sciences, Dúbravská cesta 9, SK-84228 Bratislava, Slovak Republic*

J. Hafner\*

*Institut für Theoretische Physik and Center for Computational Materials Science, Technische Universität Wien,  
Wiedner Hauptstraße 8-10/136, A-1040 Wien, Austria*

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The electronic structure of icosahedral Al-Pd-Re alloys has been calculated for a series of large approximants. For the 1/1 to 3/2 approximants with up to 2292 atoms/cell the electronic eigenstates have been calculated self-consistently via diagonalization of the Hamiltonian in a tight-binding linear-muffin-tin orbital representation. For the 5/3 and 8/5 approximants only the total and partial densities of states have been calculated using the real-space recursion method. The electronic structure of Al-Pd-Re differs from that of other icosahedral phases by (i) the appearance of a semiconducting gap for certain approximants and (ii) by a scaling behavior of the participation ratio of the states close to the Fermi level, indicating a possibly critical character of the eigenstates. [S0163-1829(99)01510-6]

Much attention has been paid to the face-centered-icosahedral quasicrystals (QC's) Al-Cu-Fe(Ru,Os) and Al-Pd-Mn(Re) because of their highly anomalous electric transport properties.<sup>1,2</sup> Among the outstanding observations made on this class of materials, those relating to icosahedral Al-Pd-Re are perhaps most exotic: (i) The resistivity is the highest ever reported for QC's and is of the same order of magnitude as that found in doped semiconductors.<sup>3-5</sup> (ii) The strong temperature dependence of the resistivity, characterized by values of the resistance ratio  $R = \rho(4.2 \text{ K})/\rho(300 \text{ K})$  which may be as high as  $R \sim 50$ .<sup>3,6,7</sup> (iii) With increasing  $R$  the magnetoresistance changes from giant positive values<sup>8</sup> to a small positive or even negative values<sup>5,9,10</sup> comparable to those registered in systems undergoing a metal-insulator transition. (iv) Extrapolations of the conductivity on a linear temperature scale from  $T > 0.4 \text{ K}$  to lower  $T$  suggest a vanishing conductivity at finite  $T$ .<sup>3,10</sup> However, the validity of these extrapolations has recently been disputed.<sup>6</sup> (v) The frequency dependence of the optical conductivity has been interpreted in terms of transitions across an indirect gap of magnitude 0.24 eV.<sup>11</sup> A gap (or at least a very deep pseudogap) of comparable width is also confirmed by tunneling spectroscopy.<sup>12</sup> (vi) At low temperatures Al-Pd-Re QC's are diamagnetic, but the observed temperature dependence of the susceptibility suggests the presence of a paramagnetic component arising from local moments on Re sites.<sup>7</sup> Again the similarity with doped semiconductors has been emphasized. (vii) All electronic transport properties are found to be extremely sensitive to the structural quality of the icosahedral phase, as well as to small variations of the chemical composition and in the thermal treatment. It is generally believed that QC's with higher structural perfection (produced at higher annealing temperatures) show higher resistivities.<sup>8,7</sup> Concerning the concentration dependence Tamura *et al.*<sup>16</sup> have found the highest resistance ratios along a line of constant nominal electron-per-atom ratio (and hence constant band filling).

While these observations might suggest that icosahedral Al-Pd-Re is on the insulating side of a metal-insulator transition, this interpretation would contradict a number of other observations: (i) The electronic specific heat measurements<sup>3,13</sup> show a finite density of states even for samples with high values of  $R$ . The carrier concentration estimated from Hall measurements also is in the delocalized regime. (ii) High-resolution photoemission experiments<sup>14</sup> and soft x-ray emission and absorption spectroscopies<sup>15</sup> observe no gap, but only a reduced density of states (DOS) at the Fermi level.

For a stable QC with a not too high resistance ratio ( $R \leq 10$ ) the magnetoresistance and the conductivity can be fitted quite well on the basis of weak localization and electron-electron interaction theories.<sup>17-19</sup> For samples with higher resistance ratios, however, a description based on quantum-interference effects breaks down.<sup>8,16</sup> If one accepts the idea that Al-Pd-Re QC's with very large  $R$  values are already on the semiconducting side of a metal-insulator transition, the natural step seems to be to apply various hopping theories that can account for the low-temperature transport theories of doped semiconductors.<sup>20</sup> However, while Basov *et al.*<sup>11</sup> claimed that the optical conductivity of icosahedral Al-Pd-Re is well explained in terms of a variable-range-hopping (VRH) mechanism, Honda *et al.*<sup>9</sup> reported that VRH fails to predict the temperature-dependence of the conductivity, and Gignoux *et al.*<sup>21</sup> found that it is difficult to account for the conductivity on the basis of nearest-neighbor hopping with constant activation energies.

Hence one is driven back to the fundamental question of the electronic structure of icosahedral Al-Pd-Re, in particular of the density and character of electronic eigenstates close to the Fermi level. This problem we address in this paper. We present detailed self-consistent calculations of the electronic structure for a hierarchy of rational approximants to icosahedral Al-Pd-Re, i.e., for crystalline structures with very large

TABLE I. Number of atoms  $N_{\text{atom}}$  and chemical composition (in at. %) of the rational approximants to icosahedral Al-Pd-Re.

Approximant	$N_{\text{atom}}$	$c_{\text{Al}}$	$c_{\text{Pd}}$	$c_{\text{Re}}$
1/1	128	68.8	15.6	15.6
2/1	544	68.4	22.8	8.8
3/2	2292	70.3	20.6	9.1
5/3	9700	70.6	20.7	8.7
8/5	41068	70.7	20.6	8.6
13/8	173936	70.8	20.6	8.6

unit cells differing from ideal icosahedral lattice by imposing a linear phason strain. We demonstrate that for a certain phason-mediated rearrangement of the atomic structure the electronic structure of Al-Pd-Re is either that of a narrow-gap semiconductor or that of metal with a pseudogap at the Fermi level. The transport properties of any macroscopic samples will therefore depend on concentration and spatial distribution of phasons.

Our structural model for icosahedral Al-Pd-Re is based on the six-dimensional structure refinement of Boudard *et al.*<sup>22</sup> for icosahedral Al-Pd-Mn and has been used in our previous electronic-structure calculations for that material.<sup>23</sup> The model is based on complex atomic surfaces centred on the even, odd- and body-centered positions of the six-dimensional hypercubic lattice with an inner shell structure that determines the chemical order on the face-centred icosahedral lattice (for all details see Ref. 23). The x-ray diffraction pattern calculated for 5/3 approximant of this model agrees very well with the pattern measured by Lin *et al.*<sup>7</sup> for icosahedral  $\text{Al}_{70}\text{Pd}_{22.5}\text{Re}_{7.5}$ . A rational approximant is constructed by imposing a linear phason strain which results in a formal replacement of the golden mean  $\tau$  in the definition of the base in the perpendicular space by the rational number  $\tau_n = F_{n+1}/F_n$  where  $F_n$  is a Fibonacci number. This creates a hierarchy of periodic structures approaching the icosahedral phase in the limit of large  $n$ ,  $\tau_n \rightarrow \tau$ . Each approximant is characterized by an ordered distribution of phasons whose concentration vanishes in the quasiperiodic limit. The tilting of the basis vectors in perpendicular space causes a deformation of atomic surfaces and hence leads to systematic changes in the stoichiometry. Lattice constants, number of atoms and composition of the lowest order approximants are given in Table. I. The space group of all approximants is  $P2_13$ .

For the 1/1 approximant with 128 atoms/cell the electronic eigenstates have been calculated self-consistently on a fine mesh of 176  $\mathbf{k}$  points in the irreducible Brillouin zone, using the tight-binding linear-muffin-tin-orbital<sup>24,25</sup> (TB-LMTO) technique. With a minimal  $s, p, d$  basis the repeated diagonalization of a  $1152 \times 1152$  Hamiltonian matrix is required. The most striking feature in the electronic density of states is the narrow gap of  $\sim 0.15$  eV immediately below the Fermi level, accompanied by a series of very deep pseudogaps in the region of the empty bands (see Fig. 1). As a consequence of this gap in the DOS, a minimal change in stoichiometry (equivalent to a reduction of the number of valence electrons per cell from 604 to 600) decides whether the 1/1 approximant is a bad metal or a narrow-gap semiconductor with a gap of 0.15 eV (we note that this corresponds

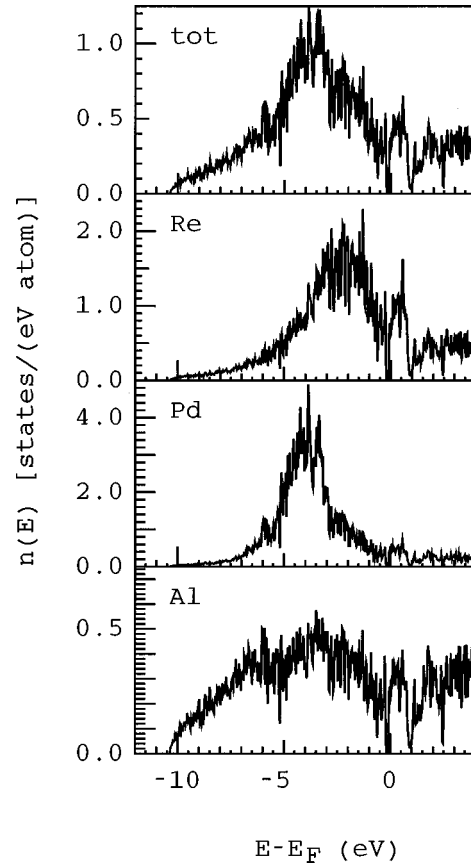


FIG. 1. Total and partial electronic density of states for 1/1 approximant to icosahedral Al-Pd-Re, calculated on a grid of 176 irreducible  $\mathbf{k}$  points.

very well to the gap of 0.24 eV deduced from the analysis of the optical properties<sup>11</sup> and from tunneling spectroscopy<sup>12</sup>). A very deep pseudogap is also found at  $\sim 0.9$  eV above the Fermi level, for this pseudogap we note the striking similarity with our results for the 1/1 approximant to icosahedral Al-Pd-Mn.<sup>23</sup> On the other hand the gap at  $E_F$  in the Al-Pd-Re has no counterpart in Al-Pd-Mn.

It is also important to analyze the character of the eigenstates on both sides of the gap. The distribution of the participation ratio of the eigenstates shown in Fig. 2(a) demonstrates that all eigenstates are delocalized and that there is not even the slightest indication for an onset of localization on either side of the gap. Hence if the Fermi level does not fall immediately in the gap, our result is also compatible with the conclusion from the Hall-effect measurements.<sup>7</sup> Close to the Fermi level, in the region where the Re-5*d* states dominate the total DOS, we find the participation ratio of Al-Pd-Re to be strikingly different from our prior results for icosahedral Al-Pd-Mn (Ref. 23): Whereas the states derived from the atomic Mn-3*d* levels (and also those derived from atomic Pd-4*d* states) have a low participation ratio of  $p_v \sim 0.2$  (indicating the more localized character of the 3*d* or 4*d* states as opposed to the Al-*s, p* states), the participation ratio of the Re-5*d* states is around  $p_v \sim 0.60$ , i.e., of the same order of magnitude as for the neighboring Al-*s, p* states. This shows that spatial correlations between eigenstates dominated by the transition-metal *d* states will be more long-ranged in Al-Pd-Re than in Al-Pd-Mn, in agreement with the observation made above.

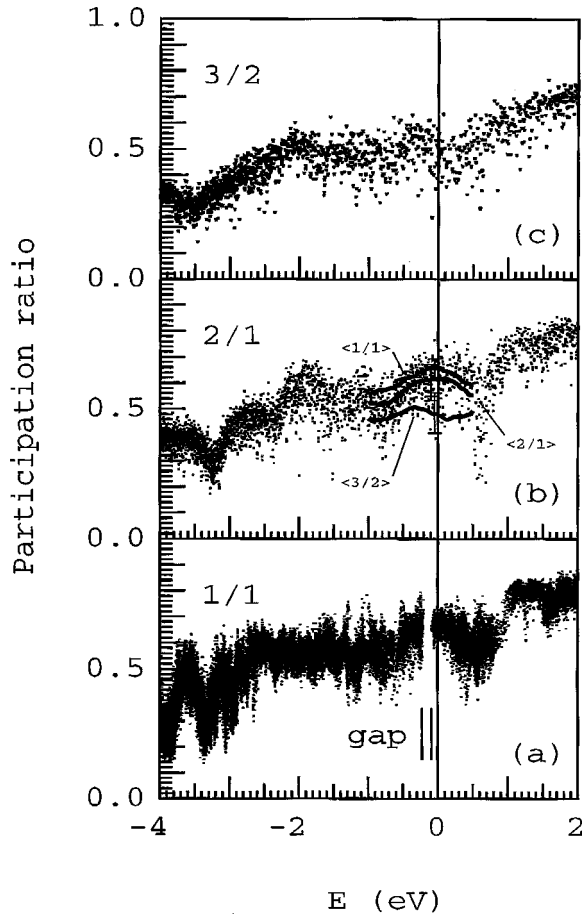


FIG. 2. (a)–(c) Participation ratio of the electronic eigenstates calculated for the 1/1, 2/1, and 3/2 approximants to icosahedral Al-Pd-Re. 176 irreducible  $\mathbf{k}$  points in the Brillouin zone have been used for the 1/1 approximant, four for the 2/1 approximant and only the  $\Gamma$  point for the 3/2 approximant. The full lines represent the participation ratio of states close to the Fermi level, averaged over intervals of  $E \pm 0.25$  eV, the error bars represent the mean-square deviations at an energy of 0.1 eV. See text.

We have calculated also the electronic structure of higher order approximants. The spectrum of the 2/1 approximant has been calculated at four high-symmetry points in the irreducible Brillouin zone, for the 3/2 approximant (2292 atoms) only the  $\Gamma$  point has been used. For the 3/2 approximant we have used the point group symmetry of the approximant to reduce the  $20628 \times 20628$  Hamiltonian matrix into diagonal blocks. The size of the maximal matrix to be diagonalized has been thus reduced by a factor 4. For the 5/3 and 8/5 approximants we used the real-space recursion method.<sup>26</sup> The potential parameters for the approximants up to 3/2 have been calculated self-consistently for all topologically non-equivalent sites. The potential parameters for 5/3 and 8/5 approximants have been transferred from the calculation of the lower order approximants.

Figures 3(a), 3(b) show the total electronic DOS of the 2/1 and 3/2 approximants; (c) shows the electronic DOS of the 5/3 and 8/5 approximants. The overall features of the band structure are in good agreement with photoemission<sup>14</sup> and soft x-ray<sup>15</sup> spectroscopy. Evidently the 3/2 approximant is metallic, although we observe a very deep pseudogap exactly at the Fermi level. The same we observed also for the

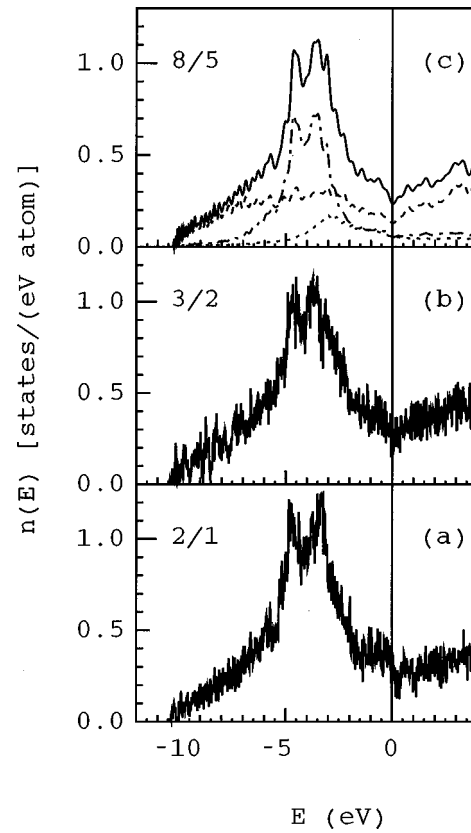


FIG. 3. (a), (b) Total electronic densities of states calculated for the 2/1 and 3/2 approximants via exact diagonalization of the Hamiltonian, using four high-symmetry points and the  $\Gamma$  point, respectively. (c) Total and partial electronic densities of states calculated using the recursion method for the 8/5 approximant (full line: total DOS, dashed line: Al, dot-dashed line: Pd, dotted line: Re-DOS).

2/1 approximant. The energy resolution of the recursion technique is limited, with about 120 recursion levels and a total band width of 15 eV the resolution is of the order of 0.1 to 0.2 eV. Hence, although we observe a rather deep pseudogap at the Fermi level, the possible existence of a semiconducting gap in the higher-order approximants can neither be confirmed nor disproved. As for the 1/1 approximant we find the fine structure of the DOS to be very sensitive to the details of the atomic structure: even small variations of the local chemical order can shift the most prominent pseudogaps on the energy-scale without, however, affecting the general spikiness of the spectrum.

Figures 2(b) and 2(c) show the participation ratio of the 2/1 and 3/2 approximants. The participation ratio suggests again a delocalized character of the eigenstates, but on average the participation ratio of the eigenstates in the range  $-1 \text{ eV} \leq E \leq 0.5 \text{ eV}$  is reduced from  $\langle p_\nu \rangle \sim 0.55$  to 0.64 for the 1/1 approximant to  $\langle p_\nu \rangle \sim 0.45$  to 0.49 for the 3/2 approximant. The calculated variation of the participation ratio  $p_\nu$  with increasing order of the approximant is compatible with the scaling behavior of critical eigenstates.<sup>27,28</sup> To improve the statistics, we estimate the scaling behavior from the participation ratio averaged over energy intervals ( $E_\nu - 0.25 \text{ eV}, E_\nu + 0.25 \text{ eV}$ ). For the participation number  $P = p \cdot N$  we find a scaling according to  $P \propto N^\beta$  with an exponent  $\beta = 0.9 \pm 0.02$ . For the eigenstates this would corre-

spond to a power-law decay,  $\psi(r) \propto r^{-\alpha}$ , with  $\alpha \sim 0.825 \pm 0.015$ . This is of the same order as the exponents calculated by Rieth and Schreiber<sup>28</sup> for the vertex model of a two-dimensional Penrose tiling, but indicates a weaker decay than observed by Fujiwara *et al.* for decagonal Al-Cu-Co (where  $\beta$  was found to vary between 0.6 and 0.9). Again this contrasts with the result for icosahedral Al-Pd-Mn where almost no variation in the participation ratio was found on going from the 1/1 to the 2/1 approximant.<sup>23</sup>

Altogether we find that the electronic structure of icosahedral Al-Pd-Re is outstanding in two respects. (i) The spectrum of all approximants is characterized by deep gaps and pseudogaps around the Fermi energy. For a certain 1/1 approximant we have even found a real gap immediately below the Fermi energy. Deep pseudogaps have been predicted for many quasicrystalline approximants, but none of these studies predicted a real gap. If we allow for a fractional occupancy of even a small number of sites (such as it often occurs in quasicrystalline structures), the Fermi energy can be placed into the gap, creating an insulating phase. A periodic

approximant can be constructed by imposing a linear phason strain. This indicates the possibility that even minimal structural rearrangements in the icosahedral phase describable in terms of inhomogeneous phason strains induce a metal-insulator transition. (ii) The participation ratio of the eigenstates in the region of the Re-5*d* band suggests scaling behavior indicative of a critical character of the eigenstates—in contrast to the behavior observed in icosahedral Al-Pd-Mn where the participation ratio of the Mn-3*d* dominated states hardly varies in the low-order approximants. To our knowledge, scaling behavior has not been observed to date in realistic icosahedral quasicrystals. Our observation supports the scaling approach to electronic transport in highly resistive quasicrystals.

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\*Present address: Institut für Materialphysik, Universität Wien, A 1090 Wien, Austria.

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