

Semiconducting Al–transition-metal quasicrystals

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We report on a class of icosahedral aluminum–transition-metal (Al-TM) alloys with true semiconducting behavior. Our description of the structure of these icosahedral quasicrystals is based on the six-dimensional Katz-Gratias-Boudard (KGB) model of the face-centered-icosahedral (fci) quasicrystal and its rational approximants. The shell structure of the atomic surfaces in perpendicular space defines the chemical order of aluminum and transition-metal (TM) atoms leading to semiconducting transport properties. In transition-metal aluminides the hybridization between the Al(s,p) and transition-metal d orbitals is responsible for the formation of a semiconducting gap in the electronic spectrum. We have analyzed the electronic charge distribution and observed an enhanced charge density along the Al-TM bonds that is characteristic of covalent bonding. The existence of an energy gap in the electronic spectrum at or in the vicinity of the Fermi level is explicitly demonstrated for several low-order approximants in the hierarchy of Fibonacci approximants which converges to the icosahedral quasicrystals of the fci class, to which also the i -AlPdRe belongs. We predict existence of truly semiconducting quasicrystalline 1/1-approximants. Our results also lead to the prediction of the existence of new semiconducting quasicrystals with specified Al-TM compositions. The possibility of the existence of a semiconducting band gap suggests an explanation for the anomalously high resistivity of the icosahedral AlPdRe quasicrystals. We demonstrate that substitutional defects violating the ideal Al-TM ordering predicted by the KGB model lead to the formation of localized states in the band gap. A real sample of i -AlPdRe thus seems to be a semiconductor with a band gap filled by the localized states.

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I. INTRODUCTION

Among the many exotic physical properties of quasicrystals, their tendency to show high electrical resistivities and negative temperature coefficients has been most extensively studied. The possible occurrence of a metal-insulator transition in highly resistive quasicrystals, and in icosahedral AlPdRe in particular, is a highly challenging and controversial subject.^{1–12} The large resistivities measured for icosahedral AlPdRe reach those of heavily doped semiconductors, making this alloy a most promising candidate for studying a metal-insulator transition.^{3–6} Delahaye *et al.*³ found that the conductivity of i -AlPdRe follows Mott's variable-range-hopping (VRH) conduction law¹³ in the temperature range 20–600 mK. Hence the i -AlPdRe phase behaves like a disordered insulator at very low temperature. Very recent magnetoresistance measurements^{9,10} also confirm the VRH mechanism, but here the Efros-Shklovskii variable-range-hopping mechanism¹⁴ incorporating the Coulomb interaction seems to be more appropriate.

The physical origin of the observed hopping conductivity in i -AlPdRe has not been satisfactorily explained so far. Many studies have been devoted to the investigation of the impact of the quasicrystallinity on the transport properties of quasiperiodic systems.^{15–22} Although these studies agree on substantial deviations from a ballistic transport regime and predict a weak metallic conductivity for infinite quasicrystals, this deviation is not strong enough to explain the anomalously high resistivities of some i -AlPdRe samples which can reach values close to 1 Ω cm. For an overview of the proposed models of anomalous transport mechanisms we

refer to the review paper 1. The existence of a VRH conductivity in certain i -AlPdRe specimens, together with tunneling experiments²³ suggesting the existence of a very deep pseudogap in the electronic density of states (DOS), leads to the question whether eventually quasicrystals with a true semiconducting gap might exist.

In this paper we demonstrate that a special Al–transition-metal (TM) ordering can lead to truly semiconducting quasicrystals. We predict the existence of semiconducting quasicrystalline 1/1 approximants with a semiconducting band gap of several tenths of an eV. Our results justify us also to predict the existence of semiconducting quasicrystals with a specified composition. We show that by a judicious selection of transition metals to be alloyed with Al, we can find alloys with a semiconducting gap at the Fermi level for a hierarchy of approximants to a quasicrystal. As the electron/atom ratio placing the Fermi level into the gap is slightly different for each approximant, this suggests that the gap persists also in the quasiperiodic limit.

The existence of a semiconducting gap is found to depend critically on a particular kind of Al-TM ordering defined by a simple rule in the six-dimensional (6D) superspace. Any deviation from this 6D order leads to the formation of strongly localized defect states in the gap. A semiconductor is characterized by the fact that a mild disorder leads to the formation of localized states in the gap which contribute to the electronic conductivity through a hopping process. The most likely disorder in quasicrystals and their approximants is chemical substitutional disorder. In Sec. IX for a 1/1 AlPtIr approximant we explore the effect of a substitution of Al by Ir and of an interchange of Al and Ir atoms. The electronic-

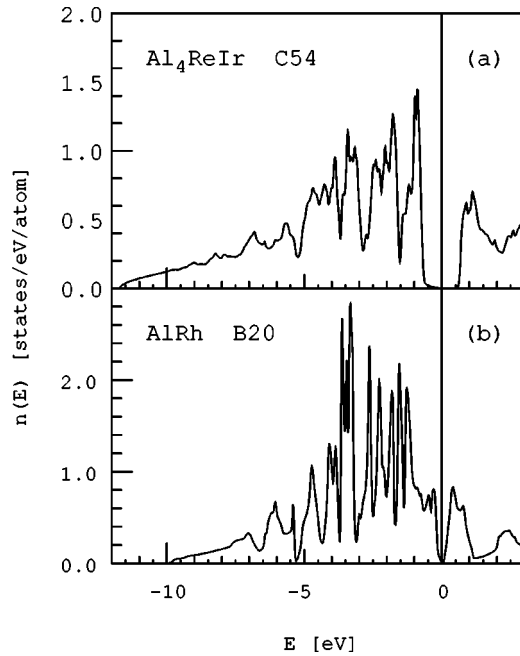


FIG. 1. Total electronic density of states of crystalline Al_4ReIr in the C54 structure (a) and AlRh in the B20 structure (b).

structure calculation shows that both processes lead to the formation of states in the gap and that these states are strongly localized. As the sequence of quasiperiodic approximants converges to the icosahedral quasicrystal with face-centered-icosahedral (fci) modulation, the structural type to which also the stable $i\text{-AlPdRe}$ phase belongs, we discuss also a possibility that a real sample of $i\text{-AlPdRe}$ is a semiconductor with a band gap filled by localized states.

II. SEMICONDUCTING INTERMETALLIC COMPOUNDS

Alloys composed of metallic elements are naturally expected to be metallic too. This expectation is fulfilled in the vast majority of cases. However, some exceptional cases of semiconducting intermetallic compounds are known. For instance, some crystalline transition-metal aluminides, such as RuAl_2 in the C54 structure were found to be semiconducting.^{24–27} The origin of this semiconducting behavior is a special metal-covalent bonding between aluminum and transition-metal atoms.^{28,29} The semiconducting behavior of transition-metal aluminides is observed mostly in specific crystalline structures. Transition-metal disilicides TMSi_2 with the C54 (TiSi_2), C40 (CrSi_2) or C11_b (MoSi_2) structures are such a family of structures favoring the formation of a gap in the valence band.²⁸ The semiconducting RuAl_2 compound belongs to this class. Other examples are the BiF_3 structure²⁶ in which TM aluminides like Fe_2VAl exhibit a nearly semiconducting behavior, or the recently reported FeGa_3 structure.³⁰ As an example of a semiconducting crystalline compound we present here Al_4ReIr in the C54 structure.²⁹ Figure 1(a) shows its total density of states. The most striking feature of the DOS is a wide gap at the Fermi level. A semiconducting behavior has also been observed in FeSi in the B20 structure.^{31–34} Various spectroscopic mea-

surements and electronic structure calculations confirm a narrow gap of ≈ 0.13 eV in the electronic spectrum just at the Fermi level. The B20 structure has $P2_13$ space-group symmetry and consists of eight atoms per unit cell in a simple cubic lattice. Atoms are located at (u, u, u) , $(u + 0.5, \bar{u} + 0.5, \bar{u})$ and the points generated by threefold symmetry about the (111) axis, $u \approx 0.16$. From the viewpoint of quasicrystals the important point is to recognize that the B20 structure is the lowest 0/1 approximant of the hierarchy of Fibonacci approximants F_{n+1}/F_n , all with $P2_13$ space-group symmetry, that for $n \rightarrow \infty$ converge to the quasicrystalline *fci* structure, i.e. the structural class to which also $i\text{-AlPdRe}$ belongs. We have found that after replacement of Si by Al and Fe by a group IX transition metal the narrow band gap in the electronic spectrum does not disappear and remains in the spectrum. In Fig. 1(b) the DOS of AlRh in the B20 structure is shown. The DOS has at the Fermi level a gap of nonzero width.

The next 1/0 approximant has 32 atoms per unit cell. We have found out that a $\text{Al}_{24}\text{Ir}_8$ compound with the structure of a 1/0 approximant is also very close to semiconducting behavior.³⁵ In Secs. V and VII we shall demonstrate that higher quasicrystalline approximants with $P2_13$ symmetry can also be intermetallic semiconductors.

III. KATZ-GRATIAS-BOUDARD MODEL OF FCI AL-TM QUASICRYSTALS

Our description of the structure of the icosahedral (i) quasicrystals of the Al-Pd-Mn(Re) class is based on a modified Katz-Gratias-Boudard (KGB) model³⁶ producing a good agreement with the experimental neutron-diffraction data for $i\text{-Al-Pd-Mn(Re)}$.³⁷ The model of three atomic surfaces was originally proposed by Katz, Gratias, and co-workers^{38,39} for interpretation of diffraction spectra of fci quasicrystals. Boudard *et al.*⁴⁰ proposed a shell structure of atomic surfaces and successfully applied the model to the description of the structure of the icosahedral AlPdMn . Our KGB model of Al-TM fci quasicrystals starts from a 6D face-centered cubic lattice with the vertices decorated by three kinds of triacontahedral atomic surfaces; see Fig. 2. The atomic surfaces have an inner shell structure determining the Al-TM chemical order of the quasicrystal: on the “even” nodes ($n_0 = [000000]$) and on the “odd” nodes ($n_1 = [100000]$) the TM core is surrounded by an outer Al shell, the body-centered bc_1 positions ($bc_1 = \frac{1}{2}[111111]$) is decorated with a TM surface. The bc_0 positions ($bc_0 = \frac{1}{2}[011111]$) are empty. The inequivalence of the atomic surfaces centered at the even and odd nodes breaks the simple cubic symmetry of the 6D lattice and leads to a face-centered superstructure. The n_0 node is truncated by its intersections with its 12 images displaced by τ^3 (the golden mean $\tau = (1 + \sqrt{5})/2$) along the fivefold axes [indicated by the dotted line in Fig. 2(a)]. The fivefold radii of the large triacontahedra at n_0 and n_1 are τ and the radius of the smaller one at bc_1 is τ^{-1} . The radii of the inner shells containing TMs only are $2\tau^{-1}$ at n_0 and τ^{-1} at n_1 . The described shell structure of the atomic surfaces defines the Al-TM ordering which has appeared to be crucial for formation of a band gap in the electronic spectrum; see Fig.

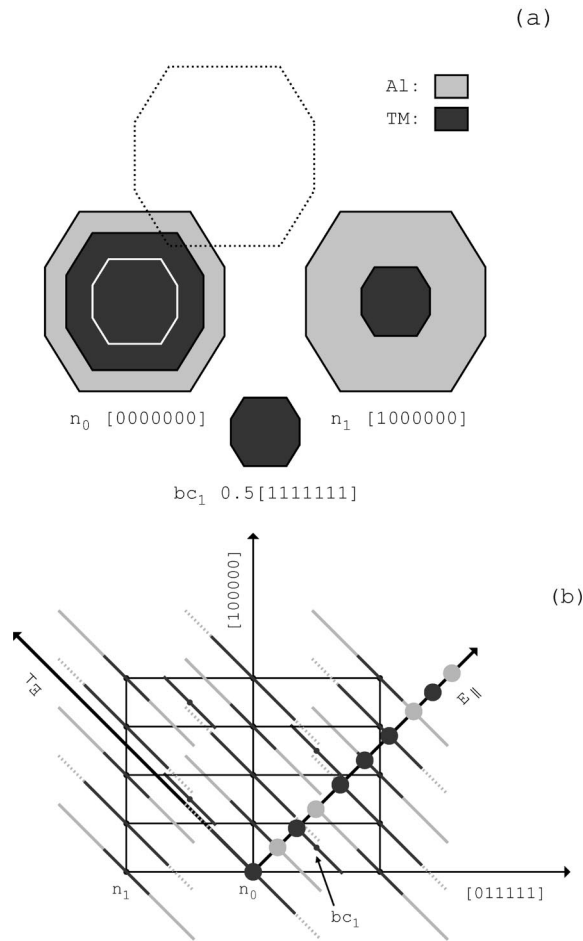


FIG. 2. A 6D Katz-Gratias-Boudard model of a fci icosahedral quasicrystal. (a) Internal structure of the three kinds of atomic surfaces in form of triacontahedra that decorate even n_0 , odd n_1 , and body-centered vertices bc_1 of a 6D cubic lattice. Internal dark regions correspond to transition-metal atoms, and outer shells correspond to Al atoms. In model of i -AlPdRe Pd atoms occupy bc_1 and the middle shell in the n_0 atomic surface, Re atoms occupy core regions in both n_0 and n_1 atomic surfaces. The odd n_0 triacontahedron is truncated by its intersections with its 12 images displaced by τ^3 along the fivefold axes (indicated by a dotted triacontahedron). (b) A schematic representation of quasiperiodic ordering and the mechanism of the Al-TM ordering. Three kinds of triacontahedra (indicated here by line segments; the three-dimensional atomic surfaces are flat in 6D) decorate even n_0 , odd n_1 and body-centered bc_1 vertices of a 6D cubic lattice. Positions of Al (light circles) and TM atoms (dark circles) in real space $E_{||}$ are defined by its intersection with the atomic surfaces. If the orientation of $E_{||}$ with respect to the 6D lattice is irrational, one obtains an infinite quasicrystal. A rational orientation corresponds to quasicrystalline approximants.

2(b). For ternary i -AlPdMn Boudard also defined a core triacontahedron inside the larger TM triacontahedron at the “even” node. In our model this core has a radius $2\tau^{-2}$. Occupation of Al and TM sites in case of i -AlPdMn is the following. A Mn core is surrounded by an inner Pd shell and an outer A shell at the “even” nodes, a Mn core and outer Al shell are at the “odd” nodes, and a Pd surface is at the bc_1 positions.

Periodic approximants are constructed by imposing a linear phason strain (i.e., a certain deformation of the atomic surfaces in the 6D hypercubic lattice) describable by a replacement of the golden mean τ in the corresponding formalism by a rational approximant given in terms of the Fibonacci numbers F_n , $\tau_n = F_{n+1}/F_n$ with $F_0=0$, $F_1=1$, $n=0,1,2,\dots$. The 1/0 approximant has 32 atoms/cell, the 1/1 and 2/1 approximants have 128 and 544 atoms/cell respectively, and the space-group symmetry is $P2_13$ for all approximants.

As i -AlPdMn and i -AlPdRe belong to the same structural class, the KGB can also be used as a structural model for i -AlPdRe if one replaces Mn atoms by homologous Re atoms. In the present work the model has been used also for generating a sequence of Al-TM approximants. In this case TM atoms occupy both TM sites of the KGB model. From the viewpoint of the eventual semiconducting behavior, a possible TM-TM' ordering has almost no effect on the existence of a band gap. The repartition of the two different TM species within the TM sites defined in this model have only a minor effect on the band gap. On the other hand, the shell structure of atomic surfaces in the KGB model defines the Al-TM ordering which has proved to be the most important prerequisite for the presence of a semiconducting band gap in the electronic structure. The KGB model provides idealized atomic coordinates. To obtain a semiconducting band gap in the electronic structure one has to allow formation of covalent Al-TM bonds. The strength of Al-TM bonds depends crucially on the structural relaxation of the model under the Hellmann-Feynman forces, which leads to small shifts of atoms (up to 0.2 Å) from their ideal positions and results in shorter interatomic distances between Al and TM atoms.

IV. COMPUTATIONAL PROCEDURE

We have used advanced local-density-functional techniques to perform a series of *ab initio* electronic structure calculations for a sequence of quasicrystalline approximants. The electronic structure of a series of approximants with different chemical compositions has been calculated using the Vienna *ab initio* simulation package VASP.^{41,42} VASP performs a variational solution of the Kohn-Sham equations in a plane-wave basis, using projector-augmented-wave potentials for describing the electron-ion interaction. The calculation of the Hellmann-Feynman forces acting on the atoms allows us to perform a full optimization of the atomic positions in the unit cell and of the lattice parameters. During the relaxation a network of chemical bonds with significant degree of covalency is formed. The full structural relaxation can result in an opening real gaps on the place of the existing pseudogaps or in a widening of the existing gaps.²⁹

The final DOSs for relaxed structures were evaluated within the tight-binding linear-muffin-tin-orbital calculations⁴³ (TB-LMTO) as here a very dense Brillouin zone (BZ) sampling necessary for resolving the fine structure of the density of states can be achieved. This is necessary for excluding the possibility that states located in a small part of the BZ that close the gap. It is well known that local density

approximation (LDA) calculations predict for ordinary semiconductors band gaps that are smaller by a factor of 2 than the experimentally observed ones. Only in a few exceptional cases the LDA predicts a larger gap than found in many-body calculations or in experiments.⁴⁴ However, this happens only for a special type of correlation interactions. Strong correlation effects arising from on-site Coulomb interaction in metallic systems with narrow bands (such as TM or rare-earth compounds) tend to broaden the gap and eventually even induce a Mott-Hubbard metal-insulator (MI) transition.⁴⁵ However, the Mott-Hubbard mechanism for the MI transition is different from the covalent bonding mechanism inducing the semiconducting behavior of quasicrystals and their approximants. On the other hand, in real systems both mechanisms can constructively cooperate in the band gap formation.

V. TRULY SEMICONDUCTING 1/1 APPROXIMANTS

The 1/1 approximant has 128 per unit cell. The structural model was generated from the 6D KGB model by the cut-and-projection method. The cubic unit cell of the model contains 14 Wyckoff positions, five with a fourfold multiplicity and nine with 12-fold multiplicity. The occupation of the sites by aluminum or transition-metal atoms is distinguished by their coordinates in the perpendicular space according to the internal structure of atomic surfaces of the KGB model. TM sites are in centers of the atomic surfaces at both even and odd 6D positions and fill the entire atomic surface at the body-centered sites. Aluminum sites correspond to the outer shells of the atomic surfaces. In the first part of our study, all TM sites were occupied by Ir atoms only. The resulting composition is $\text{Al}_{88}\text{Ir}_{40}$. Figure 3 shows the corresponding DOS for a model with ideal atomic positions as obtained from the 6D projection and a model with atomic positions optimized by Hellmann-Feynman forces. The most striking feature in the electronic DOS of the model with ideal coordinates is the existence of narrow band gaps in the vicinity of the Fermi level. The narrow band gaps open at band fillings of 600 and 648 electrons. The structural relaxation results in closing the gap at 600 electrons and a substantial widening of the gap at the band filling of 648 electrons. The band gap in the relaxed model is ≈ 0.6 eV above the Fermi level and its width is 0.59 eV. To get a band gap at the Fermi level a change of composition is necessary.

In a semiconducting quasicrystal the Fermi level must fall into the band gap. Assuming a rigid band behavior, this condition is satisfied for a certain band filling which for the 1/1 approximants is 648 electrons, i.e., the electron per atom ratio is $e/a = 5.0625$. If in the 1/1 approximant with composition $\text{Al}_{88}\text{TM}_{40}$ all TM are atoms of group IX, the band gap lies above the Fermi level; if all TM atoms belong to group X the band gap is below the Fermi level. The critical e/a ratio leading to the semiconductivity can be achieved by a combination of two types of TM atoms with different numbers of valence electrons, provided the substitution does not change the DOS. The band-filling condition of 648 electrons/cell is met for three stoichiometries: $\text{Al}_{88}\text{TM}(10)_{24}\text{TM}(9)_{16}$, $\text{Al}_{88}\text{TM}(10)_{36}\text{TM}(6)_4$, and

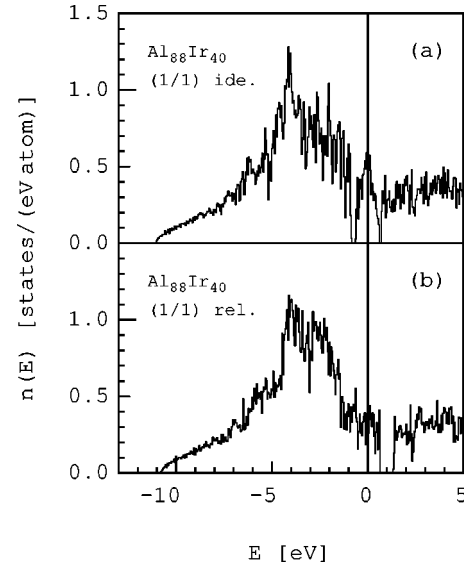


FIG. 3. The total electronic densities of states for a model with ideal atomic positions as obtained from the 6D projection (a) and a model with atomic positions optimized by Hellmann-Feynman forces (b). In model (a) two narrow band gaps open at the band fillings of 600 and 648 electrons. The structural relaxation results in closing the gap at 600 electrons and a substantial widening of the gap at the band filling of 648 electrons.

$\text{Al}_{88}\text{TM}(11)_{12}\text{TM}(9)_{28}$, where $\text{TM}(i)$ is a transition-metal atom with i number of valence electrons. Considering all combinations of TM's from the 3d to 5d rows, these rules provide the composition of 27 possibly semiconducting 1/1 approximants, e.g., $\text{Al}_{88}\text{Pd}_{24}\text{Ir}_{16}$, $\text{Al}_{88}\text{Pt}_{24}\text{Ir}_{16}$, $\text{Al}_{88}\text{Pd}_{24}\text{Rh}_{16}$, $\text{Al}_{88}\text{Pd}_{36}\text{W}_4$, $\text{Al}_{88}\text{Pt}_{36}\text{W}_4$, $\text{Al}_{88}\text{Pd}_{36}\text{Mo}_4$, $\text{Al}_{88}\text{Au}_{12}\text{Ir}_{28}$, $\text{Al}_{88}\text{Ag}_{12}\text{Ir}_{28}$, $\text{Al}_{88}\text{Cu}_{12}\text{Ir}_{28}$,

We have found that the existence of the band gap is rather insensitive to the choice of the transition-metal atoms. On the other hand, while the substitution of one TM atom by another TM atom has a minor effect on the shape and width of the gap, an interchange of Al and TM atoms has a substantial influence on the gap; the gap is filled in by some isolated groups of states and eventually disappears. The role of substitutional defects will be discussed in Sec. IX.

We have explicitly calculated the electronic structure of more than half of the 27 possibly semiconducting 1/1 approximants. The exact coordinates of atoms for every model were obtained by a structural relaxation using the VASP program. In all calculated approximants we found a semiconducting band gap or at least a very deep pseudogap in the DOS. Figure 4 shows several examples of the semiconducting 1/1 approximants. In these systems, in each stoichiometric variant, one TM constituent is varied from 3d to 5d homologous TM atoms.

The width of the gap for the 1/1 approximant $\text{Al}_{88}\text{Pd}_{24}\text{Ir}_{16}$ is 0.52 eV. The semiconducting gaps in the DOSs of $\text{Al}_{88}\text{Pd}_{24}\text{Rh}_{16}$ and $\text{Al}_{88}\text{Pd}_{24}\text{Co}_{16}$ are 0.45 and 0.22 eV, respectively. It is remarkable that in these compounds additional deep pseudogaps in the DOS are also observed. A pronounced pseudogap in the DOS of $\text{Al}_{88}\text{Pd}_{24}\text{Ir}_{16}$ is seen below E_F at the band-filling 600 electrons. This is the same gap that we

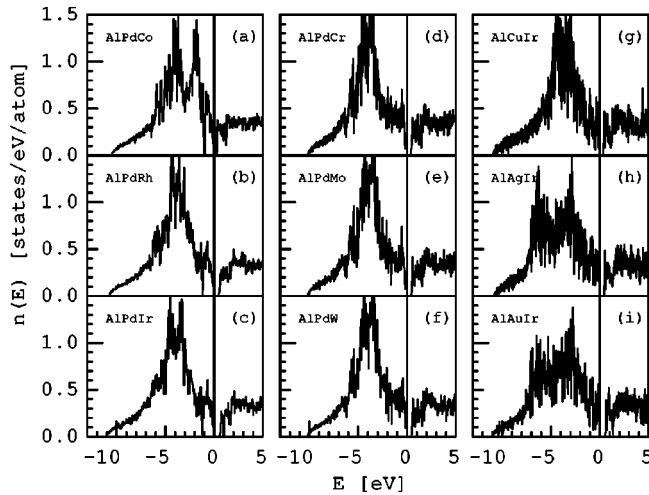


FIG. 4. Total electronic density of states of the truly semiconducting quasicrystalline 1/1 approximants. First column from top: (a) $\text{Al}_{88}\text{Pd}_{24}\text{Co}_{16}$, (b) $\text{Al}_{88}\text{Pd}_{24}\text{Rh}_{16}$, and (c) $\text{Al}_{88}\text{Pd}_{24}\text{Ir}_{16}$. Second column from top: (d) $\text{Al}_{88}\text{Pd}_{36}\text{Cr}_4$, (e) $\text{Al}_{88}\text{Pd}_{36}\text{Mo}_4$, and (f) $\text{Al}_{88}\text{Pd}_{36}\text{W}_4$. Third column from top: (g) $\text{Al}_{88}\text{Cu}_{12}\text{Ir}_{28}$, (h) $\text{Al}_{88}\text{Ag}_{12}\text{Ir}_{28}$, and (i) $\text{Al}_{88}\text{Au}_{12}\text{Ir}_{28}$. Calculated on a grid of 176 irreducible \mathbf{k} points.

observed in $\text{Al}_{88}\text{Ir}_{40}$ model with the ideal atomic positions and also in our previous results^{11,12} for $\text{Al}_{88}\text{Pd}_{20}\text{Re}_{20}$. A gap of 0.35 eV was also found in the DOS of a 1/1 approximant with the composition $\text{Al}_{88}\text{Pd}_{36}\text{W}_4$. As the content of tungsten atoms is rather small their substitution by homologous Mo or Cr has only a minor influence on the width of the gap. A remarkable gap was also found in the 1/1 approximant with the composition $\text{Al}_{88}\text{Au}_{12}\text{Ir}_{28}$. A similar result but with a narrower gap was also obtained when Au atoms were replaced by Ag or Cu. One can observe that the replacement of a 3d metal by a 4d or 5d metal always leads to the wider semiconducting gap. The width of the gaps are largest in case of 5d metals and smallest in case of 3d metals.

Although all studied approximants are stable with respect to the structural relaxation, we cannot say anything about the thermodynamic stability of these compounds. The thermodynamic stability of a phase depends on the existence of other phases with the same composition or, similar composition. Our experience with the stability of crystalline semiconducting intermetallic compounds^{28,29} indicates that in the case 3d metals magnetic interactions can destroy semiconductivity. While Al_2Os and Al_2Ru in the C54 structure exhibit a semiconducting gap, Al_2Fe adopts a metallic triclinic structure and shows a spin-glass behavior. The best chance to get real samples of the semiconducting 1/1 approximants is therefore for the compounds with 5d or 4d TM atoms only.

VI. COVALENT BONDING AND SEMICONDUCTING BAND-GAP FORMATION

The physical mechanism leading to gap formation and semiconducting behavior in quasicrystalline approximants is apparently not very different from that leading to the existence of semiconducting crystalline intermetallic com-

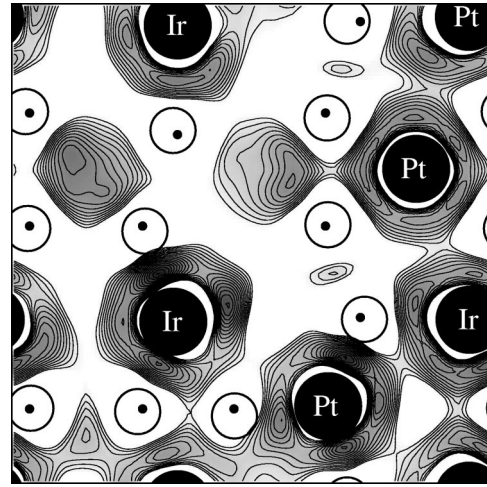


FIG. 5. The difference charge-density distribution of 1/1- $\text{Al}_{88}\text{Pt}_{24}\text{Ir}_{16}$. The figure shows a contour plot of the difference valence-charge distribution in the (x,y) plane for $z=0.345$. Positions of Al atoms close to this plane are marked by open circles, the dots slightly off center mark the positions in the ideal structure. Positions of Pt and Ir atoms are marked by filled circles. The contour plot represents the regions of positive difference electron density, in the blank space the difference density is negative. A possible covalent bonding is indicated by enhanced charge distribution along connections between atoms. The formation of metallovalent Al-TM bonds is clearly seen.

pounds. For the crystalline aluminides we have been able to demonstrate^{28,29} that the gap is a consequence of the bonding-antibonding splitting of strong (s,d) hybrid orbitals on the TM atoms and (s,p) hybrid orbitals on the Al atoms. The bonding-antibonding splitting of hybrid orbitals results in a covalent character of Al-TM bonds and in at least partially covalent Al-Al bonds. A bonding-antibonding splitting of the hybrid orbitals is of course a very general feature—the important point is that the gaps in all bands overlap so that a semiconducting behavior results.²⁹ Such a situation is realized if all atomic orbitals contribute to all relevant hybrid states—this occurs precisely for a low site-symmetry. Chemical bonds with a high degree of covalency are formed during the structural relaxation and optimization of atomic positions. The most significant consequence of the structural relaxation are smaller interatomic distances between those aluminum and TM atoms where covalent bonds are formed. It is noticeable that the observed formation of band gaps shows many symptoms of the Peierls mechanism for a band-gap formation. The covalent bonding manifests itself by distinct electron-density maxima in the bond centers.^{28,29} Recently Kirihaara and co-workers^{46,47} reported direct evidence of covalent bonds in α - AlMnSi (i.e., the 1/1 approximant to the icosahedral phase) and i - AlPdRe using a Rietveld refinement of the diffraction data. Whereas it is difficult to generalize the construction of symmetrized hybrid orbitals to the quasicrystal, the charge density analysis is readily applicable. Figure 5 shows the difference-electron density (i.e., the self-consistent density minus a superposition of the atomic electron densities) in 1/1- AlPtIr calculated in the (x,y) plane at $z=0.345$: density maxima representing

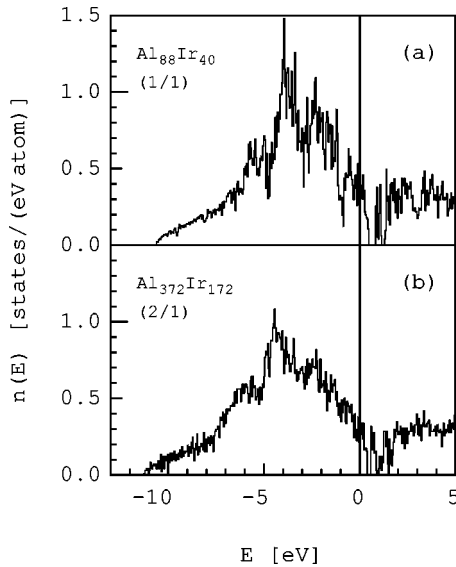


FIG. 6. Total electronic density of states of the 1/1 approximant $\text{Al}_{88}\text{Ir}_{40}$ (a) and the 2/1 approximant $\text{Al}_{372}\text{Ir}_{172}$ (b). The ideal atomic positions obtained by a 6D cut projection were relaxed using a set of classical Al-Ir interatomic potentials. The classical relaxation leads to imperfect resolution of the band gap, cf. Fig. 3(b).

metallocovalent bond charges along Al-TM bonds and partially also Al-Al bonds are readily recognized. Hence we conclude that strong hybridization plays an important role in the formation of semiconducting gaps in quasicrystals and approximants as well.

VII. SEMICONDUCTING 2/1 AND HIGHER APPROXIMANTS

Admittedly, it seems to be desirable to perform similar investigations for higher order approximants. However, as the 2/1 approximant already has 544 atoms/cell, the structural optimization of such a huge cell with Hellmann-Feynman forces requires an extreme computational effort that is close (and eventually even beyond) what is now computationally feasible. Therefore this study has been so far restricted only up to 1/1 approximants.

The electronic structure of a model of 2/1 approximant with atomic positions obtained directly by the cut-projection does not exhibit any gap.¹¹ Although, at present, we are not able to do a full structural relaxation of the 2/1 approximant and thus predict a composition of possibly semiconducting 2/1 approximants, we are at least able to demonstrate that the 2/1 approximant also can exhibit semiconductivity. We relaxed the 2/1 approximant with the Al-Ir composition using the semiempirical interatomic potentials.⁴⁸ The Al-Ir potentials were derived from the Al-Co potentials by adjusting the Al-Co interaction to a larger radius of Ir atoms.

Figure 6 demonstrates that band gaps also open in the DOS of the 2/1 approximant after its relaxation by classical interatomic potentials. Contrary to the previous cases one can see not only one large gap, but two narrower gaps. However, our experience with relaxation of the 1/1 approximants indicates that this is a consequence of the insufficiently ac-

curate description of the interatomic bonding by the semiempirical interatomic potentials used for the relaxation. Figure 6(a) shows, for comparison, the DOS of the AlIr 1/1 approximant also relaxed by the same classical interatomic potentials. Also in this case instead of one wide gap [cf. Fig. 3(b)], two narrower gaps are formed. We therefore assume that after full relaxation of the 2/1 approximant with quantum-mechanically calculated forces only a single wide band gap remains in the electronic spectrum. Nevertheless, we cannot exclude that in the 2/1 approximant a band gap in the electronic spectrum opens not only for one value of the band-filling, which, of course, does not contradict its supposed semiconductivity.

In the sequence of Al-TM quasiperiodic Fibonacci approximants to the fci quasicrystal a semiconducting behavior can exist in case of 0/1, 1/0, 1/1, and 2/1 approximants. One can quite naturally also assume the same behavior for any larger approximant.

VIII. SEMICONDUCTING QUASICRYSTALS

The extrapolation of the observed band-gap formation in the sequence of quasiperiodic approximants to infinite quasicrystals leads to an assumption that also the fci quasicrystals may be semiconducting. The sequence of approximants of our KGB model converges to the structure of *i*-AlPdRe. We therefore assume that the ideal icosahedral quasicrystal-line AlPdRe is also a semiconductor. Although this assumption seems to contradict experimental observations as no true gap in the electronic spectrum has been observed so far, in Sec. IX we shall show that in real samples of *i*-AlPdRe the semiconducting band gap is filled by localized states and thus no real gap can be experimentally observed. On the other hand, the existence of the localized states in the gap explains the experimentally observed VRH hopping conduction mechanism.

It is remarkable that the KGB model very accurately predicts the experimental composition of *i*-AlPdRe samples with the highest resistance ratio R [$\rho(4\text{ K})/\rho(295\text{ K})$] which is considered as a measure of anomalous transport properties.⁹ The KGB model predicts the asymptotic composition $\text{Al}_{0.7073}\text{Pd}_{0.2063}\text{Re}_{0.0864}$, Delahaye *et al.*³ and Srinivas *et al.*⁹ report a nominal composition of their samples of $\text{Al}_{0.705}\text{Pd}_{0.21}\text{Re}_{0.085}$.

We have already noted that as the 5d metals have more extended d-states than the 4d or 3d metals, the semiconducting behavior is more pronounced for Al-TM compounds with 5d metals than with 4d or 3d metals. As *i*-AlPdRe exhibits a behavior that is so far closest to semiconductivity, the simplest way to obtain a quasicrystal with a more pronounced semiconducting behavior is to replace Pd by its 5d homologous Pt, i.e., to prepare an alloy with the composition $\text{Al}_{0.7073}\text{Pt}_{0.2063}\text{Re}_{0.0864}$.

Experience with the semiconducting 1/1 approximants indicates that both transition metals play a symmetric role in Al-TM bonding. The choice of a different combination of transition metals from the same row of the Periodic Table has only a minimal influence on the width and the shape of the band gap. The semiconducting behavior should therefore be

observed for any combination of transition metals $TM(i)$ and $TM(j)$ with i and j number of valence electrons provided the concentrations x , and $y=0.2927-x$ satisfy the following equation: $i \times x + j \times y = 2.6677$. This equation assumes an e/a ratio of 4.7896 and the composition $Al_{0.7073}TM_{0.2927}$, both values are derived from the KGB model. Considering 5d metals from group VI to group XI, only this equation has eight solutions: $Al_{0.7073}Pt_{0.2279}W_{0.0648}$, $Al_{0.7073}Au_{0.1823}W_{0.1104}$, $Al_{0.7073}Pt_{0.2063}Re_{0.0864}$, $Al_{0.7073}Au_{0.1547}Re_{0.1380}$, $Al_{0.7073}Pt_{0.1631}Os_{0.1296}$, $Al_{0.7073}Os_{0.1840}Au_{0.1087}$, $Al_{0.7073}Pt_{0.2592}Ir_{0.0335}$, and $Al_{0.7073}Ir_{0.2759}Au_{0.0168}$. Other possibly semiconducting compounds may be derived by replacing some 5d metals by 4d or even 3d metals. Altogether one has 72 possibly semiconducting quasicrystals. However, in cases of quasicrystals with 3d and 4d TM atoms the semiconducting band gap is expected to be narrower or may even disappear.

We have demonstrated that a semiconducting Al-TM quasicrystal with a wide clean band gap at the Fermi level may exist for a certain e/a ratio. To get a clean semiconducting gap the important criterion is not only the e/a ratio, but also a precise Al-TM ordering (described by the atomic surfaces in six dimensions) and consequently the Al:TM concentration.

Although in real quasicrystals substitutional defects cannot be completely avoided, a minimal number of the defects is obtained for a certain magic Al:TM concentration. In a perfect quasicrystal a clean band gap would be created only for the magic Al:TM concentration which results from the Al-TM ordering defined in 6D space by the KGB model. For the 1/1 approximant with the $P2_13$ symmetry and 128 atoms per unit cell this concentration ratio is 11:5. For each next approximant this concentration may be slightly different. The KGB model predicts for an infinite icosahedral quasicrystal the magic composition $Al_{0.7073}TM_{0.2927}$.

IX. SUBSTITUTIONAL DEFECTS AND LOCALIZED STATES

Figure 7(a) shows the densities of states of the 1/1 approximant with the $Al_{88}Pt_{24}Ir_{16}$ composition. The DOS exhibits a clean and wide semiconducting band gap. Figures 7(b) and 7(c) show the DOSs of the same model with artificial defects: in (b) one selected Al atom is replaced by Ir and in (c) the occupations of one Al site and one Ir site are mutually interchanged. In both cases one observes the formation of groups of states in the gap. Figure 8 presents the band structure of the same three model systems as in the previous figure. In the gap some additional bands with very small dispersion appear. We shall demonstrate that the states in the gap have substantially different character from other states outside the gap. Figure 9 displays the participation ratios for all eigenstates. We remind the reader that the participation ratio $p(E_n)$ is defined as

$$p(E_n) = \frac{\left(\sum_I \sum_{\alpha} |e_{I\alpha}(E_n)|^2 \right)^2}{N \sum_I \left(\sum_{\alpha} |e_{I\alpha}(E_n)|^2 \right)^2}, \quad (1)$$

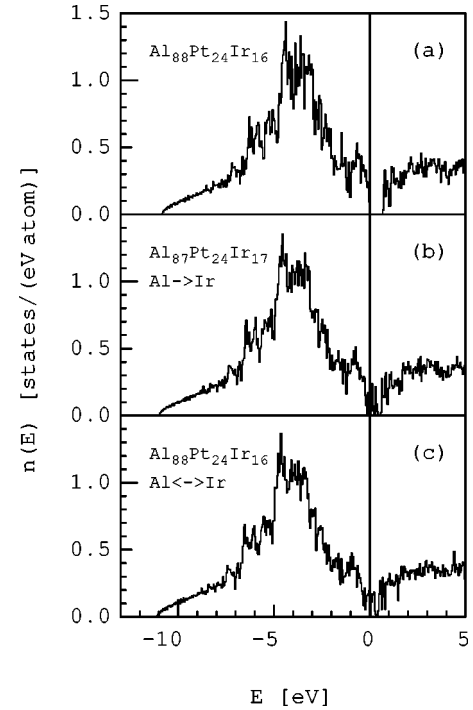


FIG. 7. The densities of states of the 1/1 approximant with the $Al_{88}Pt_{24}Ir_{16}$ composition. The DOS exhibits clean and wide semiconducting band gap (a). (b) and (c) show the DOSs of the same model with created defects: (b) one selected Al atom is replaced by Ir, and (c) occupation of one Al and one Ir sites are mutually interchanged. In both (b) and (c) cases one observes the formation of groups of states in the gap.

where $e_{I\alpha}(E_n)$ are the eigenvectors of an eigenstate with energy E_n in the LMTO basis and the sum is over all lattice sites I and quantum numbers α . N is here the number of atoms in the unit cell. For an extended state we have $p(E_n) \sim O(1)$, for a completely localized state $p(E_n) \sim O(1/N)$. In Fig. 9 one can see that while the states in the vicinity of the band gap are clearly delocalized, the average participation ratio here is ≈ 0.7 . The average participation

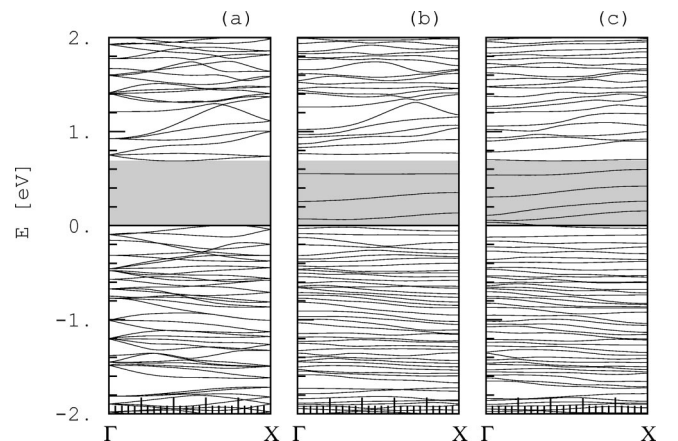


FIG. 8. The band structure of the same three model systems as in Fig. 7. In the gap of the models with defects [(b) and (c)] additional bands with very small dispersion appear. Gray regions indicate position of the band gap.

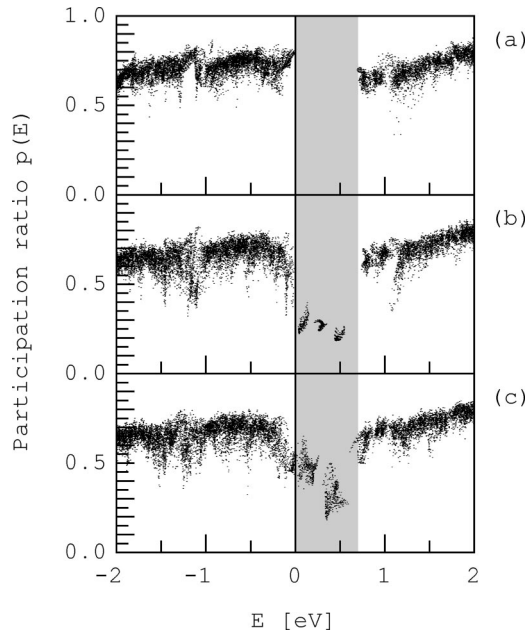


FIG. 9. The participation ratios of the states of the three models from Fig. 7. One can see that while the states in the vicinity of the band gap are clearly delocalized, low values of the participation ratios of the states in the gap indicate their tendency to localize.

ratios of the states in the gap in Figs. 9(b) and 9(c) are 0.25 and 0.40, respectively. The low values of the participation ratios of the states in the gap indicate their tendency to localize. The results presented in Figs. 7–9 correspond to defects created in a unit cell of the model. Because of the periodic repetition of the unit cell of the approximant the defects are also periodically repeated in space. One therefore also observes an interaction of the states localized at the same periodically repeated defects which manifests itself in a weak non-negligible dispersion of the localized bands, as is seen in Fig. 8. To confirm the localized character of the states in the band we constructed a supercell of eight elementary cells and created one defect per such a supercell. The picture of the participation ratios of the states in the supercell is presented in Fig. 10. The average participation ratio of the states in the gap in Figs. 10(b) and 10(c) is 0.04 and 0.09, respectively, values substantially lower than the corresponding previous values. The participation ratios of states in the band gap of the supercell scale substantially down, demonstrating the strongly localized character of these states.

The localized state corresponding to the substitutional defect is visualized in Fig. 11. The figure presents contribution to the charge density from the bands selected from the band gap as seen in Fig. 8(b). The charge density is strongly localized at the position of the introduced Al→Ir substitutional defect. One can naturally also expect the same localized character of the corresponding wave functions. At low temperature, electronic conduction in such a system will proceed by a hopping mechanism.³

X. DISCUSSION AND CONCLUSIONS

In the sequence of Al-TM quasiperiodic Fibonacci approximants to the fci quasicrystal a band gap can exist in the

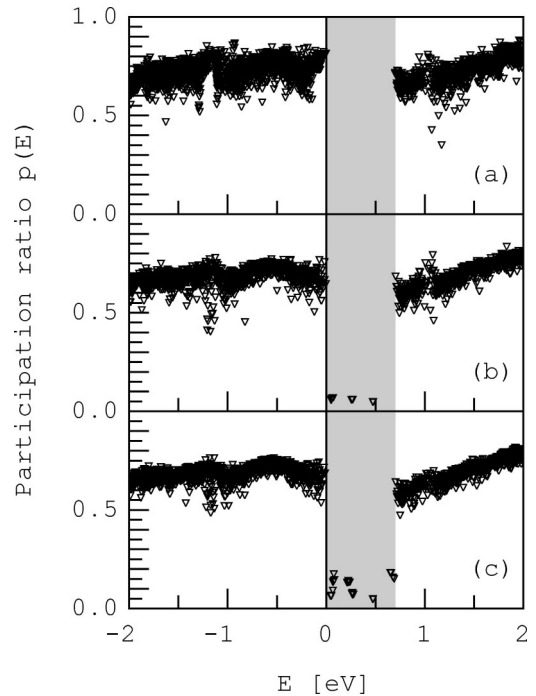


FIG. 10. The picture of the participation ratios of the states of $\text{Al}_{88}\text{Pt}_{24}\text{Ir}_{16}$ in the supercell of eight elementary cells (a). Two kinds of substitutional defects (cf. Fig. 7) are created in the supercell: (b) one selected Al atom is replaced by Ir, and (c) the occupation of one Al and one Ir sites are mutually interchanged. The participation ratios of states in the band gap scales substantially down, and demonstrate the strongly localized character of these states.

electronic spectrum of each approximant. We have demonstrated this explicitly for several lowest approximants. One can quite naturally also assume the same behavior for any larger approximant. Each approximant can thus become semiconducting for a certain stoichiometric composition that shifts the Fermi level into the band gap. The corresponding critical e/a ratio is slightly different for each approximant in the sequence.

The lattice of the lowest 0/1 approximant corresponds to the well known B20 (FeSi) structure; all higher approximants have been constructed by the 6D cut-projection method. We have observed that in the sequence of approximants the band gap can even increase with the increasing size of the approximant, when the atomic structure becomes more complex. The same behavior was observed in crystalline Al_2TM compounds in MoSi_2 , CrSi_2 , and TiSi_2 structures, where for the most complex TiSi_2 structure the semiconducting band gap was the widest.²⁸ All approximants (including higher-order ones) have a $P2_13$ space group symmetry. Out of all cubic space groups, $P2_13$ has the lowest point-group symmetry for the atomic sites: sites with multiplicity 12 have no symmetry at all, sites with multiplicity four have trigonal symmetry (point group 3). A very low point group symmetry of the atomic sites has also been found in the crystalline aluminides showing insulating or nearly insulating behavior.^{28,29}

We have presented several examples of truly semiconducting quasicrystalline 1/1 approximants with compositions

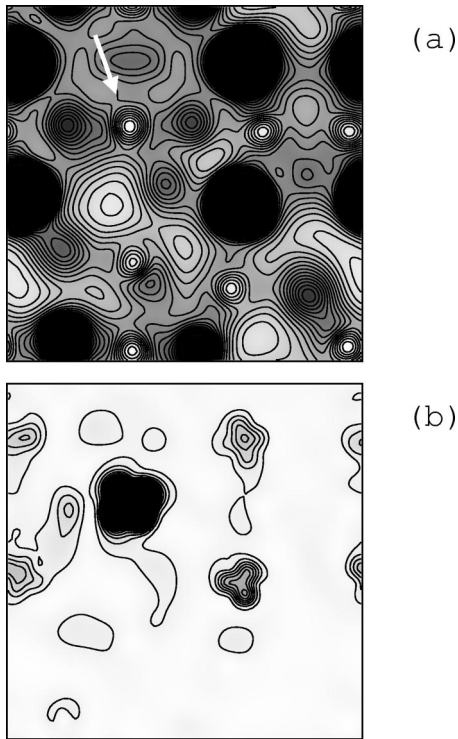


FIG. 11. Visualization of the localized state corresponding to the substitutional defect. (a) represents a valence charge density distribution of the $1/1$ $\text{Al}_{88}\text{Pt}_{24}\text{Ir}_{16}$ approximant displayed for the $z = 0.545$ plane. Dark spots correspond to the charge density of transition-metal atoms. The white arrow marks a position of the Al atom which we replaced by Ir. The introduced substitutional $\text{Al} \rightarrow \text{Ir}$ defect creates states in the band gap; also see Figs. 8(b) and 9(b). (b) presents the contribution to the valence charge density calculated from the defect states in the band gap only. The localized character of the defect states is clearly seen.

of, e.g., $\text{Al}_{88}\text{Pt}_{24}\text{Ir}_{16}$, $\text{Al}_{88}\text{Pt}_{36}\text{W}_4$, or $\text{Al}_{88}\text{Au}_{12}\text{Ir}_{28}$, and with band gaps at the Fermi level of several tenths of eV. Altogether there are 27 such approximants. As the $5d$ metals have more extended d states than $4d$ or $3d$ metals, the semiconducting band gap is larger for the Al-TM compounds with $5d$ transition metals than with $4d$ or $3d$ metals.

The origin of the semiconducting behavior is in the formation of chemical bonds between aluminum and transition-metal atoms with a high degree of covalency. The bonds in these systems are mutually correlated and form a network that incorporates all atoms. The topology of the network follows from the Al-TM ordering defined by the shell structure of atomic surfaces in the six-dimensional KGB model. So far we have not been able to fully characterize the Al-TM ordering in real space. The very low symmetry of orientations of the covalent bonds in space complicates the understanding of the real-space topology of their network. It is remarkable that the observed formation of band gaps has many symptoms of the Peierls mechanism of a band gap formation. The specific covalent bonding results in the appearance of gaps in the electronic spectrum. The observed covalent bonding and band gap formation is not specific to quasicrystals and has also been observed in crystalline Al-TM compounds.^{28,29}

The Al-TM ordering defined in 6D space has a crucial

influence on the electronic structure and transport properties of the Al-TM quasicrystals. The existence of a clean gap in the electronic spectrum is critically sensitive to the Al-TM ordering. Any deviation from the perfect Al-TM ordering, for instance the existence of substitutional defects, leads to the formation of localized states in the gap. Therefore, for real quasicrystals one cannot expect to get a semiconductor with a clean gap as in crystalline Si or Ge. A semiconducting gap of real quasicrystalline approximants is probably more or less filled by localized states.

It is remarkable that a band gap in the electronic spectrum exists (above, below, or at the Fermi level) for almost any transition-metal atom TM in the Al-TM quasicrystalline approximant with $P2_13$ space symmetry, provided Al and TM atoms occupy sites in real space according to the prescription defined by their perpendicular coordinate in 6D space. The Al-TM ordering defined in 6D space results in a critical Al:TM ratio as a prerequisite for the existence of a clean band gap of the electronic spectrum. The position of the band gap determines the critical e/a ratio of the semiconducting approximants. If TM sites are occupied by two different TM atoms, a possible TM-TM ordering has only a minor effect on the width or shape of the band gap.

Our understanding of the electronic structure of the icosahedral quasicrystal with fci modulation is based on the 6D KGB model. A real-space analysis of the structure, chemistry, and bonding in low order approximants would be very welcome. A recent study by Quandt and Elsei⁵⁰ analyzes the structure of isostructural $i\text{-AlPdMn}$ in terms of Mackay and Bergman clusters.

The sequence of approximants converges to the icosahedral quasicrystal with a fci modulation, the structural type to which also the stable $i\text{-AlPdRe}$ phase belongs. We assume that an ideal icosahedral AlPdRe alloy with the composition $\text{Al}_{0.7073}\text{Pd}_{0.2063}\text{Re}_{0.0864}$ and Al:TM ordering predicted by the KGB model would be also a semiconductor. However, for any real sample of $i\text{-AlPdRe}$ the semiconducting band gap is filled by localized states which have their origin in substitutional defects. The localized character of the states in the gap has been explicitly demonstrated.

The existence of localized states in the band gap is consistent with the experimentally observed variable-range-hopping behavior of the temperature dependence of the electronic conductivity of highly resistive samples of $i\text{-AlPdRe}$.^{3,9,10} From the viewpoint of our present results it is not surprising that the resistivity of these samples reaches values which are close to those of doped semiconductors. The electronic structure of $i\text{-AlPdRe}$ has, as we have demonstrated, the character of doped semiconductors. The observed increase of the conductivity with disorder⁴⁹ is also consistent with this picture. Icosahedral AlPdRe thus turns out to be a semiconductor with a band gap filled by the localized states.

The theoretical framework is based on the KGB model of fci quasicrystals. It allows us to predict the existence of many semiconducting approximants and icosahedral quasicrystals. The semiconducting icosahedral quasicrystals with compositions, e.g., $\text{Al}_{0.7073}\text{Pt}_{0.2063}\text{Re}_{0.0864}$, $\text{Al}_{0.7073}\text{Pt}_{0.2592}\text{Ir}_{0.0335}$ or $\text{Al}_{0.7073}\text{Pt}_{0.2279}\text{W}_{0.0648}$ could possibly

be prepared using the same metallurgical techniques as are commonly used for the preparation of high-resistive *i*-AlPdRe samples.

Our analysis sheds light on the six-dimensional character of the physical properties of quasicrystals. Seen in 3D space, the structure-property relationship remains unclear: we have a 3D network of Al-TM bonds with enhanced covalency, but, due to the low site symmetry of all atomic sites, the topology of this network looks chaotic and provides no explanation for the observed metal/semiconductor transition. However, in the 6D space in which the quasiperiodic structure can be embedded as a periodic superstructure we have identified a simple condition for the formation of a semiconducting state, and this rule can be used to predict a whole class of semiconducting approximants and quasicrystals.

The theoretical framework presented here concerns only one structural class of quasicrystals, namely, fci quasicrystals to whom the KGB model is applicable. The whole spectrum of anomalous transport properties need not and presumably

does not have only one reason. Recently, we have demonstrated²² that the quasicrystallinity itself, although not able to account for the semiconducting behavior of *i*-AlPdRe, leads to a substantial deviation from the ballistic transport. On the other hand, transport properties close to semiconducting ones have been observed in Al-Mn decagonal approximants⁵¹ for which the presented 6D theoretical framework is obviously not directly applicable. Nevertheless, here the Al-TM bonding apparently also plays a significant role and deserves a more detailed investigation.

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- ¹See, e.g., the review article by Ö. Rapp, in *Physical Properties of Quasicrystals*, edited by Z. M. Stadnik (Springer, Berlin, 1999), p. 127.
- ²S.E. Burkov, A.A. Varlamov, and D.V. Livanov, *Phys. Rev. B* **53**, 11504 (1996).
- ³J. Delahaye, J.P. Brison, and C. Berger, *Phys. Rev. Lett.* **81**, 4204 (1998).
- ⁴Q. Guo and S.J. Poon, *Phys. Rev. B* **54**, 12793 (1996).
- ⁵M. Rodmar, F. Zavaliche, S.J. Poon, and Ö. Rapp, *Phys. Rev. B* **60**, 10807 (1999).
- ⁶R. Rosenbaum, R. Haberkern, P. Häussler, E. Palm, T. Murphy, S. Hannibal, and B. Brandt, *J. Phys.: Condens. Matter* **12**, 9735 (2000).
- ⁷D. Mayou, *Phys. Rev. Lett.* **85**, 1290 (2000).
- ⁸J. Delahaye and C. Berger, *Phys. Rev. B* **64**, 094203 (2001).
- ⁹V. Srinivas, M. Rodmar, S.J. Poon, and Ö. Rapp, *Phys. Rev. B* **63**, 172202 (2001).
- ¹⁰V. Srinivas, M. Rodmar, R. König, S.J. Poon, and Ö. Rapp, *Phys. Rev. B* **65**, 094206 (2002).
- ¹¹M. Krajčí and J. Hafner, *Phys. Rev. B* **59**, 8347 (1999).
- ¹²M. Krajčí and J. Hafner, *J. Phys.: Condens. Matter* **13**, 3817 (2001).
- ¹³N.F. Mott, *J. Non-Cryst. Solids* **1**, 1 (1968).
- ¹⁴B. I. Shklovskij and A. L. Efros, *Electronic Properties of Doped Semiconductors*, Solid State Physics Vol. 45 (Springer-Verlag, Berlin, 1984).
- ¹⁵B. Sutherland and M. Kohmoto, *Phys. Rev. B* **36**, 5877 (1987).
- ¹⁶T.C. Choy, *Phys. Rev. B* **35**, 1456 (1987).
- ¹⁷G. Kasner, H. Schwabe, and H. Böttger, *Phys. Rev. B* **51**, 10454 (1995).
- ¹⁸T. Fujiwara, T. Mitsui, and S. Yamamoto, *Phys. Rev. B* **53**, R 2910 (1996).
- ¹⁹S. Roche and D. Mayou, *Phys. Rev. Lett.* **79**, 2518 (1997).
- ²⁰S. Roche, D. Mayou, and G. Trambly de Laissardière, *J. Math. Phys.* **38**, 1794 (1997).
- ²¹T. Rieth and M. Schreiber, *J. Phys.: Condens. Matter* **10**, 783 (1998).
- ²²M. Krajčí, J. Hafner, and M. Mihalkovič, *Phys. Rev. B* **65**, 024205 (2002).
- ²³T. Schaub, J. Delahaye, C. Gignoux, C. Berger, G. Fourcaudot, F. Giroud, T. Grenet, and A. Jansen, *J. Non-Cryst. Solids* **252**, 874 (1999).
- ²⁴D. Nguyen Manh, G. Trambly de Laissardière, J.P. Julien, D. Mayou, and F. Cyrot-Lackmann, *Solid State Commun.* **82**, 329 (1992).
- ²⁵S. Ögüt and K.M. Rabe, *Phys. Rev. B* **54**, R8297 (1996).
- ²⁶M. Weinert and R.E. Watson, *Phys. Rev. B* **58**, 9732 (1998).
- ²⁷M. Springborg and R. Fischer, *J. Phys.: Condens. Matter* **10**, 701 (1998).
- ²⁸M. Krajčí and J. Hafner, *J. Phys.: Condens. Matter* **14**, 5755 (2002).
- ²⁹M. Krajčí and J. Hafner, *J. Phys.: Condens. Matter* **14**, 7201 (2002).
- ³⁰U. Häussermann, M. Bostörm, P. Viklund, Ö. Rapp, and T. Björnängen, *J. Solid State Chem.* **165**, 94 (2002).
- ³¹L.F. Mattheiss and D.R. Hamann, *Phys. Rev. B* **47**, 13114 (1993).
- ³²C.-H. Park, Z.-X. Shen, A.G. Loeser, D.S. Dessau, D.G. Mandrus, A. Migliori, J. Sarrao, and Z. Fisk, *Phys. Rev. B* **52**, R16981 (1995).
- ³³J.F. DiTusa, K. Friemelt, E. Bucher, G. Aeppli, and A.P. Ramirez, *Phys. Rev. Lett.* **78**, 2831 (1997).
- ³⁴E.G. Moroni, W. Wolf, J. Hafner, and R. Podloucky, *Phys. Rev. B* **59**, 12860 (1999).
- ³⁵M. Krajčí and J. Hafner, *Phys. Rev. B* **67**, 052201 (2003).
- ³⁶M. Krajčí, M. Windisch, J. Hafner, G. Kresse, and M. Mihalkovič, *Phys. Rev. B* **51**, 17355 (1995).
- ³⁷C.R. Lin, S.T. Lin, C.R. Wang, S.L. Chou, H.E. Horng, J.M. Cheng, Y.D. Yao, and S.C. Lai, *J. Phys.: Condens. Matter* **9**, 1509 (1997).
- ³⁸A. Katz and D. Gratias, *J. Non-Cryst. Solids* **153–54**, 187 (1993).
- ³⁹M. Cornier-Quiquandon, A. Quivy, S. Lefebvre, E. Elkaim, G.

- Heger, A. Katz, and D. Gratias, *Phys. Rev. B* **44**, 2071 (1991).
- ⁴⁰M. Boudard, M. de Boissieu, C. Janot, G. Heger, C. Beeli, H.-U. Nissen, H. Vincent, R. Ibberson, M. Audier, and J.M. Dubois, *J. Phys.: Condens. Matter* **4**, 10149 (1992).
- ⁴¹G. Kresse and J. Furthmüller, *Comput. Mater. Sci.* **6**, 15 (1996); *Phys. Rev. B* **54**, 11 169 (1996).
- ⁴²G. Kresse and D. Joubert, *Phys. Rev. B* **59**, 1758 (1999).
- ⁴³O. K. Andersen, D. Jepsen, and M. Šob, in *Electronic Band Structure and its Applications*, edited by M. Yousouff (Springer, Berlin 1987).
- ⁴⁴D.W. Hess and J.W. Serene, *Phys. Rev. B* **59**, 15617 (1999).
- ⁴⁵G. A. Sawatzky, in *On the Electronic Structure and Related Physical Properties of Transition Metal Compounds*, edited by J. G. Bendorz and K. A. Müller, Springer Series Solid State Sciences Vol. 90 (Springer, Berlin, 1989).
- ⁴⁶K. Kirihara, T. Nakata, M. Takata, Y. Kubota, E. Nishibori, K. Kimura, and M. Sakata, *Phys. Rev. Lett.* **85**, 3468 (2000).
- ⁴⁷K. Kirihara and K. Kimura, *Phys. Rev. B* **64**, 212201 (2001).
- ⁴⁸I. Al-Lehyani, M. Widom, Y. Wang, N. Moghadam, G.M. Stocks, and J.A. Moriarty, *Phys. Rev. B* **64**, 075109 (2001).
- ⁴⁹J.J. Préjean, C. Berger, A. Sulpice, and Y. Calvayrac, *Phys. Rev. B* **65**, 140203 (2001).
- ⁵⁰A. Quandt and V. Elser, *Phys. Rev. B* **61**, 9336 (2000).
- ⁵¹M. Krajčí and J. Hafner, *Phys. Rev. B* **58**, 5378 (1998).