

Clusters and localization of electrons in quasicrystals

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(Received 20 August 1996)

We analyze the relationship between the tendency to electron localization, which is observed in many quasicrystals and approximants, and the local atomic order. Starting from the structural models, we consider atomic clusters that are embedded in a metallic medium, and we study their scattering properties within the multiple-scattering formalism. We show that these local environments can lead to virtual bound states for electrons, i.e., resonances of the wave function in clusters of different length scale. That is consistent with the tendency to localization shown by transport measurements or band-structure calculations. In agreement with the Hume-Rothery picture of quasicrystals, this tendency to localization has a small effect on the total energy. [S0163-1829(97)03805-8]

Quasicrystals of high structural quality reveal unusual properties, and in particular they are close to a metal-insulator transition.¹⁻³ For instance, one of the main features is the low conductivity $\sigma_{4K} = 100-200 (\Omega \text{ cm})^{-1}$ for AlPdMn and AlCuFe, and $\sigma_{4K} < 1 (\Omega \text{ cm})^{-1}$ for AlPdRe, whereas the densities of states at the Fermi level are still metallic, between one-third and one-tenth of the free electron value. This tendency to localization is a major question concerning the quantum-mechanical properties of quasiperiodic potentials. In particular, the role of the long-range quasiperiodic order is not understood. In this respect, it is interesting to study the approximant phases, which reproduce the order of quasicrystals locally, but are periodic on greater length scales.

Experiments indicate that approximant phases, like α -AlMnSi,³ α -AlCuFeSi,⁴ R -AlCuFe, etc.,³ have transport properties similar to those of quasicrystals. This suggests that the local atomic order on the length scale of the unit cell, i.e., 10–30 Å, determines their transport properties. On the theoretical side, band-structure calculations for approximants also reveal specific properties.⁵⁻⁹ The dispersion relations are flat, corresponding to small velocities. Fine peaks in density of states are associated with the flat bands. Moreover, tunneling spectroscopy studies reveal that the density of states of AlCuFe (Refs. 10 and 11) and AlPdRe (Ref. 11) quasicrystals and the α -AlMnSi (Ref. 11) approximant present a narrow pseudogap at the Fermi level of about 50 meV, which is the same order of magnitude as the fine structure of the calculated density of states. Very recently, calculations on a model of a decagonal approximant have shown that eigenstates do not have a uniform weight in the unit cell and tend to be multifractal.¹² These experimental and theoretical results suggest that the local atomic order, on a length scale of 10–30 Å, is responsible for the remarkable transport properties of approximants and quasicrystals of high structural quality.

As for local atomic order, one of the characteristics of quasicrystals and approximants is the occurrence of atomic clusters such as the Bergman type and the MacKay type.^{13,14} This can be a starting point for an analysis of quasicrystals properties. For example, Janot and de Boissieu¹⁴ propose that icosahedral clusters, arranged in a hierarchical way, are

stable entities that are nearly isolated and stabilized by magic numbers of electrons at each length scale. The role of clusters has also been emphasized by other authors (see, for example, Quémerais,¹⁵ Mayou *et al.*,¹⁶ and Jeong and Steinhardt¹⁷).

A difficulty with the model of Janot and de Boissieu is that clusters are assumed nearly isolated, whereas atomic models for quasicrystals are rather homogeneous,¹³ and calculated densities of states have a metallic character.^{3,5-8} Therefore, in this paper, we still assume that the atomic order is characterized by the occurrence of icosahedral clusters, but we consider that these clusters are embedded in a metallic medium, typically an aluminum matrix. Our aim is to check whether the scattering of electrons by clusters, on a scale of 10–30 Å, can localize some electrons.

In a standard description of intermetallic alloys, one starts from a muffin-tin potential, which varies in spheres centered on the atoms and is constant in the space between the spheres. As far as band structure is concerned, an atom is entirely characterized by its scattering properties for incident plane waves. Mathematically, the central quantity is the \mathbf{T} matrix. In the same way, the effect of a group of atoms on band structure will be characterized by its \mathbf{T} matrix, that is, by its scattering properties of plane waves.¹⁸ Starting from the \mathbf{T} matrix of various groups of atoms, we analyze the scattering properties of clusters through a calculation of the variation $\Delta n(E)$ of density of states due to the cluster. We also calculate the structural energy of a cluster, which allows us to test the validity of the Hume-Rothery picture of quasicrystals and approximants, as far as total energy is concerned.¹⁹

In this paper the scattering properties of one MacKay-type cluster and one group of MacKay-type clusters embedded in an aluminum matrix are presented. We consider the MacKay-type cluster of the actual structure of the crystalline approximant α -AlMnSi. The interest of this phase is that its structure is well known,^{20,21} and transport measurements show that it has a very high resistivity ($\rho \approx 4200 \mu\Omega \text{ cm}$ at $T = 4.2 \text{ K}$), comparable to that of high structural quality quasicrystals AlCuFe and AlPdMn.³ The MacKay-type cluster of α -AlMnSi consists of one internal icosahedron of aluminum, one external icosahedron of manganese, and one exter-

nal icosidodecahedron of aluminum, both having the same radius. There are other aluminum atoms between the clusters. The positions of the silicon atoms are not known, but they are supposed to occur as substitution on aluminum sites. As an example of a group of clusters, we consider 12 MacKay-type clusters, obtained after an inflation by a factor $G = \tau^2$ (τ is the golden mean) of the initial cluster. This structure appeared in the structural model proposed in Ref. 14 for the icosahedral AlPdMn phase. The cluster and the group of clusters studied here are not the only ones existing in quasicrystals and approximants, but they are realistic clusters which have the icosahedral symmetry.

In order to calculate the \mathbf{T} matrix of clusters, we have to simplify the model. We consider only the potential due to the transition-metal atoms, which are strong scatterers, and we neglect the potential of all the aluminum atoms that are considered weak scatterers. Furthermore, following a classical approximation,^{22,18} we retain only the potential due to the d orbital of the transition atom. This means that within the framework of the scattering theory, we consider only the phase shift for the $l=2$ component of the orbital moment. Thus, in our model, the coupling to the d orbitals of the transition atoms are the only source of scattering for the conduction electrons. We note, however, that in systems like AlLiCu, the density of states is about one-third that of free electrons, and the resistivity is about ($\rho=1000 \mu\Omega \text{ cm}$).³ This suggests that there may be a strong quasiperiodic potential, even though the quasicrystal does not contain transition-metal atoms.

The calculation of the variation $\Delta n(E)$ of the density of states due to the grouping of transition atoms in a jellium, which simulated the aluminum matrix, is performed using the Lloyd formula which is a generalization of the Friedel sum rule:¹⁸

$$\Delta n(E) = -\frac{2}{\pi} \text{Tr} \left(\mathbf{M}(E)^{-1} \frac{d}{dE} \mathbf{M}(E) \right). \quad (1)$$

The matrix elements of $\mathbf{M}(E)$ are calculated to form the \mathbf{T} matrix. The only parameters in the calculation are the geometry of the cluster and the phase shift $\delta_l(E)$ ($l=2$) due to the potential of each transition atom. We calculated the phase shift by using the formula $\tan \delta_2(E) = -[(\Gamma_d/2)/(E - E_d)]f(E)$, where E_d and Γ_d are the energy of the d orbital and the width of the resonance, respectively. For the energy near E_d , $f(E)$ is taken equal to 1, which leads to the classical approximation for $\delta_2(E)$ around the resonance.¹⁸ For $E \rightarrow 0$, $f(E) \rightarrow E^{5/2}$, so that $\delta_2(E)$ has the right asymptotic behavior at $E=0$.¹⁸ For intermediate energy, we choose a smooth interpolation between these two limits, and we have checked that this choice does not have a significant effect on the result.²³ Several *ab initio* calculations of the density of states in intermetallic alloys Al-Mn (Refs. 5 and 24) show that realistic parameters to simulate the potential of Mn in Al are $E_d=10.88 \text{ eV}$ and $\Gamma_d=3 \text{ eV}$.

Figure 1(a) shows the variation $\Delta n_0(E)$ of density of states for one transition atom (Mn). It corresponds to the classical virtual bound state of Friedel-Anderson.²² Figure 1(b) shows the result for one icosahedral cluster of transition atoms (Mn) having the same diameter as in the α -AlMnSi phase ($D=9.2 \text{ \AA}$).²⁰ This result differs from the addition of

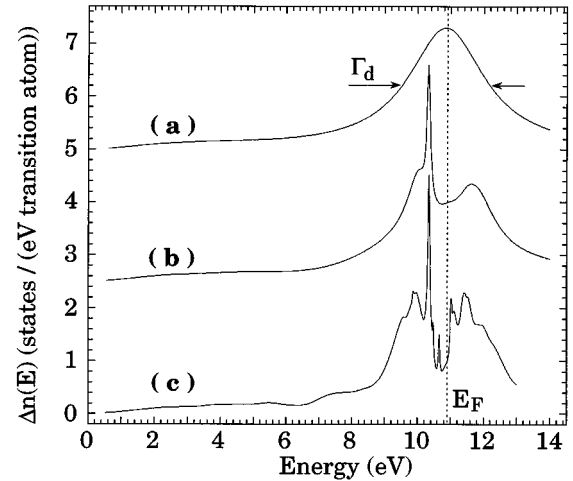


FIG. 1. Variation of the density of states $[\Delta n(E)]$: (a) for one Mn in jellium, (b) for one Mn icosahedron with diameter ($D=9.2 \text{ \AA}$) in a jellium [this is the actual Mn icosahedron of α -AlMnSi (Ref. 20)], (c) for 12 Mn icosahedra ($G = \tau^2$, see text) in a jellium. $\Gamma_d=3 \text{ eV}$, $E_d=E_F=10.88 \text{ eV}$.

12 identical contributions of an Mn atom. There is a fine peak at $E=11.3 \text{ eV}$ and also two shoulders at $E=10.0$ and 11.6 eV . Note that when Γ_d is increased, these shoulders appeared clearly as fine peaks. These structures show that there are resonances due to the scattering by the cluster. Figure 1(c) gives $\Delta n(E)$ for 12 clusters, obtained after an inflation by a factor $G = \tau^2$ (τ is the golden mean) of the initial cluster [the diameter of this cluster of clusters is about $(DG + D) \approx 35 \text{ \AA}$].¹⁴ All 12 clusters have the same orientation as the initial cluster. The density of states exhibits additional structures, which must correspond to new resonances. We expect that the resonances of Figs. 1(b) and 1(c) correspond to states that are localized on the group of atoms: cluster or cluster of clusters. These states are not eigenstates, but have a finite lifetime, of the order of $t = \hbar/\Gamma$, where Γ is the width of the resonance (Γ is of the order of a few tens of meV, which is comparable to the width of fine peaks in *ab initio* calculations⁵⁻⁷). In the case of one transition-metal atom, this resonance corresponds to the Friedel-Anderson virtual bound state. The localized state is the d orbital, and its width is much larger than for a group of atoms: $\Gamma_d=3 \text{ eV}$ in this calculation.

In the case of one Mn [Fig. 1(a)], the resonance is due to the d orbitals. But the new resonances due to the cluster and the cluster of clusters [Figs. 1(b) and 1(c)] do not result from an overlapping between the d orbitals. Indeed, the lowest Mn-Mn distance is 4.84 \AA , which does not correspond to first neighbors in actual alloys. As a consequence, these new resonances are only due to the multiple-scattering effects, i.e., to the overlapping between the d orbitals of transition atoms and the sp orbitals of the metallic matrix. The tendency to localization can be analyzed as follows. Let us recall first that scattering by transition atoms is important for energies E such that $E_d - \Gamma_d/2 < E < E_d + \Gamma_d/2$. In this energy range, the transition atoms can be considered, in a first approximation, as hard spheres with a radius of the order of the size of the d orbital, (i.e., about 0.5 \AA).^{23,24} Thus, by an effect similar to that of the Faraday cage, states can be confined in the cluster, provided that their wavelength λ satisfies

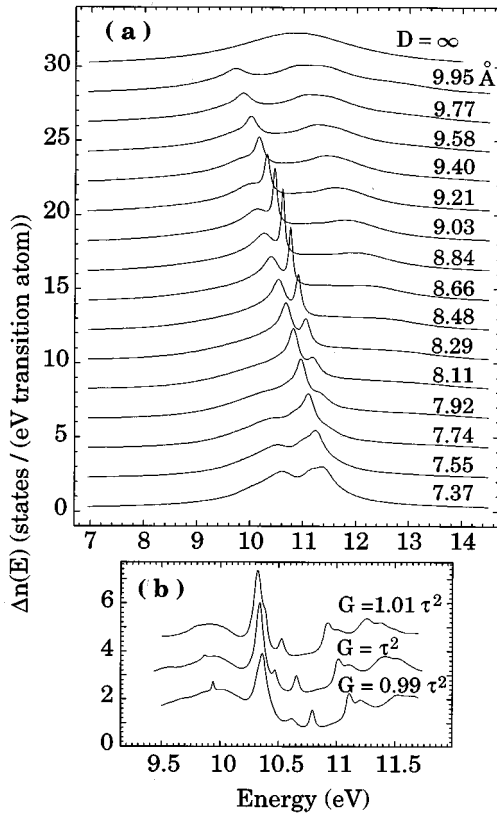


FIG. 2. Effect of the cluster size on the variation of the density of states: (a) for one Mn icosahedron in a jellium vs the diameter of the icosahedron (D). (b) For 12 Mn icosahedra in a jellium vs the inflation factor G (each Mn icosahedron has a fixed diameter $D=9.2$ Å). $\Gamma_d=3$ eV, $E_d=E_F=10.88$ eV.

$\lambda > l$, where l is the distance between the hard spheres. Since states tend to be confined in a region of extension D (diameter of the cluster), where the potential is zero, we expect that their energy should vary roughly like $1/D^2$. Indeed, Fig. 2(a) shows that when the radius increases, the energy of the states decreases. For instance, an increase (decrease) of 1% of D leads to a decrease (increase) of $\sim 0.7\%$ of the resonance energies. The $1/D^2$ law gives the right order of magnitude for the energy variation. This law is not obeyed precisely, probably because the effective scattering by d orbitals depends on energy, and also because the confinement is not perfect inside the cluster. We note also from Fig. 2(a) that resonances disappear quickly when D increases. This justifies our basic assumption that clusters cannot be treated as isolated entities in a vacuum. Figure 2(b) shows the shift of the peaks due to the localization by the cluster of clusters vs the inflation factor G (the diameter D of each Mn icosahedron is constant, $D=9.2$ Å).

Other cluster geometries have been studied elsewhere.²⁵ In particular, it has been shown that the localization by an Mn icosahedron decreases very rapidly when Mn atoms are removed from the icosahedron. Moreover, we have also calculated $\Delta n(E)$ due to other kinds of Mn clusters embedded in a matrix of aluminum: tetrahedron, cubic, and dodecahedron. In all cases, some confinement effects are present, but the strongest confinement, i.e., the narrowest peaks, are observed in the case of the icosahedron and the dodecahedron, which have the icosahedral symmetry.

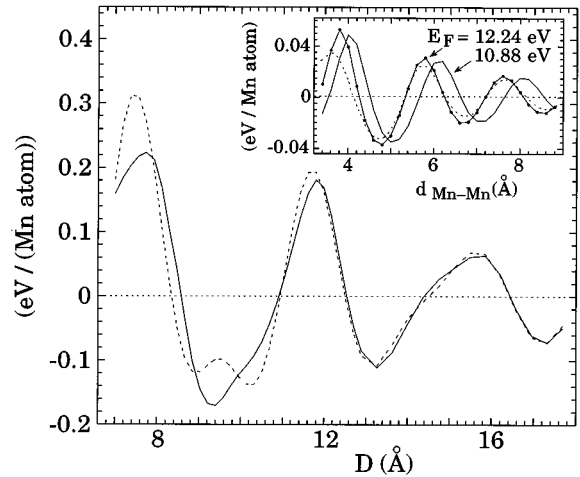


FIG. 3. Structural energy (ΔE_B) of a Mn icosahedron in a jellium vs the diameter of the icosahedron (D). Full line, exact calculation. Dashed line, sum of the Mn-Mn pair interactions. $\Gamma_d=3$ eV, $E_d=E_F=10.88$ eV. [Inset: energy of one Mn-Mn pair interaction vs the Mn-Mn distance ($d_{\text{Mn-Mn}}$). Full line, present model with $\Gamma_d=3$ eV, $E_d=10.88$ eV. Dashed line, calculated from *ab initio* calculation in Al-Mn alloys by Zou and Carlsson (Ref. 26)].

The main result of this work is the evidence for virtual bound states of groups of atoms at different length scales. For a quasicrystal, we expect that the interaction between these states is rather complex, but we propose the following renormalization-group argument. A virtual-bound state at a given energy E , which corresponds to a resonance, implies a strong scattering of electrons at this energy E . Thus a collection of virtual bound states at a given length scale can lead to the formation of virtual bound states at greater length scale. This effect is consistent with our results, since the scattering by the Friedel-Anderson virtual bound state at the atomic length scale leads to virtual bound states of a cluster or group of clusters. In the case of quasicrystals, this may lead to a hierarchical structure of the virtual bound states, in agreement with the idea of critical states. For a periodic structure, the coupling of virtual bound states should lead to the formation of bands.

Finally, we consider the role of the tendency to localization on the structural energy. We make the classical assumption²⁶ that the structural energy is given by the variation ΔE_B of the band energy and that E_d is independent of the geometry of the cluster. The structural energy of a Mn icosahedron in jellium from isolated Mn atoms in jellium is given by the formula

$$\Delta E_B = \int_0^{E_F} (E - E_f) [\Delta n(E) - \Delta n_0(E)] dE. \quad (2)$$

$\Delta n(E)$ and $\Delta n_0(E)$ are the variation of density of states due to one icosahedron of Mn and 12 isolated Mn, respectively. The Fermi level (E_F) is fixed by the metallic matrix, and we use the value calculated in the α -AlMnSi phase: $E_F=10.88$ eV.⁵ To check the validity of this structural energy calculation, we compare the energy of one pair of Mn calculated from our model with the one calculated from the *ab initio* calculation in Al-Mn alloys by Zou and Carlsson²⁶ (see inset of Fig. 3). This comparison shows a very good agreement between the two calculations.

In Fig. 3 we represent ΔE_B of one Mn icosahedron vs the diameter of the Mn icosahedron (D). This value is compared to the sum-of-pairs interactions between Mn atoms of the cluster. It appears that the main contribution to the structural energy of the cluster is the sum-of-pair interactions, as expected for an intermetallic alloy.

In summary, we have studied the role of scattering of electrons by clusters or a group of clusters in quasicrystals and approximants. A remarkable fact is that, even in a metallic medium, these clusters can lead to the formation of virtual bound states, at the length scale of a cluster or of a group of clusters. These states are associated with fine peaks

in the density of states, as found in *ab initio* calculations. We suggest that these virtual bound states are central to the electronic structure of quasicrystals and approximants. Within the present model, the structural energy is not very sensitive to this tendency to localization. The main contribution to the structural energy is the sum-of-pair interactions. This favors a Hume-Rothery picture of quasicrystals, as far as total energy is concerned.

We wish to thank J. Friedel, P. Qu  merais, C. Berger, R. Mosseri, T. Fujiwara, C. Janot, F. Cyrot-Lackmann, S. Khanna, and S. Roche for fruitful discussions.

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