

Pseudopotentials and Quasicrystals

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By pseudopotential methods the electronic properties of a quasicrystalline metal are examined from the nearly-free-electron viewpoint. The procedure results in the appearance of band gaps associated with each quasicrystal reciprocal-lattice vector, and these lead to singularities in both the density of states and the joint optical density of states. If observable by reflectivity, soft-x-ray emission, or tunneling measurements, these quantities will give information on several properties of the quasicrystalline state.

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Since the discovery of the icosahedral phase of some Al-Mn alloys¹ theoretical interest in the problem of determining the correct structure of this and other observed quasicrystalline phases continues undiminished. In addition, an understanding of what the properties of electrons and ions in such structures are, and why such a phase might be stable in the first place, is important. Thus far, the electronic problem has been attacked largely through tight-binding models on finite lattices,²⁻⁴ but in this Letter we begin from the opposite viewpoint, regarding the electrons as nearly free. The point here is to examine the implications of this model for the properties of a quasicrystal. It allows a much easier discussion not only of band gaps, the main subject of this Letter, but also of a possible Hume-Rothery explanation for the stability, a point that has already been raised by Bancel and Heiney.⁵

Since the principal component of the observed quasicrystals is often a simple metal, with no occupied *d*-electron states, most of the electrons can be well described by a nearly-free-electron picture (particularly for the Al-Zn-Mg class⁶). The other components (in the binary or ternary alloys) can have a clear *d*-electron character which may certainly be of importance, but is not central to the point being made in the Letter. We treat as a model system a hypothetical icosahedral phase for a pure nearly-free-electron metal, with aluminum as paradigm. It is also possible to reinterpret this system as a virtual (quasi)crystal in the sense implied by alloy theory,⁷ and through this picture we can then comment on the possible effect of introducing other constituents.

In the approach adopted here, we use a simple deterministic model for the structure, and with a local empty-core pseudopotential proceed to calculate the band gaps, the form of interband optical transitions, and the density of states. The band gaps produce sharp van Hove singularities in the density of states, and the increased number of interband transitions directly associated with the icosahedral structure leads to a corresponding increase in the magnitude of the optical conductivity, to an increased plasmon linewidth, and to additional features in the optical reflectivity.

Now Bak⁸ has noted that any quasiperiodic density may always be obtained by a cut through a higher-dimensional periodic density, and in the icosahedral case, this implies a three-dimensional cut through a six-dimensional lattice containing a "complementary" three-dimensional acceptance volume in each cell, thereby locating the atomic positions at the points where these objects are intersected. This leads to a quasiperiodic deterministic structure in real space, and a reciprocal "lattice" spanned by six fundamental vectors which point to the upper vertices of an icosahedron so that \mathbf{G}_k for $k=1$ to 5 surround the fivefold axis \mathbf{G}_6 , in our choice of labeling. The complementary spanning vectors \mathbf{G}_k^\perp are then determined uniquely (up to a rotation). The structure that we use is closely related to the well-known Penrose tiling model⁹ for this system except that we replace the polyhedral acceptance volume in the six-dimensional unit cells by a three-sphere of radius ρ . For aluminum, to obtain the correct atomic volume, we choose a Penrose-tiling rhombohedron edge length of 2.63 Å, and ρ is then 1.28 times this. The result is a structure that places atoms on the vertices of one of these tilings, but not every site is occupied.

Given a well-defined spatial structure of ions, we next note that in any simple metal a nearly-free-electron description of the conduction electrons can be obtained with use of perturbation theory in the total pseudopotential. Perturbation methods are justified here as long as at most a small fraction of the Fermi volume is strongly perturbed. An estimate of this fraction may be made by adding together the volume affected by each band gap, and in three dimensions this gives a finite fraction $A(V/\epsilon_F)^2$ even though the quasicrystal reciprocal lattice is everywhere dense. Here V is a characteristic potential value, ϵ_F is the Fermi energy, and A is of order unity. However, in two dimensions or fewer A diverges and each electron state is close to many zone planes. This is also true in three dimensions for states whose energy is less than or of the order of V . Thus, in fact, the two-band perturbation models used in this Letter are only valid in three or more dimensions and at larger electron energies [see Fig. 1(a)]. The important quantities in the

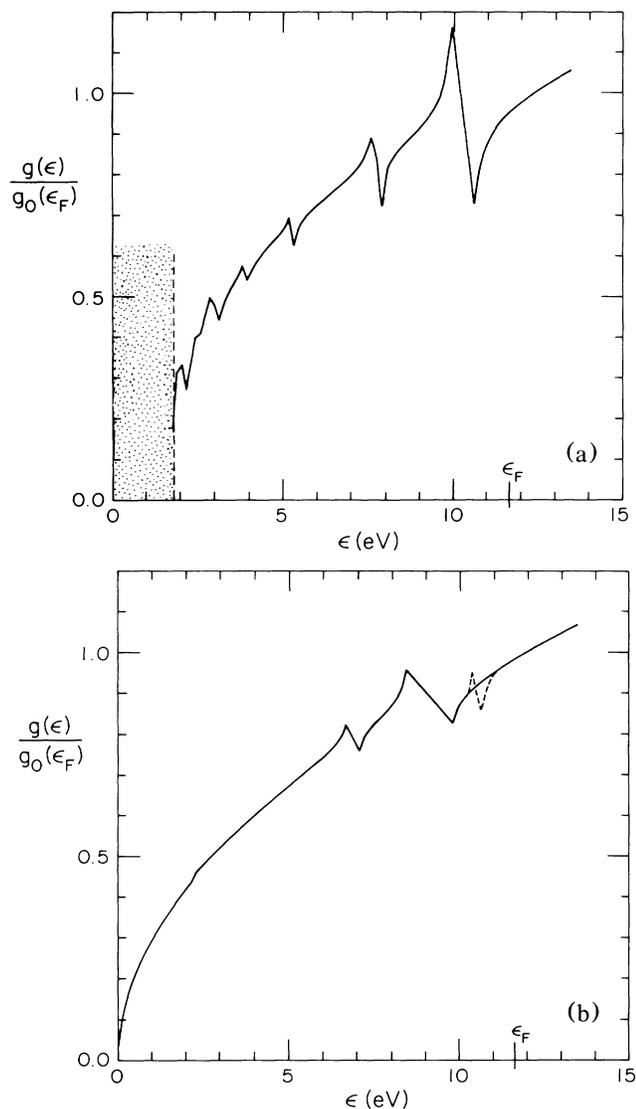


FIG. 1. One-electron density of states from two-band models: (a) Icosahedral aluminum and (b) normal fcc aluminum. Van Hove singularities appear on either side of each energy gap at a zone plane. The dashed line in (b) represents effects from indirect gap zone plane intersections, which are omitted in (a). The low-energy states in the quasicrystal are strongly perturbed by more than one potential component, and the two-band model breaks down (see text).

approach are (i) the pseudopotential values at points of the reciprocal lattice of the given structure, $V_{ps}(\mathbf{K})$, and (ii) the geometrical structure factors $S(\mathbf{K})$ given by

$$S(\mathbf{K}) = N^{-1} \sum_{\mathbf{R}} e^{i\mathbf{K} \cdot \mathbf{R}}, \quad (1)$$

where \mathbf{R} runs over all atomic positions. Note that this structure factor is the same as that usually associated to a lattice with basis, and is determined by the ion density. For a compositionally ordered alloy, we need a struc-

ture factor for each species, but in a virtual-crystal interpretation we can use only one. This is determined by evaluating the six-dimensional density in reciprocal space and then reducing to the three-dimensional result, namely

$$S(\mathbf{K}) = 3j_1(K^\perp \rho) / K^\perp \rho \\ = 3[\sin(K^\perp \rho) - K^\perp \rho \cos(K^\perp \rho)] / (K^\perp \rho)^3, \quad (2)$$

which is a simple decaying function of the magnitude of the complementary vector \mathbf{K}^\perp and the sphere radius ρ . Since in the present model S is precisely known, we can now calculate electronic properties almost as easily as with a regular crystal.

The potential seen by the electrons in the material has the Fourier transform

$$U(\mathbf{k}) = \sum_{\mathbf{K}} S(\mathbf{K}) V_{ps}(\mathbf{K}) \delta(\mathbf{k} - \mathbf{K}) \\ \equiv \sum_{\mathbf{K}} U_{\mathbf{K}} \delta(\mathbf{k} - \mathbf{K}), \quad (3)$$

and thus each reciprocal-lattice vector contributes one term. As for a regular crystal, each reciprocal-lattice vector will be associated with an energy gap of magnitude $2|U_{\mathbf{K}}|$ at the perpendicular bisecting plane ("zone plane"). Although no Brillouin zones exist in the usual sense, in three dimensions only very few of the reciprocal-lattice vectors are of importance in altering the overall electronic structure. From perturbation theory, we may start with a free-electron state of momentum $\hbar\mathbf{k}$ and then, by introducing the potential, cause a mixing of the state with plane waves of momentum $\hbar(\mathbf{k} - \mathbf{K})$ for any reciprocal-lattice vector \mathbf{K} . Except for regions very close to one or more zone planes, we expect the state to retain much of its free-electron character, and we can still ascribe to it the index \mathbf{k} .

The first quantity of interest in this approach is the density of states (Fig. 1) for the quasicrystal.¹⁰ Associated with each reciprocal-lattice vector we will have a pair of square-root van Hove singularities, separated by the energy gap $2|U_{\mathbf{K}}|$. Since the quasicrystal reciprocal-lattice vectors have large multiplicities, the magnitude of the deviation from the free-electron curve is increased by a corresponding factor, and most noticeably the slope of the portion of the density-of-states curve between the two singularities is much greater for the quasicrystal than for the regular crystal¹⁰ even though some quasicrystal band gaps may be much smaller if the corresponding $S(\mathbf{K})$ small. We expect that these distinctive features could be observed in soft-x-ray emission or tunneling measurements on the real systems to which this model might be applicable.

The general features of Fig. 1 apply both to the pure aluminum quasicrystal and to virtual-crystal alloys. The principal effects of alloying with a simple metal are to alter the pseudopotential and to move the Fermi level by changing the total number density of electrons. Both affect the band-gap magnitudes. Note that for the

chosen ρ the largest singularity is associated with \mathbf{K} along a [111001] direction which appears just below the Fermi surface. The Fermi surface itself is markedly reduced in area by this set of gaps, thus increasing the optical effective mass. If the Fermi volume were decreased (by forming a substitutional alloy) then the fraction of the Fermi surface beyond a given zone plane could be reduced drastically. The total band-structure energy of the electrons is then correspondingly lowered, enhancing the stability of the phase by the usual Hume-Rothery-Jones argument.^{7,11} For different choices of ρ and other parameters, some other band gaps could be dominant, but the general result is that this effect may contribute to the relative stability of the quasicrystal phase.

A second question of particular experimental interest is the manifestation in the optical properties of the multitude of direct interband transitions that can occur. Since only the "crystal momentum" is conserved in optical transitions, absorption of an incident photon (or photon emission) will always involve a transition of the electron in state \mathbf{k} to a state labeled by $\mathbf{k}-\mathbf{K}$ for some reciprocal-lattice vector \mathbf{K} . The transitions that will be seen will predominantly be those for which $S(\mathbf{K})$ is relatively large since this appears directly in the oscillator strength.

We obtain in this model a quantitative estimate of the optical conductivity, which determines the reflectivity (see Fig. 2). For a single zone plane, and for frequencies ω near $\omega_e = |2U_K/\hbar|$, the interband terms in the real part of the conductivity for a collisionless model are, from degenerate perturbation theory,¹²

$$\text{Re}\sigma(\omega) = \begin{cases} \frac{e^2 K}{24\pi\hbar} \frac{(2U_K/\hbar\omega)^2}{[1 - (2U_K/\hbar\omega)^2]^{1/2}}, & \omega_e \leq \omega \leq \omega_0, \\ \frac{e^2 K}{24\pi\hbar} \frac{(2U_K/\hbar\omega)^2}{[1 - (2U_K/\hbar\omega)^2]^{1/2}} \frac{(\hbar\omega + \hbar\omega_0)(\hbar\omega_1 - \hbar\omega)}{4\hbar\omega\epsilon_K}, & \omega_0 \leq \omega \leq \omega_1, \end{cases} \quad (4)$$

where $\hbar\omega_0 = \epsilon_K(2k_F/K - 1)$ and $\hbar\omega_1 = \epsilon_K(2k_F/K + 1)$. We see that the structure dependence is through both $U_K = V(K)S(K)$ and the value of K itself. The contribution is very small for reciprocal-lattice vectors with small $S(K)$. To include collision effects¹² we incorporate a relaxation time τ which smooths the singularities in the

conductivity over a scale τ^{-1} as for a regular crystal. In Fig. 2 the same τ value is used for both curves (0.8×10^{-14} s) but the minima continue to survive for τ as short as 0.1×10^{-14} s.

The imaginary part of σ is given by a somewhat more complicated expression, but again each band gap contributes. The total optical conductivity is this sum, plus the Drude (intraband) value given by

$$\sigma_D(\omega) = \frac{e^2 k_F^3}{3\pi^2 m} \frac{\tau}{1 - i\omega\tau} \frac{m}{m_{\text{opt}}}, \quad (5)$$

involving the optical mass as well as the relaxation time τ . At the plasma frequency [determined by $\text{Re}\epsilon(\omega) = \text{Re}(1 + 4\pi i\sigma/\omega) = 0$] the interband transitions produce a shift in the plasma frequency and a corresponding increase in the plasmon linewidth.¹³ This has been seen experimentally in the Al-Mn class,^{14,15} but these alloys do have some tight-binding character.

At lower frequencies the Drude contribution is large, and to obtain it we require a knowledge of the optical mass. We have an upper bound on that, however,¹⁶ namely

$$m_{\text{opt}}/m \leq [N(\epsilon_F)/N_0](S_F^0/S_F)^2, \quad (6)$$

in terms of the ratios of the density of states at the Fermi energy and the Fermi-surface area to their free-electron values, which we can easily estimate from our model. From the above we finally can calculate the reflectivity $R = |(\sqrt{\epsilon} - n)/(\sqrt{\epsilon} + n)|^2$, as shown in Fig. 2, for an interface between the metal and a material of index n . The large magnitude of the quasicrystal interband terms means that the peaks here are smaller than for the face-

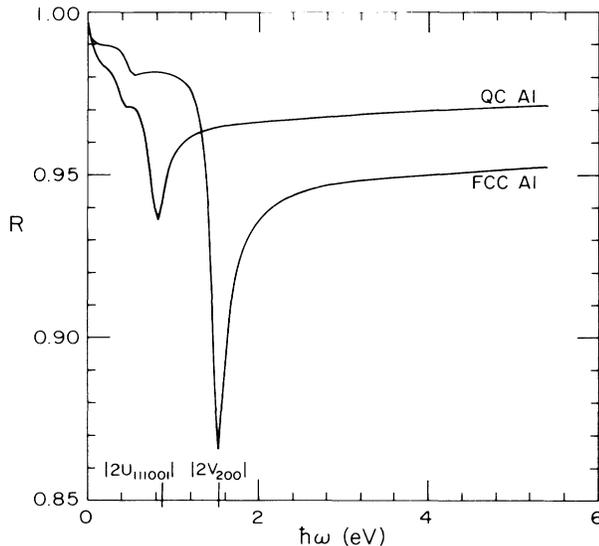


FIG. 2. Reflectivity of icosahedral and normal aluminum for a vacuum interface. The features in these curves are directly attributable to absorption at energy gaps. The values of the gaps, which give direct information on the quasicrystal structure factors, may simply be read from the positions of the observed minima. The width of the features provides a measure of the intrinsic scattering.

centered-cubic case. The energy gaps themselves are small so that these features appear only at lower energies. Alloying will increase scattering, but the observable features often survive to surprisingly high concentrations as has been seen in random lithium-magnesium alloys and other systems.^{17,18}

In conclusion, certain electronic properties of the quasicrystalline state are readily described by the pseudopotential approach. In particular, for nearly free electrons we obtain predictions for features in the density of states, in the optical conductivity, and in the reflectivity. The important result is that measurements of these will probably give further information on the structure, the electronic properties, and particularly the scattering. The large slopes of the van Hove singularities and other special features of the density of states in particular are perhaps distinctive of this state. The observed increase in plasmon linewidth¹⁴ is a consequence of the large number of allowed interband transitions, and the divergent dc conductivity for a perfect quasicrystal lattice¹⁹ results simply from the nonzero density of states at the Fermi energy. Finally, if the structure and potential are such that the largest band gap is close to the Fermi surface (as in our estimate here) we may expect that in a virtual-crystal model the observed stability of the icosahedral phase in both binary and ternary alloys might be attributable in part to a Hume-Rothery instability.

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