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Structure and electronic pseudogaps of stable quasicrystals

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A variety of geometrical, crystal chemical, statistical, and quantum-mechanical theoretical constructs provide criteria for understanding trends in quasicrystalline relative stabilities. The quantum-mechanical constructs also explain trends in transport properties. These trends have predictive value.

I. INTRODUCTION

The electronic properties of stable quasicrystals, such as Al_7Cu_2Fe and Al_7Pd_2Mn, exhibit striking semimetallic behavior, with low-temperature resistivities several orders of magnitude larger[1] than those found in ternary metallic glasses.[2] When measured in the infrared, the optical conductance is linear in frequency[3] up to $\hbar\omega = 1.0$ eV. When some crystalline rational approximants, such as α-Al-Mn-Si, are annealed, their low-temperature resistivities ρ_0 increase and their densities of states at E_F, $N(E_F)$, as measured by their electronic specific-heat coefficients γ, decrease.[4] Generally, the more stable the quasicrystal, as measured by grain size, the smaller $N(E_F)$ and the larger ρ_0, which suggests that some kind of energy gap (or pseudogap)[4] plays an important role in producing both structural stability and semimetallic electronic transport. In this paper we propose a crystal chemical model of the origin of this gap. Our present model is an extension of an earlier model,[5] but we feel that the present model is substantially superior to the earlier one in both generality and simplicity.

There have been many geometrical studies of quasicrystals, but only our own previous work systematically related the crystal chemistry of quasicrystals to that of crystalline approximants,[6] primarily by quantifying the notions of Frank-Kasper packing[7] and ternary stability in the context of quantum-structure and quantum-formation diagrams.[8] That analysis showed that the compositionally weighted ternary size $\overline{\Delta R}$ and electronegativity $\overline{\Delta X}$ differences should be small to form icosahedral building blocks either in ternary quasicrystals or ternary crystals. Our model did not show, however, why Al is overwhelmingly the most popular majority element as a basis for stable ternary quasicrystals. We suggested[6] that Al might be favored because its energy bands are well described by the nearly free electron model. However, this is not a structural model, and other metals (such as Mg) also have nearly free electron energy bands, so this suggestion is incomplete.

In principle the geometry of three-dimensional quasicrystalline atomic planes can be explained by projecting at appropriate irrational angles atomic planes in a six-dimensional antecedent space, but the decoration of these antecedent planes is uncertain. Attempts to build ideal three-dimensional decorated quasicrystals by such Penrose projections have proved only partially satisfactory, with transition metal (TM)-TM contacts where icosahedra overlap, and only qualitative agreement with observed diffraction intensities.[9] We have noted[5] that because the crystalline approximants contain $\gtrsim 10^2$ atoms/cell, this problem may not be exactly soluble, as it has much in common with the traveling-salesman problem with a very large number of customers. In fact, context-dependent decorations of Penrose tiles are required to explain diffraction data.[10]

We discuss the problems of icosahedral packing in both crystalline approximants and quasicrystals in Sec. II. Our aim is to identify the generic features of this packing which arise from the requirements of space filling with reasonable bond lengths. We find that certain topological characteristics occur both in three-dimensional crystalline approximants and in layered decagonal quasicrystals which characterize the chemical bonding near icosahedral interfaces. We use these characteristics to generate shortened or reduced crystal chemical lists of candidate element pairs or triplets in Sec. III. In fact the lists are shortened by more than an order of magnitude compared to the lists that are obtained using merely Frank-Kasper packing analogies. In Sec. IV the significance of various kinds of electronic pseudogaps is discussed together with their relationship to the crystal chemical patterns discussed in Sec. III. In Sec. V we compare the relative merits of geometrical, crystal chemical, and quantum-mechanical methodologies. In Sec. VI emerging transport anomalies found in stable quasicrystals and some crystalline approximants are related to these pseudogaps. In Sec. VII we discuss the relationship between local magnetic moments and pseudogaps, as well as the connection between the latter and enhanced orbital diamagnetism. There is an infant generic theory which connects electronic stabilization with atomic ring topology which complements the pseudogap concept, and its relation to quasicrystalline stability is reviewed in Sec. VIII. We summarize our many new results in Sec. IX.

II. GEOMETRY

Two crystalline approximants to the much simpler two-dimensional Al-Cu-Co decagonal (d) phase with large unit cells ($a \sim b \sim 50$ A) have been studied extensively,[11] and from these the relationships between the d

phase and the approximants is established. There are several interesting results. The most general one is that the strain energy associated with short bonds is reduced if the frequency of twinning is increased. Insight into the crystal chemistry is provided by analyzing the polygonal projections of the building blocks in the approximants. These are Cu- and Co-centered Al (1–10) decagons (axially projected icosahedra) with various spacings, with the regions between these decagons filled either with (1–5–10) decagons [lower half of their Fig. 1(c)] or with second decagons (1–10–10) and an atom-centered (1–5) pentagon [upper half of their Fig. 1(d)]. At the twin boundary an extra atom-centered (1–5) pentagon appears between the twinning planes, their Fig. 2, so this unit can be regarded as a building block for decagonal twinning. The extra pentagon is not a 1–10 decagon, that is, it is not an axial projection of an icosahedron. This means that the filling factor associated with icosahedra decreases as the twin filling factor increases. Thus an increased twin (or "glue") filling factor in quasicrystals compared to crystalline approximants means a reduced icosahedral filling factor, which conclusion was also reached in the Penrose projection studies.[9]

Could there be a similar nonicosahedral building block for twinning of three-dimensional crystalline approximants? It appears that the average coordination number n_c of the atom-centered (1–5) pentagons is smaller than that of the various decagons, and as the former is the twinning building block this factor may apply to three-dimensional twinning wedges. Typically in Mackay icosahedra $n_c \sim 11$ in three-dimensional models,[9] which describes almost close packing ($n_c = 12$). Alternatively we may say that in the twinning regions some pentagonal bonds are stretched, giving deformed pentagons with four short bonds. This means that while the icosahedral regions are dominated by odd-membered rings, the strained twinning regions probably contain increased fractions of even-membered rings, and this is the main mechanism for relaxing the strain energy associated with the "unfavorable local configurations" or "ULC" identified in decagonal decoration patterns.[11] In other words, near twins and especially in ULC regions, the odd ring number parity characteristic of both close packing and icosahedral packing is broken and is replaced by a mixture of even and odd parities. We note that odd parity is generally unfavorable for partially ionic bonding, but that even parity can be favored by ionic bonding.

We apply this reasoning to the structure of the most thoroughly studied[12] three-dimensional crystalline approximant, Al_5Li_3Cu, which has the *cI* 160 structure.[13] The geometrical description[12] of this Frank-Kasper structure, their Fig. 2, begins with bcc (Cu,Al) icosahedra, surrounded by Li dodecahedra, all with odd-membered rings. The next three shells which join the Li dodecahedra contain small (Al,Cu) and distorted medium (Al,Cu) triacontrahedra, and finally large Li triacontahedra, where most of the rings are even (four or six) membered. Thus the even-membered triacontahedral rings with smaller coordination numbers join together the odd-ring polyhedra, as we surmised above from the decagonal example.

The distinctive coordination environments of the atoms in the even-membered rings in *cI* 160 can be seen immediately from their radial distribution functions and their coordination polyhedra.[14] Each of the cube faces contains a Li-Al (the two Wyckoff 12*e* sites) rhombus (ring with four short bonds) at its center. These are the joining elements (analogous to the pentagons in the decagonal case) which are probably augmented with additional four-membered Li-Al rings to form the twinning wedges in *i*-Al_6Cu_3Li.

III. CRYSTAL CHEMISTRY

To proceed further with a crystal chemical analysis we need simple crystal analogues of odd and even ring parities. The Frank-Kasper crystals are excellent examples of odd ring parities, and as we showed,[6] they are favored by $|\Delta\bar{R}|$ and $|\Delta\bar{X}| \approx 0$. However, a striking feature of the recently discovered Al-Cu (Fe,Ru,Os) and Al-Mn-Pd large stable quasicrystals[15] is that they have no known Frank-Kasper cubic approximants although $|\Delta\bar{R}|$ and $|\Delta\bar{X}|$ are still small and favor icosahedral cluster formation. We therefore suspected that low twin (or ULC) strain energy[11] could be the additional factor most strongly favoring *i*-crystal stability in these ternaries, which in turn suggests we seek ternary crystalline analogues with high density and even-membered ring parity. The simplest such binary crystalline analogue would be the CsCl structure, $n_c = 8$. Energetic stabilization of twins would then be favored by existence of SM (simple metal)-TM compounds in the CsCl structure.[13] The simplest such ternary analogue is the BiF_3 structure,[13] again with $n_c = 8$; this is the structure of $AlMnPd_2$. Many ternary magnetic compounds are formed in this structure.[16]

Our hypothesis that twins in $d = 3$ quasicrystals may have atomic structures that locally resemble CsCl has received dramatic experimental confirmation.[17] Melt-spun Al-Cu-Fe alloys have been found to contain icosahedral phases which coexist in definite orientational relationships with $Al_{50}Cu_{50-x}Fe_x$ ($5 \leq x \leq 50$) in the ternary CsCl or τ phase which connects to AlFe. The simplest explanation for this full orientational coherence is that the τ phase is fully coherent because it is matched to nonicosahedral regions which also have a CsCl-like structure, with an abundance of alternating four-membered rings. Three Al-Cu-Fe quasicrystal axes match three sets of crystalline axes in two different ways, which may reflect two kinds of tiles. Similar orientational coherence between the τ phase and decagonal ($d = 2$) or $d = 1$ phases has also been reported.[17]

Partial orientational coherence of distinct phases in a rapidly quenched alloy is unusual but it is not rare. The examples of greatest relevance to our situation are between α(fcc) and β(CsCl) Cu-Zn alloy grains.[18,19] The partially coherent interfaces share two axes, an invariant and unrotated line, similar to the three fully matching quasicrystalline axes. Again the α and β Cu-Zn phases are based on three- and four-fold nearest-neighbor rings, respectively, showing that partial coherence between even- and odd-membered rings can arise even for binary crystalline alloys. It is our hypothesis that full three-axis coherence is the basic physical mechanism which stabilizes certain ternary quasicrystals compared to internally strained crystalline approximants. We believe that this full coherence is promoted by disproportionation of the third element between the icosahedral clusters and the CsCl-like regions, and that this disproportionation may reduce the strain energy and be a more important mechanism for stabilizing quasicrystals than adjustment of the electron count (and hence E_F), which merely stabilizes the pseudogap associated with icosahedral clusters.[22,23]

There is an independent test for this hypothesis.[6] In Table I we compare stable AlX compounds (CsCl structure) with the occurrence of stable icosahedral quasicrystals Al-X-Y. We see that the correspondence is very good whenever i-Al-X-Y is a quasicrystal with an fcc four- or six-dimensional antecedent (type II, seven examples, including Al-Cu-Fe and Al-Pd-Mn).[24] However, note that the correspondence is poor for the three quasicrystals of type I (sc six-dimensional antecedent), all of which are also found in the cI 162 Frank-Kasper phase. The only real failure in Table I occurs for X=Sc, but it is believed[20,21] that such an early transition metal will soak up too many s-p electrons and thereby make the average electron count too low to support a cI-162-like structure. Note that X=rare earth has been omitted from the table. It seems unlikely that the hybridization between rare earth f states and Al p states is large enough to produce pseudogap quasicrystal stabilization, as discussed in the following section.

TABLE I. Comparison of stable AlX, MgX and GaX binaries with CsCl structure with known stable quasicrystals. See also Ref. 6.

Binary CsCl	Stable quasicrystal	Type
AlAu	?	
AlCo	$Al_{65}Co_{20}Cu_{15}$	II
AlFe	$Al_{65}Cu_{20}Fe_{15}$	II
AlMn (t?)	Al_7Pd_2Mn	II
AlNi	$Al_{70}Ni_{15}Co_{15}$	II
AlOs	$Al_{65}Cu_{20}Os_{15}$	II
AlPd	Al_7Pd_2Mn	II
AlPt	?	
AlRe	Al_7Pd_2Re	II
AlRh	?	
AlRu	$Al_{65}Cu_{20}Ru_{15}$	II
AlSc	· · ·	
· · ·	Al_6Li_3Cu	I
MgAg	· · ·	
MgHg	· · ·	
MgPd	$Al_{43}Mg_{43}Pd_{14}$	I
MgRh	?	
MgSc	· · ·	
MgTl	· · ·	
· · ·	$Zn_{43}Mg_{37}Ga_{20}$	I
GaCo	?	
GaIr	?	
GaNi	· · ·	
GaRh	?	
GaRu	?	

Before proceeding to a more microscopic discussion of electronic phases, there is one tantalizing question which cannot be answered finally but is well worth discussing. Just how stable is a stable quasicrystal? Experimentally there is an unambiguous qualitative difference between the sharpness of the diffraction patterns of metastable and stable quasicrystals, and the latter are stable with respect to annealing on laboratory time scales. Note also that the known crystalline approximants all have different compositions than their corresponding stable quasicrystals, so that in practice large-scale phase separation could destabilize the latter, but this probably will not occur on laboratory time scales. Note also the remark above concerning the difference in average composition between four-membered rings and three-membered rings in a ternary alloy. In a certain sense it is the ternary character of the alloy which the experimentalist uses a lever to stabilize the quasicrystal. In fact, without this lever quasicrystals have so far not been made metastable against annealing on laboratory time scales.

IV. STABILITY AND PSEUDOGAPS

Because electronic-structure calculations require periodic boundary conditions quasicrystalline electronic spectra have been determined primarily for various crystalline approximants, for example by Fujiwara and Yokokawa.[22,23] In the crystalline approximants they find large pseudogaps ($E_p \sim 0.2-0.3$ Ry) which are primarily associated with the first and second icosahedral shells in AlMn. The projected local densities of states associated with nonicosahedral atoms do not contain such a pseudogap near $E=E_F$ and they therefore contribute a background density of states lying in the icosahedral pseudogap. They further find that when the composition of the crystalline approximants is varied, for instance in $Al_{1-x-y}Cu_xLi_y$, that E_F appears to fall at the center of E_p when x adopts a value appropriate to the crystalline approximant. This also appears to be the reason why some Al is replaced by Si in Al-Mn-Si.

The next question is whether the very small energy differences between the crystalline approximants and stable quasicrystals can be explained by these pseudogaps. It is argued[23] that "pseudogap enhancement of the cohesive energy can work more efficiently in the quasicrystalline case because the effective Brillouin zone" is more nearly spherical for quasicrystals. However, the crystalline approximants already contain more than $\sim 10^2$ atomic/unit cell, leading to a second-order aspherical correction to the cohesive energy of 10^{-4} eV, which is not only small, but actually much too small. Moreover, this argument does not explain the compositional differences between the rational approximants and quasicrystals which are of order 10% (compare c-Al_5Li_3Cu with i-Al_6Li_3Cu). Finally, when we compare the background density of states $N_b(E_F)$ in the pseudogap in the crystalline approximants with the quasicrystal, we notice that the value $N_b(E_F)$ for the latter must be larger because it has a smaller icosahedral filling factor,[9,11] and the pseudogap is associated with the icosahedra and not

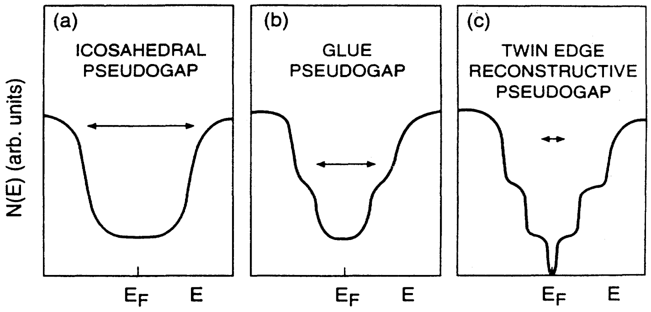

FIG. 1. A sketch of $N(E)$ which shows differences (exaggerated for clarity) between crystalline approximants, such as (a) Al_5Cu_3Li, and quasicrystals, (b) Al_6Cu_3Li, in the region of the pseudogap. In (c) we sketch a minigap within the pseudogap due to further reconstruction in twins, especially nearly twin edges.

with the nonicosahedral regions. For these reasons we believe that the E_p pseudogap correctly explains stabilization of icosahedral clusters but not the relative stabilization of one kind of icosahedral arrangement (the crystalline approximant) compared to another (stable quasicrystals). Our own model (increased twinning filling factor in the case of Mackay icosahedra with twinning regions based on AlT (T=transition metal) in a pseudo-CsCl structure) provides a much more systematic explanation of chemical and morphological trends.

These points are illustrated in Fig. 1. The density of states $N_a(E)$ with its icosahedral pseudogap E_p is sketched for a crystalline approximant as Fig. 1(a). In Fig. 1(b) we show a similar sketch for the quasicrystal $N_i(E)$, with $N_i(E_F) > N_a(E_F)$ because of the presence of more glue atoms. Finally we show in Fig. 1(c) $N_{\text{ir}}(E)$, the relaxed (annealed) density of states for a stable quasicrystal or a rational approximant obtained by annealing a metastable quasicrystal. An interesting feature of this $N_{\text{ir}}(E)$ is a minigap E_m which develops at E_F because of Jahn-Teller-like relaxation of glue atoms whose local structure is dominated by four-membered rings.

The E_m minigap shown in Fig. 1(c) has many attractive features. It is difficult to believe that the effects of annealing or the small energy differences between crystalline approximants and quasicrystals can be associated with changes in an $E_p \sim 2-3$ eV pseudogap. However, a minigap of energy $E_m \sim 0.05$ eV$\sim kT_t$, where T_t is a transformation or annealing temperature of order 600 K, could very easily explain these aspects of the data. The formation of such an E_m gap can take place much more easily for the more open and softer four-membered rings (CsCl-like) than for rigid three-membered rings (locally close packed).

V. GEOMETRY, CRYSTAL CHEMISTRY, AND PSEUDOGAPS

In early work on the atomic structure of quasicrystals (Ref. 12 and references cited therein), the problem of atomic decoration was approached by treating atoms either as points or as hard spheres. This geometrical approach is consistent with tiling constructions and projections from 2D to D dimensions. However, it is unphysical because the actual atomic structure is determined by minimization of electronic energies which must be calculated quantum mechanically in D dimensions, not 2D dimensions, and there is no reason to suppose that a high-symmetry 2D decoration when projected to D dimensions will be energetically self-consistent and stable.

In practice the quantum-mechanical requirement of energetic minimization cannot be satisfied because the computational complexities are too great, not only for quasicrystals but also for crystalline approximants containing more than $N \sim 10$ atoms/cell. (The actual values of N for known crystalline approximants is $N \sim 150$, which means that advances in computational technology are unlikely to be able to resolve this problem in the foreseeable future.) However, crystal chemical experience with simpler systems has taught us that structural stabilization can often be related to actual energy gaps or to pseudogaps in the one-electron spectra which can be and have been calculated[23] for large values of N. These calculations enable us to be much more explicit about the failures of geometrical models.[6]

Initially the geometrical models seems to promise something if only because of the close correspondence in composition and occurrence of type-I stable quasicrystals and crystalline approximants in the cI 160 structure.[6] When type-II stable quasicrystals were discovered, it became apparent that geometry had little to offer. These stable quasicrystals are much more stable than any known crystalline approximants, and in practice it has proved so difficult to prepare the latter that their unit-cell decorations are unknown. Clearly a different structural principle, essentially unrelated to crystalline approximants, is involved in stabilizing type-II quasicrystals.

We believe that the structural principle which stabilizes type-II quasicrystals is the presence of a pseudogap associated with the nonicosahedral regions. There is still a pseudogap associated with the icosahedra,[23] but the glue pseudogap is competitive so far as electronic energies near the Fermi energy are concerned. The total electronic energy also involves core-core repulsion energies, and these are more easily reduced by relaxation in the nonicosahedral regions with quadrilateral smallest rings than in the icosahedral shells with triangular rings. As a result, when the nonicosahedral region is stabilized by its own pseudogap, its filling factor increases at the expense of the icosahedral filling factor, that is, there are more twinning planes, and thus actually stabilizes the quasicrystal while it destabilizes possible crystalline approximants. It is obvious, of course, that none of these considerations arise in purely geometrical models. This is why such models are incapable of making crystal chemical predictions of the kind we have made here. It is also why the geometrical models cannot be used to discuss transport properties.

VI. TRANSPORT ANOMALIES

The issue of icosahedral and glue regions together with pseudogaps and minigaps is crucial to interpreting transport anomalies in stable quasicrystals such as *i*-Al-Cu-Fe and *i*-Al-Pd-Mn. Low-temperature resistivities in metallic glasses can be explained reasonably well by weak localization theory,[2] and the transport properties of many metastable quasicrystals[25] resemble those of metallic glasses sufficiently closely that similar fits can be made in those cases as well. However, it is obvious, if only from the fact that the resistivities near $T=0$ of stable quasicrystals can be $\sim 10^2$ larger than those of metallic glasses and metatable quasicrystals,[5] that this is not the correct approach to the former, although it has been tried.[26]

Dramatic optical measurements[3] of the conductance of stable *i*-Al-Cu-Fe from 0.01 to 3 eV have shown a remarkable linear conductance similar to that observed for partially compensated semiconductor impurity bands, but spanning a much wider energy range (up to 1.0 eV). We have suggested elsewhere[27] that the origin of this phenomenon is electronic compartmentalization, which means that the stable quasicrystal breaks up into electronic domains. The electrons near $E=E_F$ are phase coherent within each domain, but between domains in the presence of electromagnetic fields the interdomain phases are random, which gives rise to hopping conductivity, as in the partially compensated impurity band case.[3] At $T=0$ in both cases $\sigma(\omega)\rightarrow 0$ as $\omega\rightarrow 0$, so that we have a perfect semimetal at $(\omega,T)=(0,0)$. The compartmentalization analogy has the advantage that it explains both systems[3] without using explicitly the incommensurate nature of quasicrystallinity, but rather only the perfect randomness[28] which is common to both cases. It is striking that small degrees of impurity association (in melt-grown partially compensated semiconductor impurity bands) or magnetic defect clusters (Sec. VII below) are sufficient to spoil the perfect semimetallic character, and increase $\sigma(0)$. I have been able to explain this only by assuming that associated with these defect clusters there is a nonrandom length scale of order the sample dimensions, possibly produced by thermal gradients present during sample growth.

The compartmentalized model was developed to describe the transport properties of Al-Cu-Fe quasicrystals, where a convenient crystalline approximant was available to describe the domain or twinning walls, namely Al_7Cu_2Fe in the *tP*40 structure. As mentioned there, this tetragonal crystal contains AlFe layers with a local CsCl structure. In this paper we have developed many additional arguments, buttressed by dramatic new data, to show that the CsCl-like model for the structure of the twinning wedges or glue regions is valid for Al-Pd-Mn as well. The characteristic feature of the CsCl structure is the four-membered ring, and this also appears to be the key "glue" factor for *i*-Al-Li-Cu and Ga-Mg-Zn (type I) as well.

The question now arises as to what the dominant or preferred electrical paths are for transport in a two-component system consisting of icosahedral regions and nonicosahedral twinning regions. The former cannot even be locally crystalline and hence it may not be possible to define local wave packets with local crystal momentum in such regions. However, the CsCl-like glue regions, although doubtless highly defective, may still be locally periodic. Moreover almost all the background density of states at $E=E_F$, $N_b(E_F)$, is associated with the twin regions, so it is natural to picture all the current as carried quasiballistically in these regions if they are connected. The twin regions always narrow to lines where twinning planes cross. These lines will be lines of phase discontinuity, where the current carrying electrons presumably hop over a minibarrier E_b which is in the range $E_m < E_b \lesssim E_p$. These barriers are formed most completely in stable quasicrystals with a high filling factor and they may be very sensitive to annealing. We call them "edge barriers."

VII. MAGNETISM AND ENERGY GAPS

In most metallic environments (such as Heusler alloys[28,29]) Mn has a local magnetic moment of about $4.0\pm0.5\mu_B$. However, the largest average Mn moment in *i*-Al-Pd-Mn alloys is only $0.025\mu_B$, or 0.6% of the Mn in the sample if the moment is ascribed to defects.[30] This local moment decreases by a factor of order 10^2 on passing from *i*-$Al_{71}Pd_{19}Mn_{10}$ to $Al_{70.5}Pd_{22}Mn_{7.5}$, which suggests that indeed Mn possesses a local moment only at defects. The concentration of these defects decreases rapidly as the resistivity increases (with Mn concentration decreasing from 10% to 7.5% and/or annealing)[30] and develops the positive curvature as a function of T which is easily recognized as a linear conductance when studied over the wide range of optical energies.[3]

We believe that the disappearance of the local Mn magnetic moment is an indication of improved quasicrystallinity in regions near breaks of the twin edges, which breaks presumably have a filling factor in the range 10^{-3} required to explain the data. As the twin edges become more ideal, they are more effective in interrupting phase coherence and thus replacing ballistic conductance with hopping conductance.

We pause at this moment to discuss why the fraction of Mn atoms with local moments is so small in *i*-Al-Pd-Mn when such moments are so commonly observed,[28,29] for instance in the Heusler compound $AlMnPd_2$. In this crystal all rings are even-membered, which favors antiferromagnetic ordering. The large fraction of odd-membered rings in quasicrystals, some even in the glue region, tends to suppress antiferromagnetically ordered local moments. At the same time we note that while almost all (Al or Ga)MnY_2 Heusler compounds are ferromagnetic, $InMnPd_2$ is antiferromagnetic.[29] Our explanation for this is that *p*-*d* hybridization, which makes a large contribution in general to cohesive energies,[31] is larger for In than for Al or Ga. Moreover, in quasicrystals Mn is embedded in a *p*-rich (Al- or Ga-rich) environment. All of these factors, taken together with the large *p*-*d* pseudogap, tend to suppress the formation of Mn local moments except for very special defect clusters which can easily be located at twin edge breaks.

Phase decoupling and hopping conductivity may well be associated with minigaps which require perfect twin edges. Thus a very low level of defect complexes may be sufficient to fill in the minigap shown in Fig. 1(c), and this can well explain the correlation observed experimentally[30] between linear conductance and residual Mn defect local moments.

Another qualitative observation is that the diamagnetism increases with the resistivity as samples are annealed or composition is optimized. The diamagnetic susceptibility then attains a value about 50% larger than expected from ion cores alone.[30] This enhanced dimagnetism is qualitatively consistent with minigap formation and enhanced interband Larmor orbital matrix elements, that is, improved intratwin orbital confinement (compartmentalization) and enhanced intertwin phase decoupling.

VIII. ATOMIC RINGS AND ELECTRONIC STABILIZATION

We have emphasized repeatedly two qualitative aspects of the twin "glue" regions compared to the icosahedral clusters, the reduced coordination numbers and the presence of four-membered rings instead of three-membered rings. They former are characteristic of bcc-like structures, the latter of close-packed or icosahedral clusters.

There is a general tight-binding theory of the effect of ring topology on electronic structure based on the moment method. The theory was originally used to discuss the close-packed-bcc structural dichotomy as a function of d-electron count for transition elements, and it has recently been reviewed and discussed for the simplest case of s-p bonded elements.[32] As is generally the case for atomic orbital models, the density of electronic states $N(E)$ does not resemble very closely that found in more accurate calculations, especially for unoccupied states. The theory is analytically cumbersome (the density of states appears only in continued fractions) and the crystalline periodicity is not part of the theory. This makes it difficult to calibrate the results of this method against those obtained from crystalline self-consistent field calculations with much larger basis sets. However, some of these disadvantages become advantages in the present context of "icosahedra and glue" structures where crystalline periodicity may be absent.

The theory shows that although there are many contributions to the structural energy, the most distinctive ones, and the ones most likely to produce exotic structures, are the smallest rings. (If two structures have the same smallest ring energy, then one would consider the second smallest ring contributions, and so on). This is consistent with our emphasis on three-membered versus four-membered rings. For elements one finds that generally structures with odd-numbered smallest rings are favored for much less or much more than half-filled bands, whereas near half-filled bands even-membered rings are favored.[32] (The bcc structures of the heavier alkali metals are an exceptional case, which arises from Fermi surface proximity to a zone face. Similarly type-I quasicrystals may be a special case stabilized primarily by s-p electron Jones zone effects.)

We can apply these ideas to our model of stabilization of type-II quasicrystals by a CsCl-like glue, such as AlX, as follows. Instead of treating the type-II quasicrystals in the same way as type I, and assuming that we have s-p electron stabilization, we assume that the dominant factor is stabilization by the d electrons of a CsCl-like structure. The energy bands and density of states $N(E)$ has been calculated[33] for CoAl (CsCl structure). The results for the Co d and Al p states are sketched for the reader's convenience in Fig. 2(a). Both the Co d and the Al p densities of states show a large pseudogap near E_F with magnitudes of $E_p \sim 1.0$ eV (Co d) and 2.0 eV (Al, p). In Fig. 2(b) we also sketch the tight-binding approximation to a bcc p-band density of states (Fig. 2 of Ref. 32). The overall simplicity of Figs. 2(a) and 2(b) for the Al p bands is clear, as is the difference from the fcc density of states, Fig. 2(c). Although these comparisons are encouraging, when we go one step further and attempt to compare the calculated Co d bands with those obtained from model calculations[34] for pd-bonded AB compounds we had little success. The calculations were done for $\varepsilon_{pd} = E_p - E_d = 0, \pm 5$ eV and the value appropriate to AlCo seems from the self-consistent field calculations[33] to be about $+3.5$ eV.

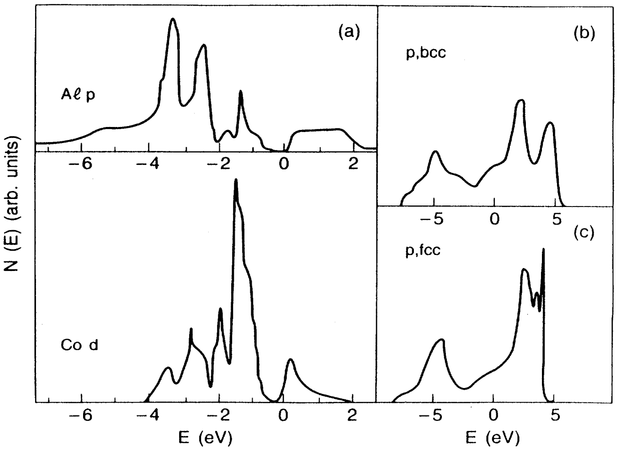

FIG. 2. Comparison between (a) projected densities of Al p and Co d states from SCF calculations for AlCo (Ref. 33) and model calculations (b), (c), for isolated p bands in hypothetical bcc and fcc Al. The Fermi energy E_F occurs at $E = 0$ in (a) and near -3.0 and -3.5 eV in (b) and (c), respectively. The peak near -5 eV in (b) and (c) corresponds to the split peaks near -3 eV in (a). In (a) there is an Al p pseudogap between -2 and 0 eV, and a Co d pseudogap between -1 and 0 eV. (The small peak near -1 eV in the Al p projection is a residue of Co d states). From these features we estimate $\varepsilon_{pd} = E_p(\mathrm{Al}) - E_d(\mathrm{Co})$ is close to 3.5 eV.

It appears from Fig. 1 of Ref. 33 that the pseudogaps arise from the Co d and Al p bands at general points of **k** space, in other words it is the result of p-d hybridization. This p-d pseudogap is probably the origin of the previously unexplained p-d contribution to the heat of formation.[31] It is possible that improvements in ring topology (especially near twin edges) can contribute to the formation of a Jahn-Teller-like minigap E_m which can explain anomalously large dependence of transport properties[1,30] and specific heat[4] on small composition shifts and annealing.

IX. CONCLUSIONS

We have used a wide variety of ideas, geometrical, crystal chemical, statistical, and quantum-mechanical, to discuss the structures and properties of stable quasicrystals. The theoretical literature largely utilizes geometrical ideas, but as we have seen, once the idea of Penrose tiling is accepted, geometrical ideas are the least useful and provide almost no insight into the origin of structural stability or trends in physical properties. This is because geometrical models are basically packing models, and it is well known that such models fail to describe structural trends even in very simple systems where directional effects are small and valence effects are excluded, such as the diatomic alkali halides.[35] Under such circumstances it would be extremely naive even to hope that packing models could successfully handle delicate questions of stability and metastability in ternary quasicrystals and crystalline approximants with $N \sim 150$ atoms/cell.

The most economical and to date by far the most successful approach utilizes crystal chemical and statistical ideas. We have used this approach here to explain differences in stability and properties of types-I and -II quasicrystals. The type-I quasicrystals are analogous to Frank-Kasper crystals in the sense that they are composed primarily of tetrahedra (smallest rings contain three atoms) and indeed there exist Frank-Kasper crystalline approximants to type-I quasicrystals. The type-II quasicrystals are stabilized by a completely different structural principal that has been identified by us here and elsewhere.[6] The unavoidable misfit engendered by icosahedral clusters is relaxed in type-II quasicrystals by a high filling factor of pseudobinary material with a local CsCl structure where the smallest rings contain not three but four atoms. Such rings facilitate low-temperature (Martensitic) transformations, for instance Na from bcc to hcp around $T \sim 50$ K, and are associated with many other bcc-based Martensitic transformations as well.[36]

From a fundamental view point, the origin of quasicrystalline stability and chemical trends in transport properties lies in pseudogaps centered on $E = E_F$. The existence of such gaps associated with icosahedra is by now well established,[23] but as we have seen the icosahedral pseudogaps, like the icosahedral clusters themselves, are insufficient to differentiate types-I and -II quasicrystals, or to explain the existence of crystalline approximants for the former but not the latter or to explain why low-temperature resistivities are much larger in the latter than in the former. We attribute all these points to the CsCl glue pseudogap, which we believe is optimized in the pseudobinary by disproportionation of the ternary composition between the icosahedra and the CsCl glue. It is the smaller, not the larger, gap that determines structural behavior, that is, the glue and not the icosahedral pseudogap. (Compare the π and σ gaps in planar hydrocarbons. The charge densities which are structurally determinative are those which are most polarizable and hence associated with the smaller energy gap.) This gap is probably the one that has been measured optically,[3] and it promises to provide us eventually with the most fundamental insight into quasicrystalline properties.

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[1] B. D. Biggs, S. J. Poon, and N. R. Munirathnam, Phys. Rev. Lett. **65**, 2700 (1990).

[2] U. Mizutani, Mater. Sci. Eng. **99**, 165 (1988).

[3] C. Homes *et al.*, Phys. Rev. Lett. **67**, 2694 (1991).

[4] B. D. Biggs, F. S. Pierce, and S. J. Poon, Europhys. Lett. **19**, 415 (1992); S. J. Poon, Adv. Phys. **41**, 303 (1992).

[5] J. C. Phillips and K. M. Rabe, Phys. Rev. Lett. **66**, 923 (1991).

[6] P. Villars, J. C. Phillips, and H. S. Chen, Phys. Rev. Lett. **57**, 3085 (1986); K. M. Rabe, A. R. Kortan, J. C. Phillips, and P. Villars, Phys. Rev. B **43**, 6280 (1991); K. M. Rabe, J. C. Phillips, P. Villars, and I. D. Brown, *ibid.* **45**, 7650 (1992); K. M. Rabe, J. C. Phillips, and P. Villars, J. Non-Cryst. Solids (to be published).

[7] F. C. Frank and J. S. Kasper, Acta Cryst. **11**, 184 (1958); **12**, 483 (1959).

[8] P. Villars, J. Less. Comm. Met. **109**, 93 (1985); **119**, 175 (1986).

[9] M. Duneau and C. Oguey, J. Phys. (Paris) **50**, 135 (1989).

[10] C. Janot, J. Pannetier, J. M. Dubois, and M. De Boisseau, Phys. Rev. Lett. **62**, 450 (1989).

[11] S. Song and E. R. Ryba, Philos. Mag. Lett. **65**, 85 (1992).

[12] M. Audier *et al.*, Physica B **153**, 136 (1988).

[13] A. Villars and L. D. Calvert, *Pearson's Handbook of Crystallographic Data for Intermetallic Phases* (ASM, Materials Park, OH, 1991), pp. 444, 467, 916.

[14] J. L. C. Daams, P. Villars, and J. H. N. Vucht, *Atlas of Crystal Structure Types for Intermetallic Phases* (ASM, Materials Park, OH, 1991), pp. 6759–6764.

[15] M. De Boisseu *et al.*, Philos Mag. Lett. **65**, 147 (1992).

[16] S. K. Paranjpe and R. J. Begum, J. Magn. Magn. Mater. **15-18**, 477 (1980).

[17] W. Liu, M. Schmücker, and U. Köster, Phys. Status Solidi (a) **124**, 75 (1991); B. Grushko and K. Urban, J. Mater. Res. **6**, 2629 (1991).

[18] A. Crosky, P. G. McDougall, and J. S. Bowles, Acta Metal. **28**, 1495 (1980).

[19] R. C. Ecob and B. Ralph, Acta Metall. **29**, 1037 (1981).

[20] A. Inoue, A.-P. Tsai, and T. Masumoto, in *Quasicrystals,* Solid State Sciences Vol. **93**, edited by T. Fujiwara and T. Ogawa (Springer-Verlag, Berlin, 1990), p. 80.

[21] N. Koshikawa, S. Sakamoto, K. Edagawa, and S. Takeuchi (unpublished).

[22] T. Fujiwara, Phys. Rev. B **40**, 942 (1989).

[23] T. Fujiwara and T. Yokokawa, Phys. Rev. Lett. **66**, 333 (1991); see also J. Hafner and M. Krajci, Phys. Rev. Lett. **68**, 2321 (1992); J. Friedel, Helv. Phys. Acta **61**, 538 (1988).

[24] C. L. Henley and V. Elser, Philos. Mag. **53**, L59 (1986); A. P. Tsai, H. S. Chen, A. Inoue, and T. Masumoto, Phys. Rev. B **43**, 8782 (1991).

[25] J. C. Plenet, A. Perez, J. Rivory, J. M. Frigerio, and O. Laborde, Phys. Lett. A **162**, 192 (1992).

[26] T. Klein, H. Rakota, C. Berger, and G. Fourcaudot, and F. Cyrot-Lackmann, Phys. Rev. B **45**, 2046 (1992).

[27] J. C. Phillips, Solid State Comun. **83**, 379 (1992); (unpublished); K. H. J. Buschow and P. G. van Engen, J. Magn. Magn. Mater. **25**, 90 (1981).

[28] T. Fujiwara and H. Tsunetsugu, in *Quasicrystals,* edited by D. P. DiVincenzo and P. Steinhardt (World Science, Singapore, 1991), p. 343.

[29] J. Kübler, A. R. Williams, and C. B. Sommers, Phys. Rev. B **28**, 1745 (1983).

[30] P. Lanco, T. Klein, C. Berger, F. Cyrot-Lackmann, and G. Fourcaudot, Europhys. Lett. **18**, 227 (1992).

[31] F. R. de Boer, R. Broom, W. C. M. Mattens, A. R. Miedema, and A. K. Niessen, *Cohesion in Metals I* (North-Holland, Amsterdam, 1988), p. 62.

[32] J. C. Cressoni and D. G. Pettifor, J. Phys. Condens. Matter **3**, 495 (1991).

[33] D. J. Nagel, L. L. Boyer, D. A. Papaconstanopoalos, and B. M. Klein, in *Transition Metals 1977,* edited by M. J. G. Lee, J. M. Perz, and E. Fawcett (Institute of Physics, London, 1978), p. 104.

[34] D. G. Pettifor and R. Podloucky, J. Phys. C **19**, 315 (1986); A. E. Carlsson and R. Phillips, in *Quasicrystals* (Ref. 28), p. 361.

[35] J. C. Phillips, in *Treatise on Solid State Chemistry,* edited by N. B. Hannay (Plenum, New York, 1973), Vol. 1, p. 1; and in *Electronic Materials,* Springer Solid State Sciences Vol. 95, edited by J. R. Chelikowsky and A. Franciosi (Springer-Verlag, Berlin, 1991), p. 287.

[36] C. S. Barrett, Acta Cryst. **9**, 671 (1956).