PHYSICAL REVIEW B VOLUME 53, NUMBER 1 1 JANUARY 1996-I

Conductivity in quasicrystals via hierarchically variable-range hopping

C. Janot
Institut Lave-Langevin, Boîte Postale 156, 38042 Grenoble Cedex 9, France

(Received 16 May 1995)

This paper takes the structure example of the AlPdMn quasicrystal, as determined from diffraction data, to derive useful self-similarity rules in consistency with composition and atomic valence constraints. These rules are then accounted for to explain inelastic-neutron-scattering data and thermal conductivity behavior. Basically, three regimes can be identified: extended low-energy phonon conductivity at low temperature following roughly a T^2 power law which transforms into a plateau of constant conductivity and, at higher temperature, a phonon assisted localized-state hopping mechanism with a $T^{3/2}$ power law and hierarchically distributed hopping distances. Electrical conductivity is also briefly analyzed along the same approach: accordingly, pure perfect quasicrystals should show a $\sigma(T)\propto T$ behavior with deviation in $T^{0.5}$ at low temperature and in $T^{3/2}$ at high temperature coming from quasiperiodicity breaking.

I. INTRODUCTION

Quasicrystals are materials presenting a new type of long-range order. Their diffraction pattern shows sharp Bragg reflections revealing symmetries which are incompatible with periodicity.[1] That quasicrystalline alloys are highly ordered systems was demonstrated with ‘‘perfect’’ quasicrystals of the AlCuFe and AlPdMn systems.[2,3] These quasicrystals exhibit extremely sharp Bragg reflections corresponding to correlation lengths of several tenths of a micrometer,[4] similar to what is obtained for good periodic crystals. Moreover, centimeter size grains can be grown in the AlPdMn system via classical methods.[5–7] The quality of these large grains is such that dynamical diffraction is observed on a macroscopic scale.[4]

The atomic structure of icosahedral quasicrystals is now well understood via higher-dimensional crystallography. Following this approach, atomic models have been proposed for AlCuFe (Ref. 8) and AlPdMn (Refs. 9 and 10) icosahedral phases. The result is only a ‘‘low resolution’’ image in that the details of the atomic structure are not yet specified. However, clear insights are obtained about the existence of well-defined atomic clusters, which are packed quasiperiodically into hierarchical aggregates.[11]

The calculation of the dynamical response of quasicrystals remains difficult, however, since atomic surfaces are not pointlike objects and the Bloch wave expansion is not an appropriate description in a quasilattice. Beyond one- or two-dimensional toy models realistic calculations have been proposed[12–14] for the derivation of the density of states and the dispersion law in periodic approximants of the icosahedral phase. From these calculations, well-defined acoustic modes are predicted to show up close to the strong Bragg reflections which can be selected as some sort of Brillouin zone centers. Accordingly, quasi-Brillouin zone boundaries are attached to high symmetry points in the reciprocal space[15,16] and are packed hierarchically around the zone centers. Far from strong reflections, acoustic modes broaden significantly.[17] Gap openings in the acoustic branches are also predicted when crossing the quasi-Brillouin zone borders. At higher energy, the calculations produce a very large density of almost flat optic branches corresponding mostly to standing modes.[12,13] Experimental results[18–21] partially support the theoretical derivations as long as low-energy acoustic modes are concerned. The point will be elaborated further in the body of the paper.

The available information on physical properties[1] include data on electrical[22–25] and thermal transport,[26,27] the complete electrodynamic response,[28] the low-temperature thermodynamic and magnetic properties,[29,30] results from photoemission and x-ray spectroscopy,[31,32] as well as mechanical behavior (elasticity/plasticity pattern, friction coefficient, surface hardness, tribology, etc.).[33]

The present paper is intended to focus on relations between structure, atomic vibrations, and anomalous transport properties of icosahedral quasicrystals, exemplified with the AlPdMn system. Basically, the very unexpected behavior of icosahedral quasicrystals is their very high electrical (and thermal) resistivity, practically that of an insulator,[34] untypical indeed for materials containing about 70 at. % of aluminium. Moreover, and conversely to usual metallic alloy properties, impurities, structural defects, and increase of the temperature improve the conductivity.[35] So far, most of the attempts to explain the origin of high resistivity in the stable quasicrystals have been linked to a combination of the existence of a deep pseudogap in the electron density of state at the Fermi level with a localization tendency of electrons near the Fermi level.[36] Along the same line of extrapolation of the models which are usually invoked for crystalline or amorphous systems, the presence of a pseudogap has been ascribed to Hume-Rothery stabilization[37] while the temperature dependence has been suggested to come from Anderson weak localization and electron-electron interactions. But these theories are unable to fully explain the experimental behavior of the best highly resistive quasicrystals: the very low density of state at the Fermi level and small mean free path are unacceptable for quantum interferences and Anderson localization to be sensibly evoked while the thermal behavior or imperfection effects on conductivity just goes the other way of that predicted by Hume-Rothery-like descriptions.[38,39] The alternative approach is to consider hopping conduction between strongly localized states. This has

0163-1829/96/53(1)/181(11)/$06.00

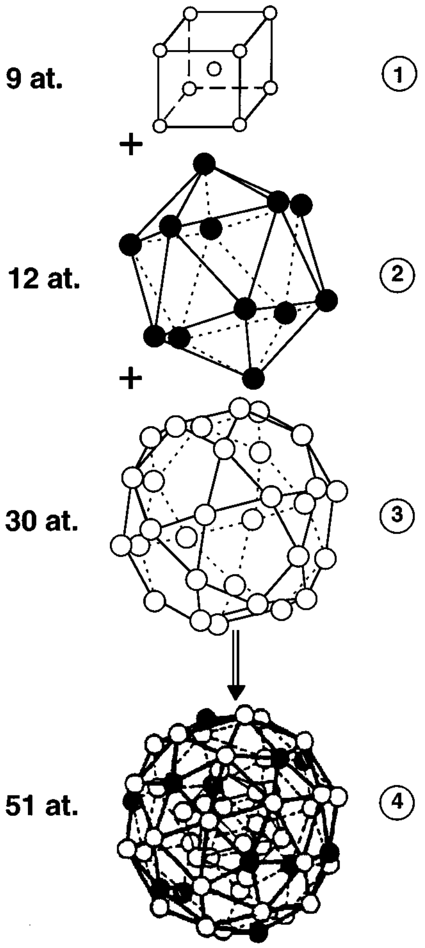

FIG. 1. Successive atomic shell of a pseudo-Mackay icosahedron (PMI).

been qualitatively suggested by several authors.[11,25,35,40,41] It is one purpose of the present paper to elaborate on such an approach, using both structure and phonon data to design a variable range hopping mechanism based on anharmonic phonon assistance and compatible with self-similarity properties. Strong localization in quasicrystals is in particular demonstrated via the observed magnetic-field dependence of the conductivity and has recently been related to the direct observation by tunneling spectroscopy that the pseudogap at the Fermi level is actually very narrow ($\sim$50 meV),[30,42,43] confirming an estimate based previously on thermal conductivity data.[27]

II. QUASICRYSTAL STRUCTURE AS A HIERARCHY OF LOCALIZATION WELLS

A. The structure from diffraction data

Details about preparation and characterization of the AlPdMn quasicrystals, including in the form of perfect big centimeter size single grains, have been published elsewhere.[5–7] Techniques relevant to quasicrystallography were also extensively and critically presented on several occasions.[1,8–10] We will then restrict the content of this section to the practically useful part of the structure, as obtained from x rays and neutron diffraction data, for the AlPdMn icosahedral quasicrystals. Though being known at a rather low level resolution only, the structure reveals several building rules which appear as astonishingly simple, with both chemical and geometrical order.

First of all, everything in the structure is based on atomic units containing 51 atoms in total, named pseudo-Mackay icosahedra (PMI) hereafter, and made of three centrosymmetrical shells as shown in Fig. 1: an inner small centered cubic core of 9 atoms, an intermediate icosahedron of 12 atoms, and an external icosidodecahedron of 30 atoms. The last two shells have practically equal radii and constitute altogether the boundary of the PMI whose diameter is slightly less than 10 Å. Apart from this well-defined geometry, the PMI's show two different chemical compositions: one family (PMI-*A*) has 6 manganese plus 6 palladium atoms on the icosahedron sites and 39 aluminium atoms elsewhere while the second family (PMI-*T*) exhibits 20 palladium atoms among the 30 of the icosidodecahedron, the rest (31 atoms) being aluminum atoms. The calculated atomic density of an individual PMI is 0.064 atoms/Å^3, which compares quite well with the measured density of the bulk material, within experimental accuracy. It is, however, fair to say that several ingredients in the description of the PMI's do not show up directly from diffraction data. The Patterson analysis strongly suggests that the PMI cores are made of about 8–9 atoms distributed into pieces of dodecahedra; it is indeed a speculation to state that these pieces are arranged in centered cubic geometry. Similarly, it is not yet possible to be definitive about the exact PMI compositions. We will see in Sec. II B that the ones proposed above allow self-consistency between structure and overall chemical composition of the alloy.

Then, these PMI units combine to reproduce a similar geometry within inflation by a scale factor τ^3 ($\tau=2\cos 36°$ is the golden mean). This is shown in Fig. 2 which presents the cut of a piece of the structure by a plane perpendicular to a fivefold axis. In the figure center, the equatorial section of a PMI shows up. Around this central PMI, there are 42 PMI's whose centers are distributed on the combined sites of the

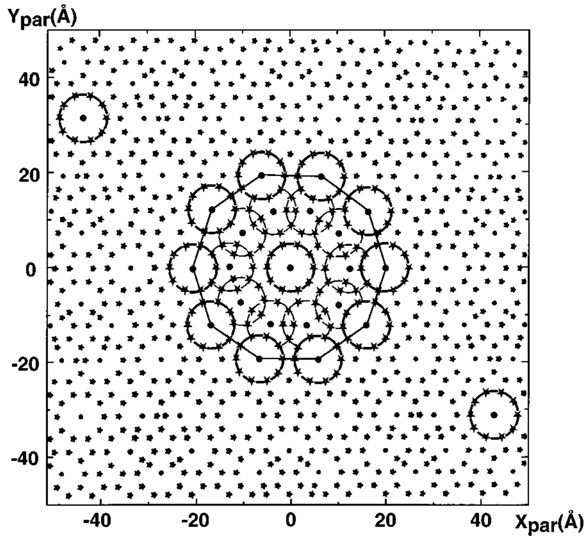

FIG. 2. Example of a planar section of the AlPdMn quasicrystal structure. Rings of ten atoms are equatorial sections of a PMI. The τ^3 inflated ring is also visible, as well as the τ^2 inflated ring of overlapping PMI's ($*$ Al; $\bullet$, Mn) (Refs. 10 and 11).

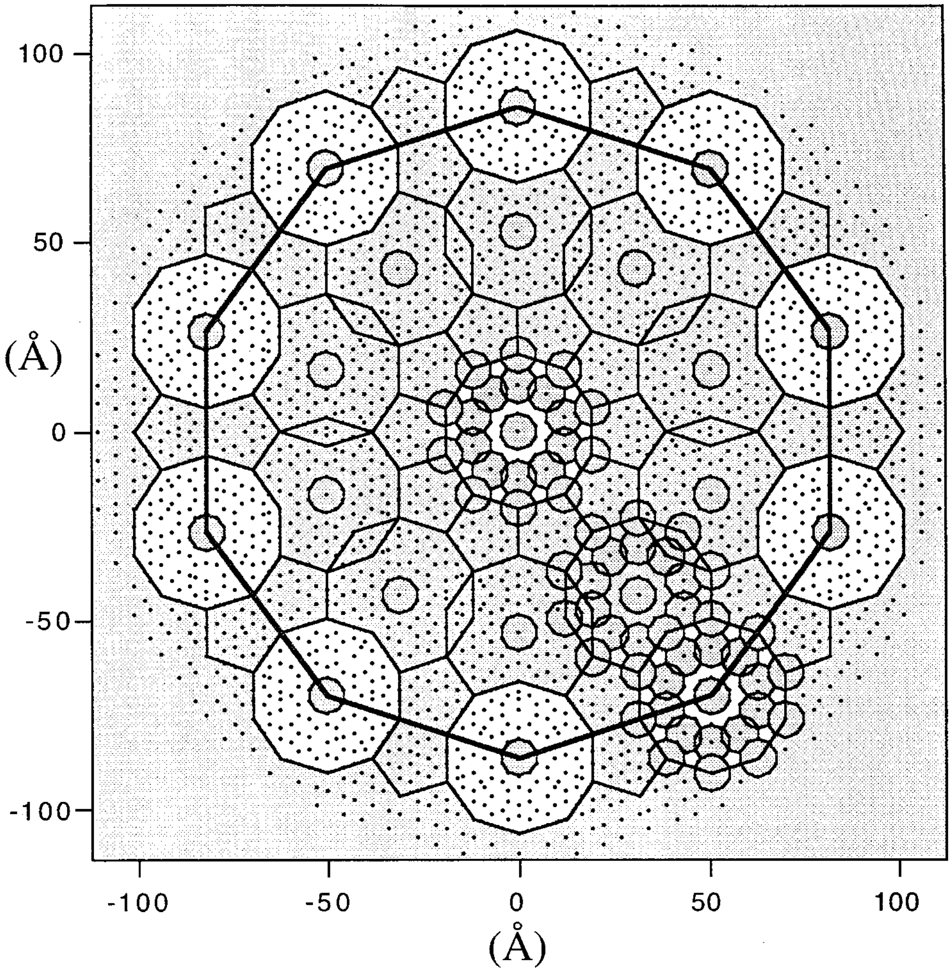

FIG. 3. Planar section of the structure identical to that shown in Fig. 2 but presenting up to the second inflation step.

icosahedron plus the icosidodecahedron of a big PMI with a radius τ^3 as large as that of the base unit (about 42 Å, namely). An intermediate shell, with τ^2 inflated radius, is also visible in Fig. 2. This shell does not reproduce the centered cube of a PMI and is made of 42 overlapping pieces of PMI units. Each of these PMI pieces contributes to the total number of atoms in the inflated τ^3-PMI with 9 atoms in the cubic core, 12 atoms in the icosahedron which do not overlap with others, and 19 (instead of 30) in the icosidodecahedron which has a 5 atom truncation in its bonding with the external shell and in which 12 atoms contribute only one half because of the overlapping geometry. Thus, the τ^2 shell brings 42×40 atoms to the inflated τ^3-PMI, in addition to the 43×51 atoms which come from the τ^3 shell of PMI's (42×51) and from the central PMI (1×51). This amounts to 75.941 effective elementary PMI's ($3\,873=51\times75.941$). It demonstrates that the big τ^3-PMI keeps the atomic density of its PMI units, with a very small residual fractality. Indeed, the τ^3-PMI volume is $\tau^9=76.013\ldots$ as large as that of the elementary PMI and contains 75.941 as many atoms; the calculated fractal dimension is then $2.999\ldots$, which is equivalent to vacancy concentration of less than 3×10^{-4}.

The structure subsequently develops via successive steps of exact τ^3inflation operations. Figure 3 shows a planar projection of a layer of atoms presenting the result of a $\tau^3\times\tau^3$ inflation, with a τ^3-PMI in the center, a shell of 42 τ^3-PMI on a $\tau^3\times\tau^3$ radius "sphere" and the $\tau^3\times\tau^2$ intermediate shell of overlapping truncated τ^3-PMI. Pentagonal "tiles" at various scales are also visible in the figure; they come from PMI and inflated PMI whose equatorial plane is not in the figure. In conclusion, at any inflation stage, we have a cluster of PMI clusters.

B. Self-similarity constraints for composition and atomic valences

The archetype of icosahedral structures is based on Penrose-like tiling. Fivefold symmetries and self-similarity force the numbers of the different prototiles to be in ratios equal to power of the golden mean τ (this is merely the extension to quasicrystals of the relations between chemical compositions and structures as currently observed in regular crystals). Then, it can reasonably be conjectured that ideal compositions for quasicrystals should obey such a τ^n law. The simplest chemical description of the AlPdMn quasicrystals would assume that we have two types of species in it: the Al atoms in the one hand, the transition atoms T in the other hand combined into Al_xT_{1-x} with $x=\tau^n(1-x)$. Experimentally, the best AlPdMn quasicrystals are obtained with x in the vicinity of 0.7, suggesting that we have a "τ^2" quasicrystal ($\tau^2/1+\tau^2=0.7236\ldots$) whose ideal composition may be refined as $\mathrm{Al}_{0.7236}T_{0.2764}$. Now, if the self-similar structure described in the previous section is a robust view of reality, the relative concentrations of the two types of PMI (PMI-*A* concentration n_A, PMI-T concentration n_T) should also obey the τ^2 law ($n_A = \tau^2 n_T$). If so, we should have consistency relations satisfied to account for PMI chemical composition and structure altogether such that

$$\frac{39n_A + 31n_T}{51} = 0.7236$$

and

$$\frac{12n_A + 20n_T}{51} = 0.2764$$

with $n_A = 0.7236$ and $n_T = 0.2764$; these are indeed compatible within less than 1%. Interest in such a conclusion is twofold. First, it contains a consistent validation of both the structure described above and the τ^2 law for composition. But it also allows to calculate individual concentrations of manganese and palladium in the alloy by using the composition of the PMI's (A and T), namely

$$C_{\mathrm{Mn}} = \frac{6n_A}{51} = 0.0828,$$

$$C_{\mathrm{Pd}} = \frac{6n_A + 20n_T}{51} = 0.1935.$$

The ideal composition of the perfect quasicrystal thus should be $\mathrm{Al}_{0.7236}\mathrm{Pd}_{0.1936}\mathrm{Mn}_{0.0828}$.

[*Note:* an interesting and somewhat mysterious fact may be worth being mentioned here. Writing the chemical formula $\mathrm{Al}_x\mathrm{Pd}_y\mathrm{Mn}_z$ of the quasicrystal, we assumed without proper justification that the τ^2 rule applied in cascade, namely:

$$y = \tau^2 z, \quad x = \tau^2(y + z)$$

with

$$x + y + z = 1.$$

There is, then, a single solution such as $\mathrm{Al}_{0.7236}\mathrm{Pd}_{0.2000}\mathrm{Mn}_{0.0764}$.

A similar rule, applied to the AlFeCu quasicrystal which is a τ compound instead of τ^2, gives $\mathrm{Al}_{0.618}\mathrm{Cu}_{0.237}\mathrm{Fe}_{0.145}$. None of these compositions correspond exactly to those experimentally deduced from phase diagrams.[44,45] The AlPdMn real quasicrystal has slightly less aluminum and slightly more palladium while the AlFeCu one contains 2% less iron and 2% more copper; these experimental compositions are very close to that of the 3/2 and 2/1 periodic approximants, respectively, when calculated with the above cascade rule but with 3/2 or 2/1 instead of τ. At this stage, it is difficult to reach definitive conclusions. The experimental compositions, after all, are partly mastered and corrupted by noncongruent melting effects and kinetics of the phase transitions. The best AlFeCu quasicrystals, with the so-called canonical composition, are even prepared via a procedure which associates melt quenching and annealing in sequence, far enough from equilibrium casting. AlPdRe and AlCuRu quasicrystals have compositions that obey more closely the τ^2 and τ rule, respectively.]

One can even go further and take benefit of the self-similarity properties to calculate the apparent atomic valences of the three metals in the compound. This is based on the idea that metallic clusters with icosahedral symmetry can be stable entities to the point that they mimic the chemistry of atoms, with the valence electrons distributed in states which are the energy levels of the cluster instead of those of the atoms. Such an idea has been supported by self-consistent quantum-mechanical calculations[46] which demonstrate the point. Independently it has also been verified that strong resonances occur when such an icosahedral cluster is immersed into a free electron gas, thus confirming the stability of the cluster levels.[47] Formally, these cluster energy levels can be obtained by solving the problem of the valence electrons into the potential due to ionized atoms in the cluster, or equivalently, to find the electronic eigenstates of an appropriate potential well. In a naive jelliumlike approximation of this problem[11] it has been shown that the cluster would have very stable structure, comparable to that of rare gas atoms with saturated levels containing 2,8,20,40,92,138,156, . . . electrons into the cluster states. As far as the PMI clusters of the AlPdMn quasicrystal are concerned, with their 70 at. % or so of aluminum, and their 51 atoms, the state corresponding to 92 electrons must be reasonably selected. However, to be bonded to each other, the PMI must contain slightly more or slightly less electrons than the 92 saturated configuration. Moreover, we have, as we know, two types of PMI's (A and T) which are constrained to self-similarity and, then, must reproduce the behavior of the atomic species. It means that the two prototypes of PMI's contain $92 + V_{\mathrm{Al}}$ and $92 + V_T$ electrons, respectively, in which $V_{\mathrm{Al}} = 3$ is the aluminium atomic valence and V_T is the average atomic valence of palladium and manganese, i.e.,

$$0.2764V_T = 0.0828V_{\mathrm{Mn}} + 0.1936V_{\mathrm{Pd}}.$$

Proper balance of electrons, as written for PMI-A and PMI-T, gives

$$92 + V_{\mathrm{Al}} = 39V_{\mathrm{Al}} + 6V_{\mathrm{Mn}} + 6V_{\mathrm{Pd}},$$

$$92 + V_T = 31V_{\mathrm{Al}} + 20V_{\mathrm{Pd}}.$$

The only unknown quantities are V_{Mn} and V_{Pd}, the atomic valences of the two transition metals; going through the arithmetic gives $V_{\mathrm{Pd}} = -0.107$ and $V_{\mathrm{Mn}} = -3.559$.

As by products of the calculation we get also the average atomic valence of the transition metal, $V_T = -1{,}141$ and the global average atomic valence $\langle V \rangle = 1.855$. Interestingly, we see that $V_{\mathrm{Al}} \simeq -\tau^2 V_T$, which means that the τ^2 rule would apply here for both concentrations and atomic valences. This is in favor of the existence of a very strong chemical order with ionocovalentlike self-similar bonding between atoms and cluster at any inflation stage. Noteworthy, if both the concentration and the valence rules are taken for granted ($C_{\mathrm{Al}} = \tau^2 C_T$ and $V_{\mathrm{Al}} = -\tau^2 V_T$ or $V_T = -1.1459$), there is no need of any model anymore to fix the number of electrons into saturated PMI cluster levels; the value 92 emerges naturally from calculations in wonderful consistency with the model. To summarize the electronic structure of these quasicrystals: 51 atoms are packed into PMI's, each Al atom giving 3 electrons to the cluster and each T atom "trapping"

-1.1459 electrons from the pool; the remaining "free" electrons are distributed into cluster levels, 92 of them being into saturated states to stabilize the cluster and bonding between cluster being ionocovalentlike with again $+3$ and -1.1459 effective cluster valences; the same scheme repeats for the PMI's at subsequent inflation steps: saturated cluster levels plus electrons for bonding and generating the next inflated clusters. The elementary PMI's, as we said, have 51 atoms and 92 electrons (± valences); the inflated PMI's have 76 PMI's of the previous generation and then 138 electrons (± valences), which, being also a saturated configuration, adds to the self-consistency of the electronic and atomic structures described above.

The negative effective valences for the transition atoms are not surprising and currently understood for intermetallic compounds.[48] They manifest the strong interaction of the d states with the conduction band. These negative valences have not "universal" values and depend on both the chemical species and the structure in which they are engaged. Thus, it is agreeable to have them derived from a physical analysis of the structure.

In conclusion, the quasicrystal appears as some sort of a hierarchically packed pseudomolecular solid, with strongly localized states into PMI clusters; any wandering particles (electrons) or quasiparticles (phonons) are then expected to have mostly very short mean-free path Λ of the order of the PMI diameter; small and decreasing fractions of them $(1/\tau^9, 1/\tau^{18}, \dots, 1/\tau^{9n}, \dots)$ have a hierarchy of increasing mean-free paths $(\tau^3\Lambda, \tau^6\Lambda, \dots, \tau^{3n}\Lambda, \dots,$ respectively). Consequences on properties are expected to be fairly dramatic.

III. ATOMIC VIBRATIONS AND THERMAL CONDUCTIVITY

A. A heuristic description of the critical states

In periodic crystals, atomic vibrations and electronic states are analyzed in terms of independent plane waves and Bloch waves, respectively. Any wave of that sort with wave vector $\mathbf{k}$ propagates ad infinitum except for wave vectors that obey the Bragg law $2\mathbf{k}\cdot\mathbf{G}\pm|\mathbf{G}|^2=0$ for which one has standing waves, steady state, zero group velocity, and gap opening in the dispersive law $\omega(\mathbf{k})$ or band structure $E(\mathbf{k})$. This is a rather rare circumstance and remains, in any case, an extended state in real space since the Bragg law can be satisfied with a single $\mathbf{G}$ for a given $\mathbf{k}$ (exceptionally with a small number of $\mathbf{G}$ as deduced, for instance, from the classical Ewald sphere construction).

In quasiperiodic structures, the $\mathbf{G}$ vectors define a dense set of points. Formally $\mathbf{G}$ depends on more than three linearly independent basis vectors (six for icosahedral quasicrystals).[1] As a consequence the Bragg law is satisfied for any $\mathbf{k}$ vector with a subset of $\mathbf{G}$ which extends roughly like the Ewald sphere size. Thus, the steadylike state becomes the rule rather than the exception: there is no actual propagation (zero group velocity) but all the atoms contribute collectively. It looks like localized states that would repeat coherently again and again at distances scaling with $1/|\mathbf{k}|$: this may be a simple description of what is currently called critical states. The important consequence is observed when states or excitations are tentatively analyzed using the usual spectroscopy methods: the momentum transfer to the solid being not properly defined, eigenmodes in the current sense cannot be measured; a distribution of energy (or frequency) values are found in the response to fixed momentum excitation, and vice versa, the width of the distributions scaling with either $|\mathbf{k}|$ or E (or ω).

An equivalent definition for the critical state of wave function ψ_i (Ref. 49) is expressed in the answer to the following question: How system size dependent is the number of sites $n(\varepsilon)$ on which $|\psi_i|^2$ is larger than any small value ε? For a strictly localized state $n(\varepsilon)$ is bounded and does not increase when the system expands: $n_l(\varepsilon)=n_0 d^0$ where d is a length typical of the system size. For an extended state, ψ_i is observed equivalently at any site; thus, $n(\varepsilon)$ is proportional to the system volume: $n_{\mathrm{ex}}(\varepsilon)\simeq d^3$. The critical state is just formally in between with $n_{\mathrm{cr}}(\varepsilon)\simeq d^{3\beta}$ where $0<\beta<1$ is a measure of the criticality of the state. The coherent communication between sites where vibrations or electrons are in identical states forces the wave function to be space transmitted with nothing else than some damping, i.e.,

$$\psi_{2d}(x)\sim z(x)\psi_d(x) \tag{1}$$

in which $z(x)$ is the damping factor and we have accounted for identical zones of extension d being $2d$ apart in the quasiperiodic structure. Solutions of the above equation are of the form

$$\psi_d(x)\sim\frac{1}{d^{\alpha(x)}} \tag{2}$$

with $\alpha(x)=-\ln z/\ln 2$ [for an extended mode we would have $z(x)=1$ and $\alpha=0$ since there is no damping]. It is interesting to emphasize that in the case of critical modes, the wave functions decay as a power law of the distance instead of the exponential decay typical of strictly localized modes. The conductivity is expected to be proportional to the overlap of two identical states at isomorphic sites and then to decrease as a power law $1/d^{2\alpha}$. A macroscopic piece of quasicrystal, consequently, is an insulator at 0 K. This is consistent with the description of the structure in terms of stable atomic clusters, trapping most of the electrons into their own energy levels, rigidly bonded into a self-similar packing such that the charge (or thermal) carrier density decays as a power law of their mean free path (number of electrons that can travel over distances scaling like τ^{3n} scales like τ^{-9n} as explained in the previous section).

Eigenfunctions of the form given by Eqs. (1) and (2) apply to one-dimensional systems only. But extension to three dimensions is straight-forward. Short-range propagation without damping in a three-dimensional medium gives rise to spherical waves whose total intensity integrated on a sphere of any radius must remain constant, i.e.,

$$4\pi r^2|\psi(r)|^2=\text{const}$$

or

$$\psi(r)\sim 1/r.$$

Damping results in $\psi(r)$ scaling as $r^{-\alpha}$ with $\alpha>1$. In the case of the hierarchical structure of the AlPdMn quasicrystal, the density of modes per atom is divided by τ^9 when the length scale for localization is multiplied by τ^3. The flux of $|\psi(r)|^2$ must be damped accordingly, i.e.,

$$\tau^{-9}r^2|\psi(r)|^2=(\tau^3r)^2|\psi(\tau^3r)|^2$$

or

$$\tau^{-9}r^{2(1-\alpha)}=\tau^{6(1-\alpha)}r^{2(1-\alpha)}$$

and finally

$$\psi(r)\sim r^{-2.5}. \tag{3}$$

B. Phason jumps and thermally activated transport

In incommensurate modulated crystals phason modes correspond to fluctuations of the phase difference between the periodic structure and the modulation function. For quasicrystals this translates easily in the high-dimensional periodic image of the structure:[1] phasons are due to fluctuations (positions or/and shapes) of the atomic surfaces in the complementary (perpendicular) space. The resulting observable effects of phasons are jumps of atoms over positions which are almost energetically equivalent and at short distance apart. As an example it is very easy to check on a Fibonacci sequence of large (L) and short (S) segments that permuting nearest-neighbor LS segments into SL requires only small atom displacements and allows identical (isomorphic) zones to communicate directly instead of being twice their size apart. As a consequence, if phason jumps are thermally activated, the conductivities will increase with temperature.

Looking back at Figs. 2 and 3, one remember that the structure of the AlPdMn quasicrystal is a self-similar packing of atomic clusters, with intermediate zones in which the clusters are truncated and overlap partially. The critical states are within the rigid nonoverlapping full clusters which form insulator zones at 0 K. The sandwiched zones of overlapping pieces of cluster are softer and may be reasonably credited of a sizable conductivity. At 0 K there is no exchange whatsoever between insulator and conductive zones and the whole packing behaves as an insulator. Now, we can see in Figs. 2 and 3 that sort of double atomic positions would possibly accommodate short-distance thermally activated atom jumps, thus allowing in particular the boundaries to fluctuate between insulator (solid clusters) and conductive (pieces of clusters) zones. Such a mechanism would at least account qualitatively for improved conductivity with temperature increase. Static defects or impurities would also help in bypassing insulator zones.

If phason jumps are obviously involved in thermal activation of the conductivity mechanism for quasicrystals, they may be not strictly at the origin of the phenomena. In this section, anharmonicity effects which describe nonlinear interactions between phonons and may initiate phason jumps, are going to be considered.

The self-similar structure of quasicrystals and the presence of "big molecules"-like atomic clusters suggest indeed that transport phenomena may be mastered by phonon-assisted delocalization effects. Such an approach is reminiscent of what has been proposed to explain the dynamical properties of fractal structures.[50] In fractals, a crossover is predicted, and sometimes observed, in the dynamical spectrum. At low energy (large wavelength) excitations are phononlike and extended. Conversely, at high energy (wavelength smaller than or of the order of an isolated fractal "blob") the vibrations are localized and dubbed fractons. Accordingly, fractons would not contribute to transport properties and, for instance, thermal transport $\kappa(T)$ would only be accomplished by the extended normal modes. If $\kappa(T)$ is calculated under these conditions, $\kappa(T)$ increases with increasing temperature because both mode-density occupancy and Bose factor increase. This will continue until all of the extended phonon states are exhausted. The thermal conductivity from phonon transport will then saturate in the Dulong-Petit regime ($k_BT \gg \hbar\omega_{\mathrm{ph}}$). This is not the case actually and $\kappa(T)$ continues to increase above the phonon saturation in real fractal materials.[50] To explain such a peculiar and unexpected experimental fact, nonlinear anharmonicity effects have been evoked. Nonlinearity allows vibrational modes to interact (Fig. 4) and, in the particular case of phonon-fracton coupling, may result in fracton "hopping" in much the same sense as the "phonon-assisted electronic hopping" of Mott[51] for localized electronic states. Calculations demonstrate that, at temperature greater than the crossover energy, the thermal conductivity from fracton hopping increases linearly with temperature, which is reasonably well in agreement with experimental data.[50]

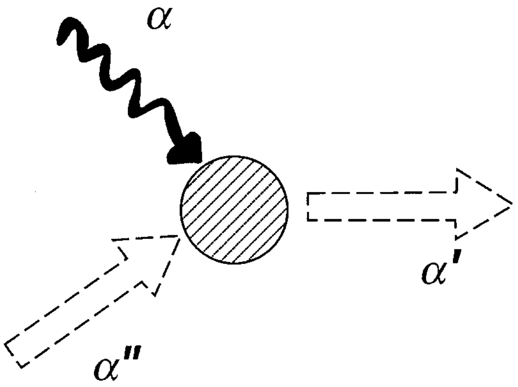

FIG. 4. Schematic diagram of the nonlinear anharmonic interaction phonon+"fracton"→"fracton". The wavy symbol is the phonon, arrows in dashed lines are the fracton states.

One may be tempted to formally use the same derivation for quasicrystals, just substituting some "localized modes" in PMI clusters to fractons. But it is not as simple as that. In quasicrystals the nonextended states are critical rather than strongly localized, such as fractons. This implies, as derived in the previous sections, that the eigenfunctions decay as a power law of the distance and not exponentially. On the other hand, the Mott-like calculation must here account for hopping distances being strictly defined and hierarchically distributed due to the deterministic self-similarity of the structure; the most probable hopping distance of Mott[51] in its original sense relies instead on some random disorder.

C. Experimental data for vibrational modes and thermal conductivity

In good consistency with the analyses presented in the previous sections, inelastic-neutron-scattering measurements[20,21] show that extended phonons are observed only for very small wave vectors in the vicinity of strong Bragg re-

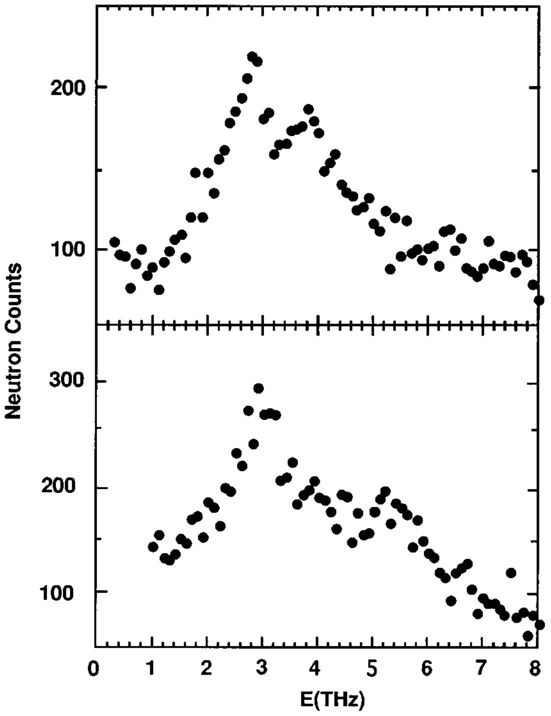

FIG. 5. Energy dependence of the inelastic-neutron-scattering signal measured at constant wave vectors, at two different places in the reciprocal space, away from any strong Bragg peak.

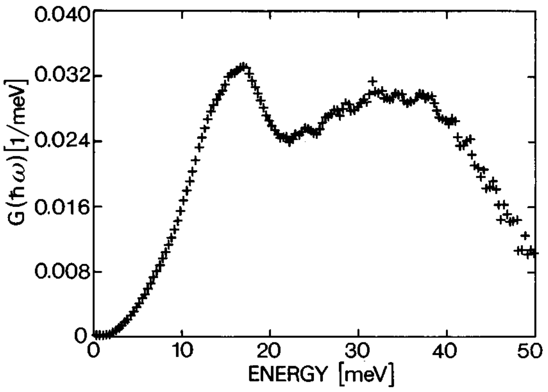

FIG. 6. Vibrational density of states of the icosahedral AlPdMn quasicrystal measured with thermal neutron energy loss spectroscopy (Ref. 52) (courtesy of J. B. Suck).

flections. These phonon modes have an acoustic character. The corresponding dispersion curves allow one to deduce the sound velocity and Young modulus which compare quite well with those obtained directly (from ultrasonic and mechanical investigations) and with values typical of aluminum metal (v_s=3593 ms^{-1} and 6520 ms^{-1} for transverse and longitudinal modes, respectively; Young modulus of 70–80 GPa in compression). When wave vectors larger than about 0.35 Å^{-1} are selected by the triple axis spectrometer, the observed excitations broaden in energy; they also broaden in wave-vector space if scans are carried out at constant energy. This strongly confirms that plane wave modes are not relevant anymore to describe the atomic vibrations in quasicrystals, except for the acoustic small domain close to strong Bragg reflections. The point may even be better illustrated with Fig. 5, which shows the energy dependence of scattered intensities at constant wave vector, somewhere in reciprocal space, away from any sizable Bragg peak. The observed signals cover an energy range which resembles and is as large as that corresponding to the total "phonon" density of state (Fig. 6).[52] This is obviously due to a lack of momentum conservation which allows the interaction of neutrons not only with one selected "phonon" but with all vibrational excitations. However, the excitation intensity appears as strongly modulated in the reciprocal space, contrary to what would be observed for strictly localized states: criticality contains a certain amount of coherent interference effects which show up here in the reciprocal space modulation. This has also been observed in infrared spectra,[53] all modes becoming active regardless of selection rules, which is a direct experimental evidence of the charge transfers between Al and transition-metal atoms as resulting from the hierarchical cluster structure described in the previous section. Wave-vector scans originating from a strong Bragg peak, at constant energies, give several flat branches in the dispersion curves with some intensity modulation. Interestingly, the minimum wavelength (or maximum wave vector) at which true unbroadened acoustic modes can be observed (18 Å and 0.35 Å^{-1}, respectively) corresponds to the largest standing wave that can settle into a cavity of about 9 Å size, which is very close to the diameter of the PMI units. Possible standing waves and optic modes being built in the successive generations of inflated clusters have not been observed actually. But this may be hampered by experimental resolution which allow one to pick only the "low-hanging fruit." The modes also recover, to some extent, extendedlike character when the localization length scale reaches 50–100 Å or so, i.e., roughly after the second inflation step. In conclusion, we observed extended phonons with small wave vectors (smaller than 0.35 Å) and low energy (below 1.5 THz~6 meV) and fractonlike critical ("localized") modes at larger energies.

Such a reduced range of real extended phonons should result in very poor thermal conductivity of the quasicrystals, with a temperature dependence showing a saturation behavior in the Dulong-Petit regime as previously explained. The 6 meV limit for existing phonons would then force the thermal conductivity $\kappa(T)$ to keep a constant value above about 60 K. These predictions are partially verified experimentally. The observed $\kappa(T)$ values are indeed very small, much smaller than expected from purely metallic compounds: at room temperature $\kappa(T)$ for an AlFeCu or AlPdMn quasicrystal is more than two orders of magnitude smaller than for aluminum, more than one order of magnitude smaller than for steel, and about half that of zircon, which is currently considered as one of the best thermal insulators.[54]

On the other hand, the phonon saturation plateau has also been observed in AlPdMn (Ref. 26) and AlFeCu (Ref. 27) quasicrystals (Fig. 7), covering a temperature range from about 25 to 100 K again in good agreement with the energy range of extended phonons. But at higher temperatures $\kappa(T)$ resumes its increasing trend, though with another T dependence;[26,27] $\kappa(T)$ follows the power laws T^n with n approximated by 2.5 below 0.1 K, $n \simeq 2$ between 0.4 to a few K and $n \simeq \frac{3}{2}$ above room temperature (Fig. 8). It is then rather clear that we have all ingredients in hand to try to extrapolate the fracton hopping mechanism to an appropriate variable-range hopping scheme.

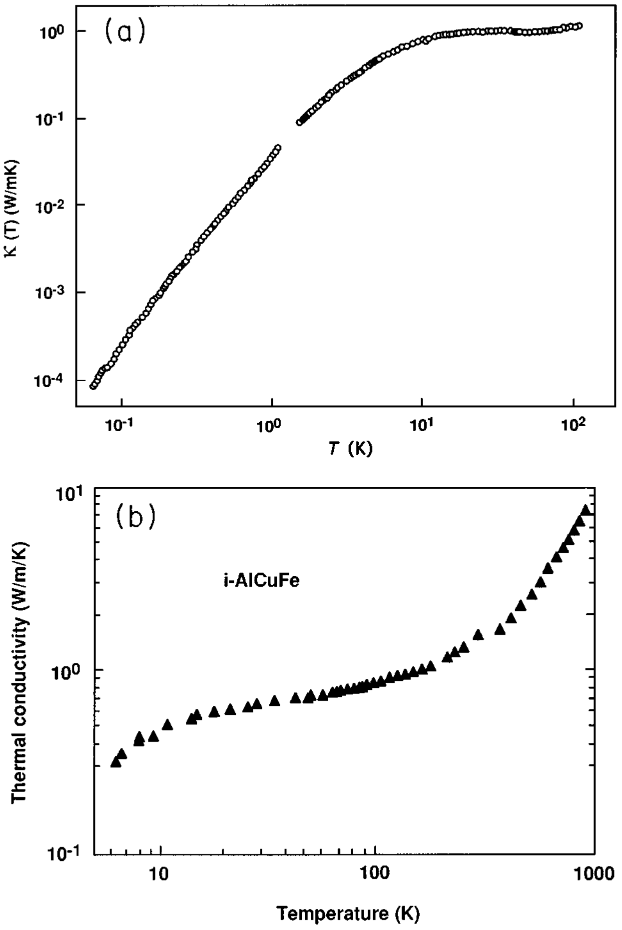

FIG. 7. Thermal conductivity measured with AlPdMn (Ref. 26) (a) and AlFeCu (Ref. 27) (b) icosahedral quasicrystals as a function of temperature (redrawn).

D. A variable-range hopping conductivity for quasicrystals

A formal simplified expression for the thermal conductivity is

$$\kappa(T)=\tfrac{1}{3}Cv\Lambda \tag{4}$$

in which C is a specific heat, v a velocity, and Λ a mean free path for the thermal transport modes of interest. An exact calculation would require a summation over the mode distribution. At low temperature, only the low-energy modes can be excited. We are in the linear regime and thermal transport occurs via the existing extended phonons. In a mean-field Debye-like approximation, the specific heat scales as T^3, the mean free path as T^{-1}, and the velocity is constant. This gives correctly the observed T^2 law for $\kappa(T)$, which culminates to a plateau when all available phonons are saturated in the Dulong-Petit limit (both C and Λ keep constant values when $k_BT \simeq \hbar\omega_{p,\max}$). At very low temperature, the mean free path tends to become constant when limited by extrinsic defects (surfaces, grain boundaries, defects, . . .); then the T^2 law changes progressively into $\kappa(T)\propto T^3$.

To explain the further increase of $\kappa(T)$ at temperature above the saturated phonon state, we must now enter the nonlinear regime corresponding to interaction of the high-energy critical modes with the low-energy extended phonons. This interaction allows critical states to communicate within the network of equivalent sites of the structure, in a way similar to that of fracton hopping. For the sake of simple wording we will call clustrons the hopping modes in quasicrystals. Their contribution to the thermal conductivity is given by a formula similar to that of Eq. (4), which can be rewritten as

$$\kappa_f(T)=\tfrac{1}{3}C\Lambda^2\tau_l^{-1}, \tag{5}$$

in which Λ is here the distance over which clustron jumps occur and τ_l^{-1} is the jump frequency. If the overlap between initial and final states is written $|\psi(\Lambda)|^2$ and if ΔE is the energy barrier to be overcome, the jump frequency is formally given by

$$\tau_l^{-1}=|\psi(\Lambda)|^2\exp\left(-\frac{\Delta E}{k_BT}\right). \tag{6}$$

We have demonstrated that the self-similarity of the structure forces $\psi(\Lambda)$ to scale as a power law $1/\Lambda^{\alpha}$ [Eq. (3)]. In the structure of the AlPdMn quasicrystal distances between equivalent sites scale as τ^{3n} and ΔE as τ^{-6n}; thus, ΔE is a power law β/Λ^2 of the jump distance Λ which, in turn, can take any value in the series $\Lambda_0\tau^{3n}$. A new expression for the jump frequency is then

$$\tau_l^{-1}\propto\frac{1}{\Lambda^{2\alpha}}\exp\left[\frac{-\beta}{\Lambda^2k_BT}\right]. \tag{7}$$

Jump distances which are effectively explored are temperature dependent; at a given temperature, jump distances are selected to produce the maximum jump frequency, i.e.,

$$\Lambda_{\max}^2=\frac{\beta}{\alpha}\frac{1}{k_BT} \tag{8}$$

and

$$\tau_{l,\max}^{-1}\propto\left(\frac{\alpha}{\beta}k_BT\right)^{\alpha}\exp(-\alpha)\propto T^{\alpha}. \tag{9}$$

The specific heat to be considered here is the one of phonons in the Dulong-Petit regime, i.e., a constant value, the contribution from the clustrons being zero since initial and final

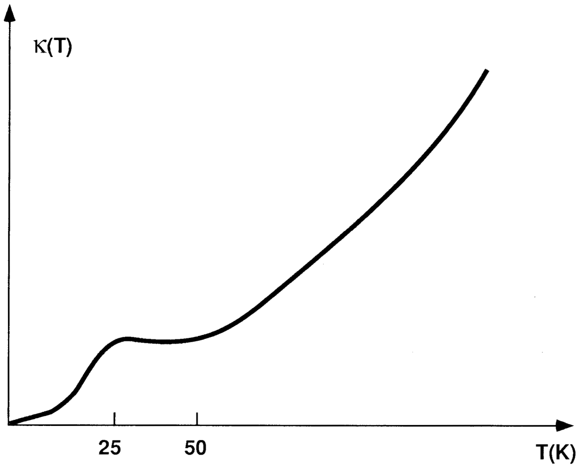

FIG. 8. Schematic presentation of temperature dependence of the thermal conductivity in quasicrystals.

states are identical and, thus, have equal energies. The number of sites corresponding to a given hopping distance Λ decreases as the power law Λ^{-3} but the number of atoms concerned and, thus, the number of modes concerned, increases as Λ^3. Accordingly the weighting factor for individual phonon-clustron modes in Eq. (5) does not depend on temperature. Substituting the temperature dependences of Λ and τ_l^{-1} [Eqs. (8) and (9)] into the expression of the thermal conductivity gives $\kappa(T) \sim T^{\alpha-1}$ or $\kappa(T) \sim T^{1.5}$ when the value of α is accounted for [Eq. (3)].

However, the $T^{1.5}$ power law should not hold ad infinitum; Λ decreases as $T^{-1/2}$ [Eq. (8)] down to its minimum value $\Lambda_{\min}$ corresponding to the distance between two elementary PMI; at this stage, both the energy barrier ΔE and $\psi(\Lambda)$ stop injecting temperature effects into the jump frequency τ_l^{-1} [Eq. (6)]; then the thermal conductivity increases exponentially up to saturation such that

$$\kappa(T) = \kappa_{\max} \exp\left(-\frac{E_0}{k_B T} \right). \tag{10}$$

Of course, the various regimes may overlap in certain temperature ranges because of a distribution of the effective modes involved. The exponential regime has not been observed actually, perhaps because of structure changes close to the melting point, as suggested by recent diffraction measurements (unpublished, by this author and co-workers). Finally, it is fair to say that, at least at high temperature, electrons should also contribute to thermal conductivity and modify the $T^{1.5}$ law.

The analysis which has just been carried out for the thermal conductivity $\kappa(T)$ can easily be extended to understand the temperature dependence of the dc electrical conductivity $\sigma(T)$. As previously explained in the paper and detailed elsewhere,[11] valence electrons of the atoms are distributed in hierarchical cluster levels; most of them, being in the relatively narrow levels of the elementary PMI's, are "localized" in these PMI's (mean free path of about 10 Å); smaller and smaller parts of them scaling as $1/\tau^{9n}$ (n any integer) are less and less localized with mean free paths increasing as τ^{3n} up to some extrinsic limitation due to symmetry breakings (defects, disorder, impurities, surfaces, . . .). Localization, or more precisely hierarchical localization, occurs because the atomic valence electrons are in resonance with the cluster energy levels[46,47] while the Coulomb repulsion prevents the electrons to coalesce and forces them to occupy all equivalent localization sites. The density of states then shows a very spiky self-similar profile with a steep square-root envelope towards the Fermi level.[11] In such a description, intrinsic conduction states cannot exist at all and all electrons remain paired into the self-similar distribution of the hierarchical cluster levels. Unavoidable symmetry breaking by surface or other structural defects may create a very flat conduction band, right beyond the Fermi level, inducing a weak semimetal contribution with thus a very small conductivity scaling roughly as $T^{3/2}$.[11] But most electronic transport should come from phonon-assisted collective electron hopping between sites of the same generation of inflation.

For electron hopping, in a Drude-like approximation, the conductivity $\sigma(T)$ is still given by a formula similar to Eq. (4); C is only the specific heat for the low-energy assisting phonons since electron hopping occurs between identical initial and final states; v is basically a constant since $k_B T$ is always small with respect to the electron kinetic energy; the mean free-path Λ can be calculated as previously done for the thermal conductivity derivation and is then given by Eq. (8); the number of hopping modes with mean-free path Λ scales as $1/\Lambda^3$. The result is Λ^{-2} or equivalently a linear T dependence of $\sigma(T)$. This $\sigma(T) \propto T$ law should hold over most of the temperature range for very pure and perfect quasicrystals. It may be corrupted at low or very low temperature if extrinsic effects due to defects of some sort bound the mean-free path to a maximum value; then the hopping probability decreases as the number of states having the energy $E = E_F - k_B T$, i.e., as $\sqrt{E}$,[11] or $1/\Lambda$, which gives a $\sigma(T) \propto T^{1/2}$. The linear $\sigma(T)$ behavior may also be corrupted to some extent with the overall weak $T^{3/2}$ semi-metal-like contribution already mentioned. Finally, we should also observe the very high-temperature behavior corresponding to Λ having reached its minimum value (i.e., distance between elementary PMI's, so that $\sigma(T)$ saturates exponentially according to a law similar to Eq. (10).

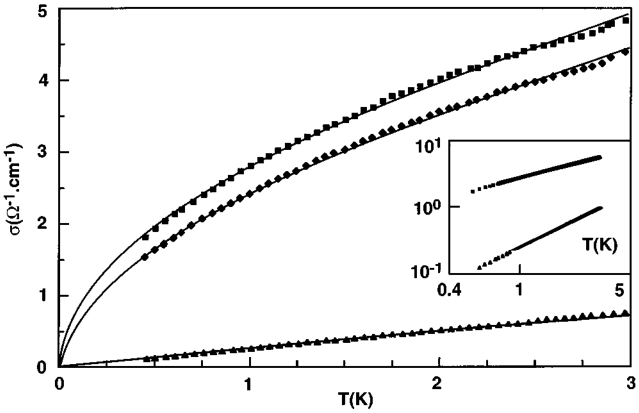

FIG. 9. The low-temperature part of the $\sigma(T)$ curves for AlPdRe quasicrystals showing the $\sigma \propto T$ behavior for a perfect icosahedral phase (▲) and the $\sigma \propto T^{0.5}$ law for a slightly less good sample (■). A log-log plot is also shown in the inset for $T < 2$ K. Redrawn from Ref. 56.

From the experimental point of view, one cannot say that a universal behavior of $\sigma(T)$ has been reported so far.[22–25,34,35,55,56] But for the best quasicrystals of the AlPdRe system,[56] those having the more pronounced insulator character at 0 K exhibit a T^n electrical conductivity with $n \sim 1$ at low or medium temperature and $n \sim 1.2$–1.3 anywhere above cryogenic temperature up to the highest ($\sim$1000 K). Samples with slightly lower resistivity have exponent $n \sim 0.5$–0.6 below 3 K (Fig. 9). If one accepts that the $n \sim 1.2$–1.3 values result from a corruption of the $\sigma(T) \sim T$ basic intrinsic law by the weak extrinsic $T^{3/2}$ contribution, there is a reasonably good agreement between experiment and modeling. Recent results with x-ray spectroscopy investigation of the same AlPdRe quasicrystals[57] also support the present model by showing an almost vanishing "conduction band" beyond the Fermi level.

According to this hierarchically variable-range hopping mechanism, the frequency dependence of the conductivity $\sigma(\omega)$ at a given temperature should show a broad resonance centered at $\nu_c \simeq \tau_l^{-1}(T)$ with τ_l^{-1} given by Eq. (9). Such a

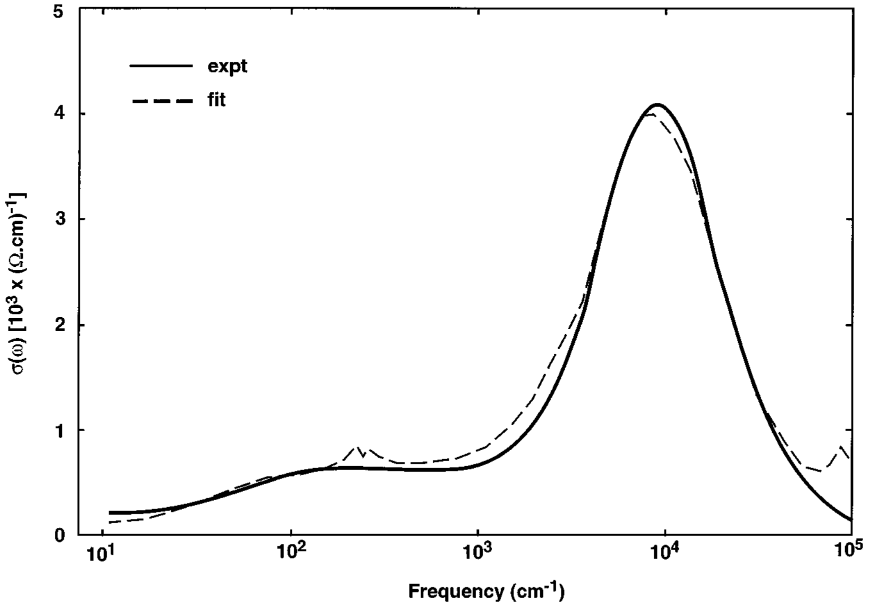

FIG. 10. Optical conductivity $\sigma(\omega)$ of the icosahedral AlPdMn quasicrystal at room temperature. A broad "resonance" shows up, centered close to 10 000 cm^{-1} (1.12 eV or 290 THz) (Ref. 53) (redrawn).

behavior has actually been observed with the AlPdRe and AlPdMn good quasicrystals[28,53] (Fig. 10). Assuming that the electron energy is purely kinetic during hopping, one can easily derive the relation between the observed resonance in $\sigma(\omega)$ and the most represented hopping distance, i.e.,

$$E_e = \tfrac{1}{2} m v_e^2 = \tfrac{1}{2} m \Lambda \nu_c^2 = h \nu_c$$

or

$$\Lambda = \left(\frac{2h}{m \nu_c} \right)^{1/2}.$$

If ν_c is taken equal to 9679 cm^{-1} or 290.2 THz as measured by Degiorgi *et al.*,[28] one gets $\Lambda = 22.4$ Å, which is very close to the distance between two PMI centers in the AlPdMn structure.

In a slightly different approach, Moulopoulos and Cyrot-Lackmann[58] have recently proposed to treat electronic transport properties of quasicrystals in terms of electron/fracton scattering in a strict formal sense. This gives good qualitative interpretations of the observed thermal and electronic conductivities. Fracton superconductivity is also a theoretical possibility resulting from matching model to resistivity data.

IV. CONCLUSION

The description of quasicrystals in terms of hierarchical clustering of atomic clusters in a self-similar structure as deduced from diffraction data appears to be self-consistently related to composition and atomic valences. Such a structure implies that electrons and vibrational states have mostly localized characters. A hierarchical variable-range hopping mechanism, compatible with inelastic-neutron-scattering data, gives a satisfying explanation of the thermal and electronic transport phenomena in quasicrystals. The electronic conductivity in particular should be basically a linear function of the temperature, but with $\sqrt{T}$ and $T^{3/2}$ contributions coming from extrinsic effects due to symmetry breaking. Strong deviation from the law $\sigma(T) \sim T$ and absence of a thermal conductivity plateau at some temperature are definitive good reasons to suspect sample quality.

ACKNOWLEDGMENTS

I am very pleased to thank Dr. M. de Boissieu, Dr. J. M. Dubois, and Professor J. Friedel for their critical reading of the manuscript. I am also endebted to Dr. F. Cyrot-Lackmann, Dr. M. Chernikov, Dr. D. N. Basov, and Dr. M. Boudard for valuable discussion and informing me of their works prior to publication.

---

[1] C. Janot, *Quasicrystals: A Primer*, 2nd ed. (Oxford University Press, Cambridge, 1994).

[2] A. P. Tsai, A. Inoue, Y. Yokoyama, and T. Masumoto, Mat. Trans. JIM **31**, 98 (1990).

[3] A. P. Tsai, A. Inoue, and T. Masumoto, Philos. Mag. Lett. **62**, 95 (1990).

[4] S. W. Kycia, A. I. Goldman, T. A. Lograsso, D. W. Delancy, M. Sutton, E. Dufresne, R. Brüning, and B. Rodricks, Phys. Rev. B **48**, 3544 (1993).

[5] M. de Boissieu, M. Durand-Charre, P. Bastie, A. Carabelli, M. Boudard, M. Bessiere, S. Lefebvre, C. Janot, and M. Audier, Philos. Mag. Lett. **65**, 147 (1992).

[6] Y. Yokoyama, T. Miura, A. P. Tsai, A. Inoue, and T. Masumoto, Mater. Trans. JIM **33**, 97 (1992).

[7] M. Boudard, E. Bourgeat-Lami, M. de Boissieu, C. Janot, M. Durand-Charre, H. Klein, M. Audier, and B. Hennion, Philos. Mag. Lett. **71**, 11 (1995).

[8] M. Cornier-Quiquandon, M. Quivy, S. Lefebvre, E. Elkaim, G. Heger, A. Katz, and D. Gratias, Phys. Rev. B **44**, 2071 (1991).

[9] M. Boudard, M. de Boissieu, C. Janot, J. M. Dubois, and C. Dong, Philos. Mag. Lett. **64**, 197 (1991).

[10] M. 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**, 10 149 (1992).

[11] C. Janot and M. de Boissieu, Phys. Rev. Lett. **72**, 1674 (1994).
[12] J. Hafner and M. Krajci, J. Phys. Condens. Matter **5**, 2489 (1993).
[13] M. Windisch, J. Hafner, M. Krajci, and M. Mihalkovic, Phys. Rev. B **49**, 8701 (1994).
[14] J. Los, T. Janssen, and F. Gähler, J. Phys. (France) I **3**, 107 (1993).
[15] K. Niizeki, J. Phys. A **22**, 4295 (1989).
[16] K. Niizeki and T. Akamatsu, J. Phys. Condens. Matter **2**, 2759 (1990).
[17] G. Poussigue, C. Benoit, A. Azougarh, M. de Boissieu, and R. Currat, J. Phys. Condens. Matter **6**, 659 (1994).
[18] A. I. Goldman, C. Stassis, M. de Boissieu, C. Currat, C. Janot, R. Bellissent, H. Moudden, and F. W. Gayle, Phys. Rev. B **45**, 10 280 (1992).
[19] M. Quilichini, G. Heger, B. Hennion, S. Lefebvre, and A. Quivy, J. Phys. (France) II **2**, 125 (1992).
[20] M. de Boissieu, M. Boudard, R. Bellissent, M. Quilichini, B. Hennion, R. Currat, A. I. Goldman, and C. Janot, J. Phys. Condens. Matter **5**, 4945 (1993).
[21] M. Boudard, M. de Boissieu, S. Kycia, A. I. Goldman, B. Hennion, R. Bellissent, M. Quilichini, R. Currat, and C. Janot, J. Phys. Condens. Matter **7**, 7299 (1995); Phys. Scr. **T57**, 84 (1995).
[22] P. Lanco, T. Klein, C. Berger, F. Cyrot-Lackmann, G. Fourcandot, and A. Sulpice, Europhys. Lett. **18**, 227 (1992).
[23] S. Takeuchi, H. Akiyama, N. Naito, T. Shibuya, T. Haskimoto, K. Edagawa, and K. Kimura, J. Non Cryst. Solids **153-54**, 353 (1993).
[24] M. A. Chernikov, A. Bernasconi, C. Beeli, and H. R. Ott, Europhys. Lett. **21**, 767 (1993).
[25] F. S. Pierce, S. J. Poon, and Q. Guo, Science **261**, 737 (1993).
[26] M. A. Chernikov, A. Bianchi, and H. R. Ott, Phys. Rev. B **51**, 153 (1995).
[27] A. Perrot and J. M. Dubois, Ann. Chim. (France) **18**, 501 (1993); in Proceedings of the 5th International Conference on Quasicrystals, 1995, edited by C. Janot and R. Mosseri (World Scientific, Singapore, in press).
[28] L. Degiorgi, M. A. Chernikov, C. Beeli, and H. R. Ott, Solid State Commun. **87**, 721 (1993).
[29] M. A. Chernikov, A. Bernasconi, A. Schilling, C. Beeli, and H. R. Ott, Phys. Rev. B **48**, 3058 (1993).
[30] T. Klein, C. Berger, D. Mayou, and F. Cyrot-Lackmann, Phys. Rev. Lett. **66**, 2907 (1991).
[31] G. W. Zhang, Z. M. Stadnik, A. P. Tsai, and A. Inoue, Phys. Lett. A **186**, 345 (1994).
[32] E. Belin, Z. Dankhazi, A. Sadoc, and J. M. Dubois, J. Phys. Condens. Matter **6**, 8771 (1994).
[33] S. S. Kang and J. M. Dubois, Philos. Mag. A **66-1**, 151 (1992); J. M. Dubois, S. S. Kang, and A. Perrot, Mater. Sci. Eng. **A179-A180**, 122 (1994).
[34] S. J. Poon, Adv. Phys. **41**, 303 (1992).
[35] D. Mayou, C. Berger, F. Cyrot-Lackmann, T. Klein, and P. Lanco, Phys. Rev. Lett. **70**, 3915 (1993).
[36] T. Fujiwara, S. Yamamoto, and G. Trambly de Laissardière, Phys. Rev. Lett. **71**, 4166 (1993).
[37] S. Burkov, T. Timusk, and N. W. Ashcroft, J. Phys. Condens. Matter **4**, 9447 (1992).
[38] R. Tamura, A. Waseda, K. Kimura, and H. Ino, Mater. Sci. Eng. **A181-A182**, 794 (1994).
[39] G. W. Zhang, Z. M. Stadnik, A. P. Tsai, and A. Inoue, Phys. Rev. B **50**, 6696 (1994).
[40] K. Kimura, H. Yamene, T. Hashimoto, and S. Takeuchi, Mater. Sci. Forum **22-24**, 471 (1987).
[41] F. S. Pierce, S. J. Poon, and B. D. Biggs, Phys. Rev. Lett. **70**, 3919 (1993).
[42] T. Klein, H. Rakoto, C. Berger, G. Fourcadot, and F. Cyrot-Lackmann, Phys. Rev. B **45**, 2046 (1992).
[43] T. Klein, O. G. Symko, D. N. Davydov, and A. G. M. Jansen, Phys. Rev. Lett. (to be published).
[44] D. Gratias, Y. Calvayrac, J. Devaud-Rzepski, F. Faudot, M. Harmelin, A. Quivy, and P. A. Bancel, J. Non-Cryst. Solids **153-154**, 482 (1993).
[45] M. Audier, M. Durand-Charre, and M. de Boissieu, Philos. Mag. B **68**, 607 (1993).
[46] S. N. Khanna and P. Jena, Chem. Phys. Lett. **219**, 479 (1994).
[47] D. Mayou, in Proceedings of the 5th International Conference on Quasicrystals, 1995 (Ref. 27).
[48] J. Friedel, Philos. Mag. B **65**, 1125 (1992).
[49] C. Sire, in *Lectures on Quasicrystals*, edited by F. Hippert and D. Gratias (Les Editions de Physique, Les Ulis, France, 1994), p. 505.
[50] T. Nakayama, K. Yakubo, and R. L. Orbach, Rev. Mod. Phys. **66**, 1 (1994).
[51] N. F. Mott, Adv. Phys. **16**, 49 (1967); Philos. Mag. **19**, 835 (1969).
[52] J. B. Suck, J. Non-Cryst. Solids **153-154**, 573 (1993).
[53] D. N. Basov, F. S. Pierce, P. Volkov, S. J. Poon, and T. Timusk, Phys. Rev. Lett. **73**, 1865 (1994); D. N. Basov, S. J. Poon, and T. Timusk (unpublished).
[54] J. M. Dubois, S. S. Kang, P. Archambault, and B. Colleret, J. Mater. Res. **73**, 38 (1992).
[55] R. Tamura, A. Waseda, K. Kimura, and H. Ino, in *Aperiodic '94*, edited by G. Chapuis (World Scientific, Singapore, 1995), p. 212.
[56] F. S. Pierce, Q. Guo, and S. J. Poon, Phys. Rev. Lett. **73**, 2220 (1994); S. J. Poon (private communication).
[57] E. Belin, Z. Dankhazi, A. Sadoc, S. J. Poon, A. M. Flank, H. Müller, and H. Kirchmayer, in Proceedings of the 5th International Conference on Quasicrystals, 1995 (Ref. 27).
[58] K. Moulopoulos and F. Cyrot-Lackmann (unpublished); in Proceedings of the 5th International Conference on Quasicrystals, 1995 (Ref. 27).