

## Universal Pseudogap at the Fermi Energy in Quasicrystals

Takeo Fujiwara and Takeshi Yokokawa

*Department of Applied Physics, University of Tokyo, Bunkyo-ku, Tokyo 113, Japan*

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The electronic structures are calculated for several crystalline approximants of quasicrystals, AlCuLi and AlFe. The densities of states of these systems, and also of AlMn, suggest universality of the pseudogap at the Fermi energy in quasicrystals. The pseudogap satisfies a Hume-Rothery-type relation. The origin of the pseudogap is attributed to strong electron scattering by the lattice and the pseudogap causes an enhancement of cohesive energies. The characteristics of the states in the pseudogap and the electric resistivity are also discussed.

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Since the discovery of quasicrystals,<sup>1,2</sup> theoretical investigations have focused mainly on their structures and phasons. Recently, the electronic properties have received much attention. The main interest is twofold: One is electronic transport or localization<sup>3-5</sup> and the other is the electronic mechanism of cohesion.<sup>6-9</sup> The diffraction pattern in quasicrystals is a sum of densely distributed  $\delta$  functions with crystallographically disallowed orientational symmetry. The anomalous diffraction pattern suggests that electrons in quasicrystals may be always and everywhere scattered strongly and the electron wave functions oscillate at all scales. This is the case in the one-dimensional Fibonacci lattice and the energy spectrum has gaps at almost every energy value.<sup>3</sup> In the two-dimensional case, the situation is not essentially changed. The energy spectrum of the two-dimensional Penrose lattice is not smooth and most of the wave functions are critical, i.e., neither extended nor exponentially localized, and presumably with power-law decay.<sup>4</sup> Recently, high quality samples of stable quasicrystals with only small amounts of structural disorder and phasonlike defects were prepared, and their electric resistivity has been observed to be anomalously large. The electric resistivity in icosahedral AlCuLi is 6 times larger than in crystals, whereas the coefficient of the linear-temperature-dependent term of the specific heat is almost the same in two phases.<sup>10</sup> The electric resistivity of stable icosahedral AlCuRu has been observed to increase drastically, up to  $2500 \mu\Omega \text{ cm}$  or more at 4.2 K.<sup>11</sup> Therefore, we presume that electronic states in three-dimensional quasicrystals are also critical. The anomalous diffraction pattern also suggests a strong electron-lattice interaction and one may expect it has a crucial role for stability, such as in the Hume-Rothery or Peierls mechanism.

In this paper, we present the electronic structures of crystalline approximants of realistic quasicrystals, AlCuLi and AlFe, and discuss an electronic mechanism of cohesion and stability in realistic quasicrystals. Discussions are concerned with *R*-AlCuLi and Al<sub>14</sub>Fe<sub>3</sub>, together with  $\alpha$ -AlMn.<sup>8</sup> These are the crystalline approximants of typical quasicrystals: the stable icosahedral

quasicrystal *i*-AlCuLi, the metastable icosahedral quasicrystal *i*-AlMnSi, and the metastable decagonal quasicrystal *d*-AlFe. The crystalline phase of AlCuLi, i.e., *R*-AlCuLi, reveals the typical structure of the Frank-Kasper phase. The lattice of the crystalline approximants can be constructed by the optimal rational approximation of the golden mean  $\tau = (\sqrt{5} + 1)/2$  in the three-dimensional (icosahedral phase) or the two-dimensional (decagonal phase) Penrose lattice. Furthermore, the local atomic structure of the crystalline approximants is quite similar to that of the quasicrystals, and it is believed that this resemblance is generic. The icosahedral atomic structures of AlCuLi and AlMnSi could be obtained by locating atomic clusters of triacontahedra and Mackay icosahedra on the twelvefold vertices in a three-dimensional Penrose lattice, respectively.<sup>12</sup> The *R*-AlCuLi contains 80 atoms in a unit cell and is *Im*3, whose structure is a bcc aggregation of triacontahedra of 136 atoms. The  $\alpha$ -AlMnSi contains 138 atoms in a unit cell and is *Pm*3, whose structure is a simple cubic aggregation of icosahedra of 54 atoms, called Mackay icosahedra. These clusters are common aggregation units in both quasicrystals and crystalline approximants. The atomic structure of decagonal AlFe may be constructed by locating Fe atoms on the vertex positions of a two-dimensional Penrose lattice when the structure is projected along the *c* axis.<sup>13</sup> The Al<sub>13</sub>Fe<sub>4</sub> is the base-centered monoclinic structure *C2/m* of 51 atoms in a unit cell. The atoms on puckered layers are a decoration of the rational approximant of a two-dimensional Penrose lattice and the two penetrating icosahedral clusters bridge a gap between these layers.

The self-consistent electronic structures of these crystalline approximants were calculated by the linear muffin-tin orbital method with the atomic sphere approximation (LMTO-ASA),<sup>14</sup> which is a typical linear method of band-structure calculation originating from the Korringa-Kohn-Rostoker method. This method is the most suitable for densely packed systems, and usually, within a reasonable computational time, one can get self-consistent band structures of crystals with up to a few hundred atoms in a unit cell. No atoms are experi-

mentally observed at the centers of the triacontahedra in AlCuLi or the Mackay icosahedra in AlMn. The calculated local density of states at the centers of clusters vanishes over a wide energy range of width 0.2~0.3 Ry around the Fermi energy.<sup>8,9</sup> If some atoms are located there, there is not enough space for additional valence electrons and surplus charges should be distributed in the surrounding spatial regions in an energy range just above the Fermi energy. Therefore, interstitial atoms at the centers of clusters cause an increase of energy and energetic instability.

In real  $R$ -AlCuLi, the atomic contents are given by fractional numbers ( $\text{Al}_{88.7}\text{Cu}_{19.32}\text{Li}_{52}$ ), and atomic occupancies at several atomic sites are disordered. The electronic densities of states (DOS) and integrated densities of states in several simplified models of  $R$ -AlCuLi are shown in Fig. 1. In the model structure  $\text{Al}_{96}\text{Cu}_{12}\text{Li}_{52}$  of  $Pm3$ , the half of the Wyckoff sites  $24g$  on one bcc sublattice are occupied by Al atoms, and the other half on the other bcc sublattice by Cu atoms. Other sites are assumed to be occupied by Al and Li atoms. Then the resultant space-group symmetry of the model system is  $Pm3$  with 160 atoms, but not  $Im3$  with 80 atoms. The density of states has a very apparent wide pseudogap and the Fermi energy is just 0.05 Ry above the minimum of the pseudogap. The high DOS peak at 0.3 Ry below  $E_F$  comes from the Cu  $3d$ . The narrow width of the Cu- $3d$  peak indicates a very small mixing between Cu  $3d$  and other orbitals. In order to understand the role of Cu

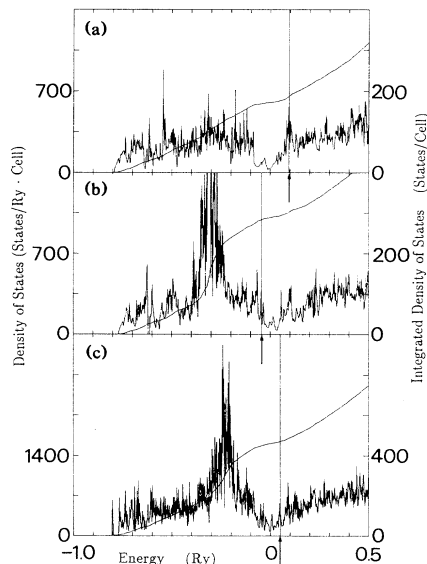


FIG. 1. Densities of states and integrated densities of states for (a)  $\text{Al}_{108}\text{Li}_{52}$ , (b)  $\text{Al}_{84}\text{Cu}_{24}\text{Li}_{52}$ , and (c)  $\text{Al}_{96}\text{Cu}_{12}\text{Li}_{52}$ . The Fermi energies are indicated by arrows and vertical lines. The size of the unit cells in (a) and (b) is half of that in (c), and the ordinate scales in (a)–(c) are the same if scaled for the same volume 1.

atoms and the origin of the pseudogaps, the densities of states in two other models,  $\text{Al}_{108}\text{Li}_{52}$  and  $\text{Al}_{84}\text{Cu}_{24}\text{Li}_{52}$ , were calculated. All Wyckoff sites  $24g$  are occupied by Cu in  $\text{Al}_{84}\text{Cu}_{24}\text{Li}_{52}$  and by Al in  $\text{Al}_{108}\text{Li}_{52}$ , respectively. The following facts were found: (1) In all three cases, the positions of the minimum of the pseudogap do not shift and the energies measured from the bottom of the valence band and the widths of pseudogap do not alter; (2) even in  $\text{Al}_{108}\text{Li}_{52}$ , the pseudogap does not disappear and Cu atoms play no role in the formation of the pseudogap; (3) the Fermi energy shifts according to the concentration of valence electrons depending on the Cu concentration; (4) for the exact Cu concentration of  $R$ - $\text{Al}_{88.7}\text{Cu}_{19.3}\text{Li}_{52}$  and  $i$ -AlCuLi, the Fermi energy seems to locate just at the exact minimum of the pseudogap.

The electronic density of states and the integrated density of states of  $\text{Al}_{13}\text{Fe}_4$  are shown in Fig. 2. The density of states in  $\text{Al}_{13}\text{Fe}_4$  also shows a pseudogap at the Fermi energy  $E_F$  though the density at  $E_F$  is high. The finite density of states mainly originates from Fe- $3d$  states. The  $E$ - $\mathbf{k}$  curves, especially around  $E_F$ , are flat for momenta  $\mathbf{k}$  within a plane perpendicular to the  $c$  axis. On the other hand, several parallel  $E(\mathbf{k})$  curves have been seen with relatively large  $\mathbf{k}$  dependence along the  $c$  axis which also mainly originate from Fe- $3d$  states. The electron density of states of  $\alpha$ -AlMn has been calculated in a model where Al atoms are substituted for Si atoms.<sup>8</sup> The substitution of a proper amount of Si atoms for Al atoms would make  $E_F$  climb up to just the exact minimum of the pseudogap and enhance the stability of AlMnSi. The existence of the pseudogap at the Fermi energy is generic in these systems, crystalline approximants of realistic quasicrystals. In AlFe and AlMn, the pseudogap divides the transition-metal  $3d$  band into two, occupied and unoccupied, and the Fermi energy is located near the minimum of the pseudogap. Considering the existence of the pseudogap even in AlLi and the similarity of the crystalline structures of AlCuLi and AlMn, we

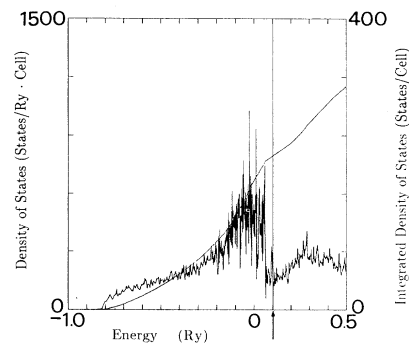


FIG. 2. Density of states and integrated density of states for  $\text{Al}_{13}\text{Fe}_4$ . The Fermi energy is indicated by an arrow and a vertical line.

can conclude that the pseudogap here could not be due to antiresonance of the transition-metal  $d$  band in the Al  $sp$  band. In contrast to the case of AlCuLi, the pseudogaps are rather narrow in AlMn and AlFe and the transition-metal  $d$  states smear out the pseudogap. The values of the density of states at the Fermi energy are 2 or 3 times larger.

The clusters, either icosahedra or triacontahedra, are generally stable constituent units of icosahedral quasicrystals and crystalline approximants. These clusters are placed on twelffold vertices of the three-dimensional Penrose lattice. The local structures determine cohesive properties and their electronic properties except electric transport. Therefore, several electronic properties may be common in both crystals and quasicrystals. The most crucial point is whether the pseudogap at the Fermi energy observed in crystalline approximants also exists in quasicrystals.

The energy position of the pseudogap measured from the bottom of the valence band is about 0.8 Ry and the corresponding Fermi wave vector  $k_F$  is about  $1.7 \text{ \AA}^{-1}$  in a free-electron model (more specifically,  $1.75 \text{ \AA}^{-1}$  in AlMn,  $1.64 \text{ \AA}^{-1}$  in AlCuLi, and  $1.73 \text{ \AA}^{-1}$  in AlFe). On the other hand, the strongest characteristic scattering peaks in quasicrystals are at about  $Q=3.0 \text{ \AA}^{-1}$  [ $2.896 \text{ \AA}^{-1}$  of (211111) and  $3.043 \text{ \AA}^{-1}$  of (221001) in AlMn,  $2.793 \text{ \AA}^{-1}$  of (211001) and  $3.189 \text{ \AA}^{-1}$  of (222100) in AlCuLi, and  $3.017 \text{ \AA}^{-1}$  in  $\text{Al}_4\text{Mn}_{0.72}\text{Fe}_{0.28}$ ]. Similar strong scattering peaks exist in the crystalline phase and always satisfy the relation  $Q \approx 2k_F$ . From these scattering wavelengths, the relevant atomic planes can be assigned.<sup>15</sup> The strong scattering peaks or the large geometrical structure factor can be explained by the existence of atomic planes shared by the nearest- and next-nearest-neighbor pairs of clusters. The relation  $Q \approx 2k_F$  and the pseudogap at the Fermi energy attribute the origin of the pseudogap to a touching of the Fermi surface at the effective Brillouin zone, which may be defined by the bisection planes perpendicular to the scattering vectors with the strongest intensity. The pseudogaps, lowering the energy of occupied states and raising that of unoccupied states, lead to an enhancement of the cohesive energy and can work more efficiently in the quasicrystalline case because the effective Brillouin zone should be almost spherical in its polyhedron shape. This band mechanism of enhancement of the cohesive energy has much in common with the Hume-Rothery mechanism. This mechanism of stabilizing quasicrystalline structures was argued by Friedel<sup>7</sup> and calculated by Smith and Ashcroft and Vaks, Kamyshenko, and Samolyuk<sup>6</sup> in weak scattering approximation. A crucial factor determining a stable structure, a stable quasicrystal or a crystalline approximant, may be the atomic compositions and their small energy differences. The favorable structure, for a given atomic composition, may be determined so that the Fermi energy coincides with the

minimum of the pseudogap and the cohesive energy is enhanced.

As already mentioned, the coefficient  $\gamma$  of the linear-temperature-dependent term of the specific heat  $C = \gamma T + \alpha T^3 + \dots$  is almost the same in the two phases, crystalline and quasicrystalline, especially in  $sp$  alloys, without any exception.<sup>10,16</sup> This fact supports our starting assumption that the electronic structure is mainly determined by the local or intermediate-range atomic structure. One can evaluate from the value of  $\gamma$  the density of states at the Fermi energy by using the equation  $D(E_F) = (\frac{1}{3} \pi^2 k_B^2)^{-1} \gamma$ . A typical example of the similarity of  $\gamma$  values is in AlCuLi,<sup>10</sup> 0.13 state/eV atom ( $i$  phase) and 0.12 state/eV atom ( $R$  phase). They agree well with the present calculated result, 0.12 state/eV atom. The free-electron value is estimated to be, on the other hand, 0.33 state/eV atom (Ref. 10) and is 3 times larger than the above values, which suggests the existence of a strongly enhanced pseudogap of the density of states. These large discrepancies between observed and free-electron values are not found in metastable quasicrystals such as AlCuMg,<sup>16,17</sup> which is understandable in that the valence of the Mg atom is larger than that of the Li atom and the Fermi energy shifts to the higher-energy side above the pseudogap. Disagreement between positions of  $E_F$  and the pseudogap may be a cause of the metastability of several quasicrystals. The pseudogap in the occupied valence bands may be observed in photoemission spectra.

Though the values of  $\gamma$  coincide with each other in quasicrystals and crystalline approximants, the values of resistivity differ from each other, sometimes by a large factor; for example, in AlCuLi, they are  $870 \mu\Omega \text{ cm}$  ( $i$  phase) and  $150 \mu\Omega \text{ cm}$  ( $R$  phase).<sup>10</sup> Kishi *et al.*<sup>18</sup> observed a systematic change of electric resistivity in  $\text{Al}_5(\text{Mg}_x\text{Li}_{1-x})_{3.5-4}\text{Cu}_1$  which is much enhanced at  $x=0$ , by a factor of 13, presumably caused by a pseudogap and critical character of the electronic states. In decagonal AlCoNi,<sup>19</sup> the resistivity within a quasiperiodic two-dimensional plane is 7 times larger than that along the direction perpendicular to the plane. We observed that the states outside the pseudogap rapidly change their orbital character with changing wave vector and that, on the contrary, the states in the pseudogap are relatively pure and more like a plane wave in  $R$ -AlCuLi and AlFe. Therefore, though localization is a future problem in three-dimensional quasicrystals, we might argue that a state in the pseudogap is more influenced by the quasiperiodicity and seems to have a stronger tendency to be critical, i.e., neither extended nor localized, in the quasicrystalline phase.

In conclusion, we presented the electronic densities of states for several crystalline approximants of quasicrystals, showing the universality of the pseudogap at the Fermi energy in quasicrystals. The origin of the pseudogap is attributed to strong electron scattering by the lat-

tice, and the existence of the pseudogap causes an enhancement of cohesive energies. Similar calculations extended to crystalline approximants with successively larger unit cells would be highly desirable but are impossible at the present state of our computational facility.

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