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Occupancy of central sites in the $Zn_{49}Mg_{32}$ quasicrystal from total-energy computations on its crystal approximant

R. S. Rao, B. K. Godwal, S. K. Sikka, and R. Chidambaram
High Pressure Physics Division, Bhabha Atomic Research Centre, Bombay, 400 085, India

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First-principles electronic-structure and total-energy calculations related to the 1/1 crystal approximant to the Al-Zn-Mg quasicrystal are carried out with different possible atoms at the center of the packing unit. The linear muffin-tin-orbital (LMTO) method with the atomic-sphere approximation and the muffin-tin correction to the Coulomb energy is employed. The density of states shows a very shallow minimum near the Fermi level, supporting the view that the pseudogap exists in the crystal approximants to quasicrystals even in the absence of a *d*-state contribution to the valence electrons. It is shown that packing units with Al or Zn at the centers are more stable than those with empty centers, supporting the recent positron-annihilation data and pseudopotential calculations, but disagreeing with qualitative conclusions from some LMTO calculations for crystal approximants to other quasicrystals.

INTRODUCTION

Ever since the discovery of quasicrystals, that is quasiperiodic systems with long-range bond orientational order, there has been increasing interest, both experimentally and theoretically, to explore them for their structure, stability, and various physical properties.[1,2] Krajci and Hafner[3] used idealized structure models for quasicrystals on the basis of three-dimensional Penrose tiling with Henley-Elser decoration of the basic structural units, and investigated the stability of these structures by an isothermal molecular dynamics annealing of a hierarchy of crystalline approximants, with realistic pair potentials derived from pseudopotential theory. Based on such studies they proposed a modulated tiling model for the structure of an icosahedral quasicrystal of Al-Zn-Mg class and found that such structures are stable only at compositions leading to an electron per atom ratio in the range 2.1–2.2, indicating the existence of a Hume-Rothery criterion for the stability of quasicrystals. However, these studies do not address the question of occupancy of the centers of the packing units in view of recent positron-annihilation lifetime measurements[4,5] which reveal that these centers are occupied, in contradiction to earlier x-ray diffraction findings.[6]

Attempts have been made using self-consistent electronic-structure calculations on various crystal approximants like Al-Mn-Si and Al-Cu-Li to argue that the centers of the packing units should be empty.[7,8] Although these calculations do not evaluate the total energies explicitly, the conclusions are mainly based on charge-density distributions, or in some systems like the Al-Cu-Li alloy, on the nonconvergence of self-consistent solutions. These estimates are at variance with the recent pseudopotential computations of the cohesive energies[9,10] in Al-Mn-Si and Al-Zn-Mg systems with and without atoms at the centers of the packing units.

Studying physical properties of quasicrystalline systems, like unusual transport properties,[1,2] is another active area of research and the knowledge of electronic structure is a prerequisite for it. It is well known that stable quasicrystals show semimetallic behavior and exhibit low-temperature resistivities orders of magnitude larger than those of metallic glasses.[1] In general, the more stable a quasicrystal is (measured by grain size), the higher will be its low-temperature resistivity, and the smaller will be the density of states $D(E_F)$ at the Fermi level E_F. These observed features suggest that some kind of energy gap plays a significant role in the electronic and transport properties of stable quasicrystals. In this connection, it is interesting to note that the empty core pseudopotential method used by Smith and Ashcroft[11] to examine electronic properties of the Al-Mg-Zn alloy showed the appearance of band gaps associated with each quasicrystal reciprocal lattice vector which resulted in singularities in both the density of states and the joint optical density of states. A few other theoretical models[12,13] have also been employed to explain the pseudogaps and the background density of states in the pseudogap. Further, Fujiwara and co-workers[7,8] carried out first-principles electronic-structure calculations using the linear muffin-tin-orbital method[14] within the atomic-sphere approximation (LMTO-ASA) for several crystalline approximants of quasicrystals, AlCuLi, AlFe, and AlMn, etc. By observing the densities of states of these systems, they suggested universality of the pseudogap at the Fermi energy in quasicrystals. The pseudogap was found to satisfy a Hume-Rothery–type relation and its origin is attributed to the proximity of the Fermi surface to the pseudo-Brillouin zone.[15,16] Recently Hafner and Krajci[17] have made LMTO calculations on higher-order rational approximants to the icosahedral Al-Zn-Mg quasicrystal and found a structure induced pseudogap at the Fermi level. These calculations included the 3*d* electrons of Zn in the valence band.

Thus all these calculations which show the existence of the pseudogap are either for quasicrystalline systems having a transition-metal alloy or with the inclusion of a *d* character in the valence states. This raises the doubt whether the existence of the pseudogap is related to the

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valence d electron composition in quasicrystals because the recent experimental studies on electronic properties of a large number of quasicrystals as discussed by Poon[1] show almost free-electron-like specific-heat behavior in some of them.

Our interest is to improve upon the existing pseudopotential[9] and LMTO[7,8] calculations, and to check whether the limitations of those calculations, mentioned earlier, can affect their conclusions about the occupancy of the centers of the packing units. In view of the sensitivity of the LMTO-ASA results in some systems to the muffin-tin (MT) corrections[18,19] to the electrostatic Coulomb contribution in the total energy, we have employed these correction terms (details given below) in our calculations. We have also used these self-consistent electronic-structure calculations to investigate the pseudogap characteristics of a crystal approximant to a quasicrystal system with no transition-metal component or a d character of the valence electrons.

DETAILS OF CALCULATION

Calculations were intended to correspond to 1/1 crystal approximants to the $[Al_xZn_{1-x}]_{49}Mg_{32}$ quasicrystal (generally $0.3<x<0.35$). As the $[Al/Zn]_{49}$ site distributions are not known, and Zn atoms are in majority at these sites, we studied the model systems ©-$Zn_{48}Mg_{32}$ in the primitive cell, where ©- denotes the central site of the packing unit. The calculations were carried out with Al, Zn, Mg, and vacancy (empty sphere) at the center ©-. The packing units, the cubo-octahedra at the bcc lattice sites,[2] give efficient close packing, and the LMTO-ASA results should be quite reliable, especially as all the calculations were performed on identical atomic positions and atomic-sphere radii ratios. Even in this model, as the crystal approximant has 162 atoms per unit cell (81 atoms per bcc primitive cell), the calculations demand powerful computers. Hence these calculations were carried out on a parallel processor[20] with eight nodes. As our computations involve evaluation of eigenvalues at many **k** points in the Brillouin zone, and the calculations for different **k** points are independent, we have parallelized the relevant matrix construction and eigenvalue routines. As this part of the calculation takes more than 95% of the computational time, the **k** point parallelization is quite efficient in our calculations. With seven processors, our code gives a speedup of about 6.7 on this machine as compared to the corresponding sequential machine computation. Further details of our LMTO computations on this parallel processor will be reported elsewhere.[21]

Nonrelativistic LMTO-ASA computations have been performed with frozen cores, and with s and p muffin-tin orbitals. Valence electron configurations have been chosen as Mg:$3s^2$, Al:$3s^23p^1$, and Zn:$4s^2$. The lattice constant of the bcc lattice is taken as 14.16 Å, and the 81 atom basis associated with each lattice point can be divided into eight types as described below[22] (coordinates in units of lattice constant): type A at the central site (0,0,0); 12 atoms of type B [Zn/Al] at $(\pm0.0908,\pm0.1501,0)$ and cyclic permutations (CP); 12 atoms of type C [Zn/Al] at $(\pm0.1748,\pm0.3007,0)$ and CP; eight atoms of type D [Mg] at $(\pm0.1836, \pm0.1836, \pm0.1836)$; 12 atoms of type E [Mg] at $(0,\pm0.2942,\pm0.1194)$ and CP; 24 atoms of type F [Zn/Al] at $(\pm0.1680,\pm0.1860,\pm0.4031)$ and CP; six atoms of type G [Mg] at $(\pm0.4002,0,0.5)$ and CP; and six atoms of type H [Mg] at $(\pm0.1797,0,0.5)$ and CP. Barth-Hedin exchange was used for all the calculations. The so-called combined correction terms in LMTO-ASA computations have been applied, and the irreducible wedge of the Brillouin zone is sampled at 30 **k** points. Zn(Al) atomic spheres are chosen as 0.84 times that of Mg which correspond to near minimum mismatch in the potentials at the atomic-sphere radii of different types of atoms, and also minimum overlap between neighboring atomic spheres. The muffin-tin correction terms, mentioned above, for the total energy are employed according to the following formulas (for n atoms per primitive cell; see Ref. 19 for details):

$$\Delta E=1.8\sum_i \frac{q_{0i}^2}{s_i}+\sum_{ij}\frac{q_{0i}M_{ij}q_{0j}}{2\langle s\rangle} +\sum_{ij}(Z_i-q_i)\frac{M_{ij}}{2\langle s\rangle}(Z_j-q_j) +\sum_{ij}(Z_i-q_i)\left[\frac{M_{ij}}{\langle s\rangle}+\frac{3}{s_i}\delta_{ij}\right]q_{0j}\ , \tag{1}$$

where Z_i is the atomic number of ith atom and s_i is the corresponding MT radius; $\rho_i(r)$ is the spherically averaged charge density inside the MT sphere of ith atom;

$$q_i=\int_0^{s_i}4\pi r^2\rho_i(r)dr\ ;$$

ρ_0=constant charge density in the interstitial region

$$=\sum_i(Z_i-q_i)\Big/\left[V-\sum_i\Omega_i\right]\ ;$$

$$\Omega_i=(4\pi/3)s_i^3$$

=nonoverlapping MT sphere volume of ith atom ;

$$q_{0i}=\Omega_i\rho_0\ ;$$

V=cell volume$=(4\pi/3)n\langle s\rangle^3$;

$$M_{ij}={\sum_{\mathbf{R}}}'\frac{2\langle s\rangle}{|\mathbf{h}_i-\mathbf{h}_j-\mathbf{R}|}-\frac{1}{V}\int d^3r\left[\frac{2\langle s\rangle}{|\mathbf{r}|}\right]\ ;$$

$\mathbf{h}_i$=position of ith atom in the primitive cell ;

$\mathbf{R}$=direct lattice vector .

The prime over the summation indicates exclusion of zero denominator. In a further ASA approximation to these MT correction terms, all the MT radii in Eq. (1) are replaced by the corresponding ASA radii.[18,19]

RESULTS AND DISCUSSION

Results of our 0-K ground-state total-energy calculations are presented in Table I, which shows that the occupation of the central site by an Al or Zn atom is preferred

TABLE I. Frozen-core total energies for ©-$Zn_{48}Mg_{32}$ for various atoms at the center (©-). Valence electron total energies per primitive cell in columns 3(a) [3(b)] and 4(a) [4(b)] compare the stabilities of occupied and unoccupied centers of the packing units, respectively. Column 2 corresponds to similar frozen-core energies of well separated atoms. All energies are in rydbergs.

Atom at central site ©- of the packing unit	Total energy (valence) of atom (Ref. 24) (Ry)	Total energy per primitive cell (Ry)		Total energy of empty centered crystal plus well separated atom (Ry)	
		(a) no MT correction	(b) MT corrected	(a) no MT correction	(b) MT corrected
Empty sphere		−171.816	−169.122	−171.186	−169.122
Al	−4.050	−175.746	−173.280	−175.236	−173.172
Mg	−1.763	−173.256	−170.861	−172.949	−170.885
Zn	−2.247	−173.752	−171.434	−173.433	−171.369

to the vacant center.[23,24] We also observe from the last column in Table I that a Mg atom is not a probable occupant of the central site due to its larger size. These results are in qualitative agreement with the remarks made by Bergman, Waugh, and Pauling[22] who attributed Al-like occupancy for the electron density at the center in the x-ray Fourier map. We also note that our calculations fully support the positron-annihilation experiments.[4,5] However, our estimates of total-energy differences between occupied and unoccupied centers are in disagreement with pseudopotential results.[9] This discrepancy can be attributed to the perturbative approach and non-self-consistency of the pseudopotentials. Nevertheless, we are in complete agreement with their conclusion that the centers of the packing units are occupied.

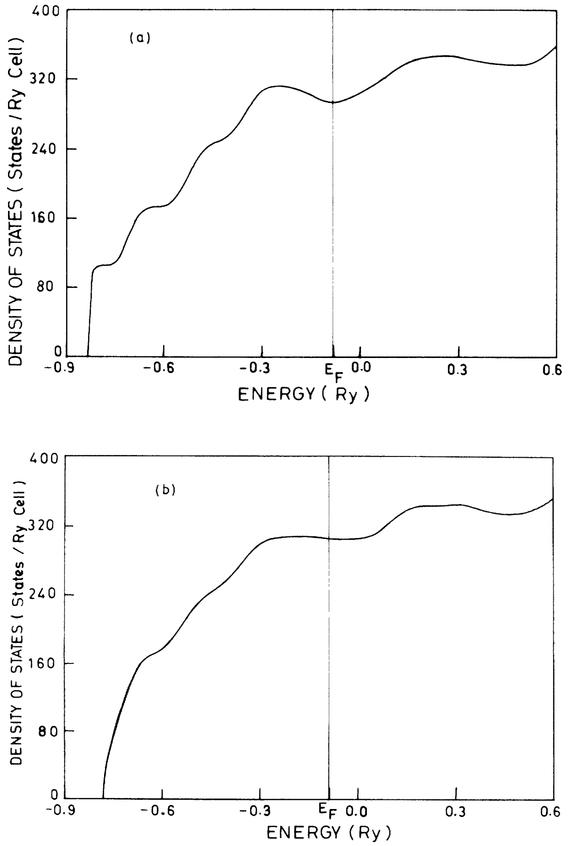

FIG. 1. Electron density of states for (a) Al-$Zn_{48}Mg_{32}$ and (b) empty sphere-$Zn_{48}Mg_{32}$. The Fermi level E_F in each case is shown by a vertical line.

Figure 1 shows the electronic density of states and the Fermi level E_F for the crystal approximants. The density of states, obtained by 30 **k**-point sampling of the Brillouin zone, were smoothened and shown for cases with Al-centered and empty-centered packing units. The density of states for the Zn-centered and Mg-centered cases (not shown) is similar to that shown in Fig. 1(a). These density of states curves show only a shallow minimum (valley) near E_F (indicating a small so-called pseudogap) which is consistent with the fact that experimental specific-heat data for the Al-Zn-Mg quasicrystal is almost free electron like. In Table II we compare our calculated density of states at the Fermi level[25] with the free-electron value. It is seen that the resulting electron specific-heat constants, γ, are close to the experimental values.[1] The shallowness of the minimum in the density of states at E_F explains the experimental observation that these quasicrystals are relatively less stable.[1] Even though some recent studies show that the pseudogap minimum in the density of

TABLE II. Electron density of states at the Fermi level for $Zn_{49}Mg_{32}$ by LMTO-ASA calculations and by the free-electron model. Resulting electronic specific-heat constants γ are compared with experimental data (Ref. 1) on $Al_{17}Zn_{32}Mg_{32}$.

Quantity	LMTO	Free-electron model	Experiment
$D(E_F)$ electrons/Ry (per primitive cell)	291	385	
γ mJ $mol^{-1}K^{-2}$	0.98	1.07	1.04

states might become more pronounced for higher-order approximants,[12] it is not expected to happen for the present system in view of the specific-heat data. Also the calculations of Hafner and Krajci,[17] which consider 3*d* electrons of Zn in the valence configuration show that the pseudogap hardly changes as the order of the crystal approximant is increased for the Al-Zn-Mg quasicrystal.

CONCLUSIONS

The LMTO-ASA total-energy calculations with muffin-tin correction terms to the intercellular Coulomb contribution show that the centers of the packing units in Al-Zn-Mg quasicrystals are occupied. These observations are in agreement with the positron-annihilation data[4] and pseudopotential results.[9] However, they disagree with LMTO-ASA results on other quasicrystal approximants,[7,8] which are not based on explicit evaluation of total energies, regarding the occupancy of the centers of the packing units. The fact that our densities of states show a shallow minimum even when the 3*d* electrons in Zn are considered as frozen in the core confirms that the pseudogap exists in the Al-Zn-Mg system even in the absence of valence *d* electrons. The shallowness of the minimum in the density of states at Fermi level is consistent with the nearly free-electron-like specific-heat data. This supports the existing view that the pseudogap is universal in quasicrystals or their crystal approximants for their stability.

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[23] When symmetry breaking structural changes are not involved, estimates of total energy changes by LMTO-ASA with combined corrections are quite reliable, especially for cubic crystals, and have been used extensively for structural stability studies.[14,18,19] Our calculations involve comparisons of total energies (Table I) with changes in the occupancy of only one site at the center of the packing unit, and the accuracy limitations are of the order of 10 mRy or less.

[24] Atomic total enegies were estimated by expanded lattice calculations, and extrapolated to large lattice constants by least-square fitting; the method is hoped to lead to significant cancellation of numerical and model dependent errors between bulk and atomic calculations.

[25] Theoretical values of γ are renormalized with the electron-phonon enhancement factor $1+\lambda$ (where $\lambda=0.3$) for direct comparison with experimental data of Table I (p. 313) of Ref. 1.