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Detailed *ab initio* electronic structure study of two approximants to Al-Mn based icosahedral quasicrystals

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The electronic structure of three available models of α-AlMnSi and of three models of a hypothetical approximant in the Al-Pd-Mn system are studied by means of the linear muffin-tin orbital method in the atomic sphere approximation. The effect of the atomic sphere approximation is investigated. The energy resolution of our best calculation is estimated to be 50–100 meV. By comparing the available models the importance of accurate atomic positions for the electronic structure is demonstrated. In the density of states of α-AlMnSi and the AlPdMn approximant a wide pseudogap ($\sim$1 eV) is found near the Fermi energy. Total energies for various possible positions of the Si atoms in α-AlMnSi are compared. It is found to be favorable for the Si atoms to partially occupy three of the classes of inequivalent Al atoms. The full charge density of α-AlMnSi is calculated and compared with available experimental results. In contrast to the experimental results the strongest bonding is found to be between Si and Mn atoms.

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I. INTRODUCTION

Stable icosahedral quasicrystals (i-QCs) show unusual electronic properties.[1–3] The low temperature electric conductivity σ_0 often is of the order of 100 $\Omega^{-1}\,\mathrm{cm}^{-1}$,[3] which is about a hundredth of the typical conductivity of metallic glasses. In i-AlPdRe σ_0 is even two orders of magnitude lower.[1] The conductivity increases with increasing temperature[4,5] and with disorder.[6] Both the low value of the conductivity and its temperature and disorder dependence are opposite to what one would expect for metallic alloys. Although attempts have been made to understand the atomic and electronic structure of these QCs, there are still open questions. The atomic structure cannot be resolved by means of standard crystallographic methods because of the absence of lattice periodicity. The extension of crystallography to six dimensional space[7,8] has led to models that describe about 80% of the atom positions conclusively ($R=0.14$).[9] This is far from what can be done for lattice-periodic crystals.[9] The electronic structure has been studied by means of ultrahigh energy resolution photoemission spectroscopy (PES),[2,10,11] tunneling spectroscopy,[12–15] and specific heat measurements.[1,16,17] These studies indicate strongly the presence of a pseudogap in the electronic density of states (DOS) at the Fermi energy. Whereas the PES results indicate that this pseudogap is 500–1000 meV wide (full width at half depth), tunneling spectroscopy has given evidence that it is much narrower, typically 50–100 meV. *Ab initio* electronic structure calculations of realistic models of i-QCs give sometimes very different results for the same structure models.[18–22] An added problem is that the calculated electronic structure depends sensitively on the modeled atom positions.[23]

The remarkable electronic properties of stable i-QCs are shared by so-called approximant phases,[24,25] lattice-periodic crystals with large unit cells and a local atomic structure similar to that of the parent QC. α-AlMnSi,[26] a 1/1 approximant[27] to i-AlMn, is such a phase that reproduces the observed electronic properties of stable i-QCs.[24] Its conductivity $\sigma_0=235\ \Omega^{-1}\,\mathrm{cm}^{-1}$.[24] There are 138 atoms per unit cell: 24 Mn, (114-x) Al, x Si, $11\lesssim x\lesssim 22$.[26,28,29] Its space group is $Pm\overline{3}$ (No. 200).[26] α-AlMnSi is nonmagnetic.[30] Soft x-ray emission (SXE) spectroscopy gives evidence of the presence of a pseudogap at the Fermi energy E_F in the electronic DOS,[29,31] approximately 600 meV wide.[29] Tunneling spectroscopy[13] indicates a width of 50 meV. Specific heat measurements[17,32] show that DOS(E_F) is at most $\approx$0.75 of its free-electron value. By means of standard crystallographic methods the atomic structure has been determined[33,34] up to an R factor of 0.031, which makes it one of the best-known structures amongst the approximants. It can thus be argued that α-AlMnSi is an ideal system for a detailed *ab initio* study that aims at increasing our understanding of stable i-QCs.

In this paper we present a detailed *ab initio* study of the electronic structure of α-AlMnSi and of a hypothetical approximant[35] in the Al-Pd-Mn system. In Sec. II we describe three available models of α-AlMnSi. It is important to understand to what extent various approximations made during the calculations affect the final results. Section III is devoted to this aspect. In Sec. IV A we compare the DOSs of the available structural models of α-AlMnSi. In Sec. IV B we compare the DOSs of three models of the AlPdMn approximant. In the models of α-AlMnSi there is some uncertainty in the positions of the Al and Si atoms.[34] With the hope of finding an optimum structure, in Sec. V we investigate the effect of the interchange of Al and Si positions. In Sec. VI we make some remarks about the fine structure in the DOS of α-AlMnSi. The charge density of α-AlMnSi is calculated and compared with experiment in Sec. VII. A summary of our results is presented in Sec. VIII.

II. MODEL

Three structural models of α-AlMnSi are considered. The most accurate one is probably the structure that was determined by Sugiyama *et al.*,[33] and confirmed by Kirihara *et al.*[34] This structure is a refined version of an older model of Cooper *et al.*[26] A third model of α-AlMnSi is the Elser-Henley model.[27] It has been used in almost all electronic structure studies of this system.[18–20,36–43] The Elser-Henley model was obtained in several steps. The starting point was the model of Cooper *et al.*,[26] where no distinction was made between Al and Si atoms. We will refer to α-AlMnSi as α-AlMn whenever Al replaces Si in the real structure. It was pointed out by Elser and Henley[27] that α-AlMn is a 1/1 approximant to *i*-AlMn, for which they constructed a six dimensional (6D) model. The 1/1 approximant to this model QC is obtained by making a rational cut in the 6D space and projecting it onto the physical 3D space.[18,27] In order to avoid short distances between the atoms in the 1/1 approximant, some Al atoms had to be moved slightly.[18] The resulting structure is the Elser-Henly model, also called 1/1 AlMn. The main difference between the Elser-Henley model and the original structure of Cooper *et al.* is that the atoms in the Elser-Henley model occupy idealized positions, as prescribed by the projection method. The atom positions of the Cooper model are based on X-ray diffraction data. As already mentioned above, the Sugiyama model is a refined version of the Cooper model. In Sec. III we use the Elser-Henley model to study the effects of various approximations usually made in *ab initio* electronic structure calculations of QCs. In Sec. IV we compare the electronic DOSs of the above-mentioned models. In the remaining sections we restrict ourselves to the model of Sugiyama *et al.*[33]

III. METHOD

We used the tight-binding linear muffin-tin orbital (LMTO) method in the atomic-sphere approximation (ASA).[44] For the exchange-correlation potential we used the local density approximation of von Barth and Hedin.[45] The LMTO method is a minimal basis method. Space is divided into nonoverlapping (muffin-tin) spheres and the interstitial region. The muffin-tin spheres are centered about the atomic positions. In open structures they can also be centered about interstitial sites (empty spheres). The ASA replaces the muffin-tin spheres with volume-preserving, and therefore partially overlapping atomic (Wigner-Seitz), spheres. If r_1 (r_2) is the radius of atomic sphere 1 (2), and d_{12} is the distance between atom 1 and 2, then the radial overlap of sphere 1 and 2 is given by[46]

$$O_{12}=\max\left(0,\frac{r_1+r_2-d_{12}}{d_{12}}\right). \tag{1}$$

For a system with many atoms per unit cell the important quantity is the maximum of the overlap of the various neighboring spheres:

$$O=\max_{i,j}(O_{ij}). \tag{2}$$

In *ab initio* electronic structure calculations the Poisson equation and the Schrödinger equation are solved self-consistently. If $O\lesssim 0.3$, finding the solution to the Schrödinger equation does not pose a major problem.[46] The largest errors are due to the sphere overlap and the interstitial regions, and can to lowest order be taken care of by including the so-called combined-correction term[47] in the Hamiltonian. In the ASA the charge density that enters the Poisson equation is approximated by a superposition of spherically symmetric charge densities inside the spheres.[46] This is the main cause of error in the LMTO-ASA method.[46] The situation can be improved by placing empty spheres in the largest interstitial regions,[46] and simultaneously reducing the atomic sphere radii, so that the atom-centered and empty spheres are volume preserving. In this way the overlap O is reduced and extra degrees of freedom are introduced for the charge density.

We found empty spheres in the following way. First the maximal allowed overlap between any two spheres was specified:

$$O\leqslant O_{\max}. \tag{3}$$

The atomic sphere radii were scaled so as to satisfy this condition. In general the scaled atomic spheres were not volume preserving. In this case we checked the positions in the interstitial region between the atomic spheres by subsequently placing an empty sphere on each point of a grid, making it as large as condition (3) allowed. After trying all positions on the grid the largest empty sphere was selected. Its position was refined to make the empty sphere larger. The refinement allowed us to use a rather coarse grid to begin with. If the atom-centered spheres and the newly found empty sphere(s) were still not volume preserving, the next empty sphere position was determined in the same way. This was repeated until the spheres (empty and atom-centered) were volume preserving. This procedure is a slightly modified version of the standard procedure,[48] which works with touching spheres instead of partially overlapping spheres. By decreasing the parameter $O_{\max}$ the number of empty spheres is increased. We usually decreased $O_{\max}$ to the extent possible, without using empty spheres of radii $r\lesssim 0.6$ Å.

Ab initio electronic structure calculations for the Elser-Henley model have been performed by Fujiwara,[18,36–40] by Fujiwara and co-workers,[19,41,42] and by Solbrig and co-workers.[20,43] They use the LMTO method at various levels of approximation. As a consequence, the calculated DOSs have different levels of accuracy. In the above-mentioned papers 16 empty spheres are included in the unit cell.[18] The maximum overlap O of the atom-centered spheres is 0.264, and that between any two spheres is 0.275. In order to understand the differences between the various published results we performed a systematic study, varying the basis set, with and without the combined correction. From this study we concluded the following: Fujiwara[18] does not include the combined-correction term in the Hamiltonian.[42] His basis set consists of *sp* states for the Al atoms and the empty spheres and *spd* states for the Mn atoms. We reproduced his result [Fig. 1(a)] with 45 inequivalent **k** points in the self-consistent calculation and 9951 inequivalent **k** points for the final result. The calculation of Fujiwara *et al.*[19] is the same as above, except that Al-*d* states are also included in the basis. We reproduced this result [Fig. 1(b)] with 45 inequivalent **k**

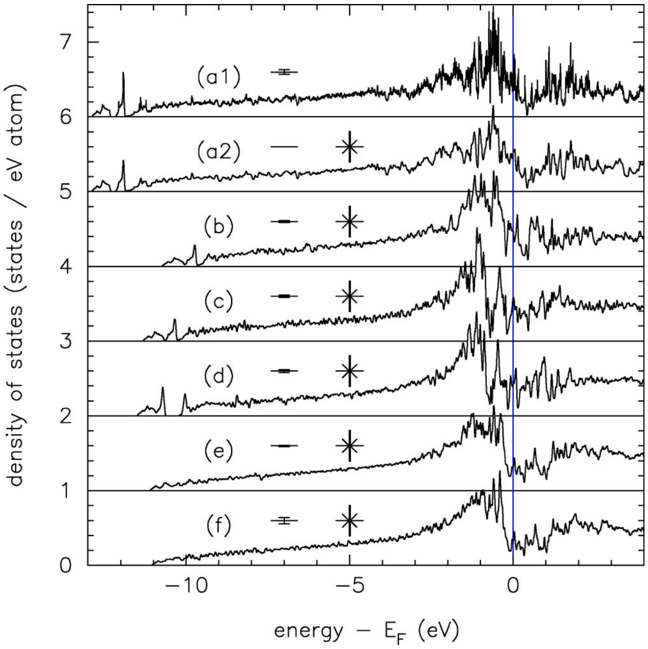

FIG. 1. DOS of α-AlMn. (a1)–(d) are results for the Elser-Henley model calculated at various levels of approximation. (a1) reproduces the calculation of Fujiwara. (Ref. 18) (a2) is the same result convoluted with a Gaussian of full-width at half-maximum of 30 meV. (b) reproduces the calculation of Fujiwara *et al.* (Ref. 19). In calculation (c) we have included the combined-correction term in the Hamiltonian. (d) is a calculation with 56 empty spheres. This is the most accurate calculation for the Elser-Henley model. At the same high level of approximation (e) and (f) are results for the Cooper and the Sugiyama model, respectively. An estimate of the maximal **k**-space integration error is indicated in each subfigure (error symbol). When a DOS was convoluted with a 30-meV-wide Gaussian, this is indicated (resolution symbol).

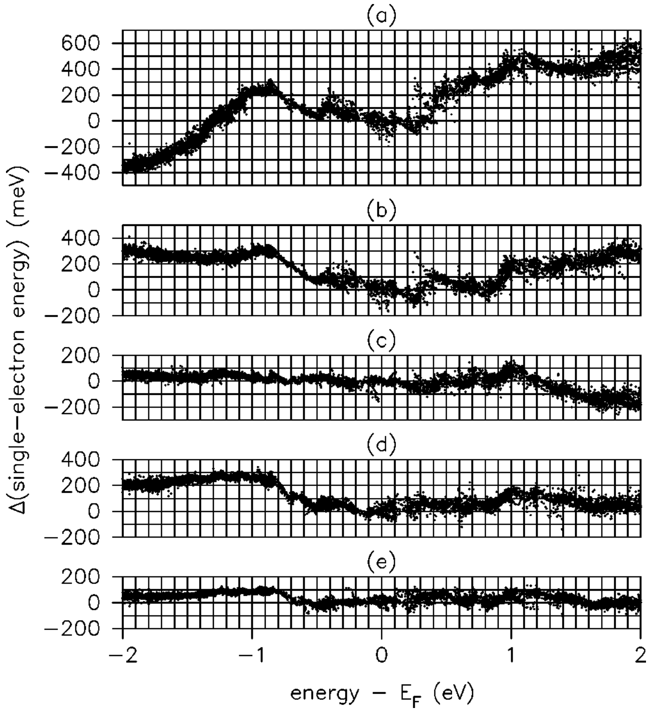

FIG. 2. Differences of the single-electron energy eigenvalues of five calculations from those of a reference calculation (vertical axes) vs the single-electron energy eigenvalues of the reference calculation (horizontal axis). All calculations are for the Elser-Henley model. (a) Calculation with parameters according to Fujiwara (Ref. 18). (b) Calculation with parameters according to Fujiwara *et al.* (Ref. 19). (c) Calculation including the combined-correction term in the Hamiltonian. (d) Calculation without empty spheres. (e) Calculation with 24 empty spheres. The reference calculation has 56 empty spheres. Its DOS is shown in Fig. 1(d). The DOSs of (a), (b), and (c) are shown in Figs. 1(a), 1(b), and 1(c), respectively.

points in the self-consistent calculation and 741 inequivalent **k** points for the final result.[63] Solbrig *et al.*[20] include the combined-correction term in the Hamiltonian. In addition they assume that some atoms are equivalent even though they are not related by symmetry. We repeated the calculation of Solbrig *et al.*[20] without this assumption. The DOS, which was calculated self-consistently with 45 inequivalent **k** points [Fig. 1(c)], shows only minor differences from the results of Solbrig *et al.*[20]

We performed additional calculations with an increasing number of empty spheres: no empty spheres ($O = 0.262$), 24 empty spheres ($O = 0.225$), and 56 empty spheres ($O = 0.201$). For all spheres we included *s*, *p*, and *d* states in the basis set. For Al atoms with $r > 1.6$ Å, *f* states were also included. These were downfolded.[49] The DOS of the calculation with 56 empty spheres is shown in Fig. 1(d). The DOSs in Figs. 1(e) and 1(f) will be discussed in Sec. IV.

The purpose of all these calculations is to gain an understanding of the energy scales on which features of the DOSs in Fig. 1 are significant. Therefore, in Fig. 2 we plot differences of the single-electron (Kohn-Sham) energy eigenvalues[50] at 45 inequivalent **k** points from those of a reference calculation. The reference calculation employs 56 empty spheres. Assuming that the reference calculation has relatively small errors, we note the following. Single-electron energies that are almost equal in the reference calculation are scattered over an energy range of about 200–400 meV in the calculation of Fujiwara[18] [the spread in the single-electron energies corresponding to a given energy in the reference calculation in Fig. 2(a)]. This is the energy resolution of this calculation. By the same argument the energy resolution of the calculation of Fujiwara *et al.*[19] [Fig. 2(b)] is only marginally better. The combined correction [Fig. 2(c)] improves the resolution to 100–200 meV. The resolution improves with increasing number of empty spheres. Without empty spheres [Fig. 2(d)] it is 200−400 meV, with 24 empty spheres [Fig. 2(e)] it is 100–200 meV. Extrapolating these numbers we estimate the resolution of the reference calculation with 56 empty spheres to be 50–100 meV.[64]

We conclude that the standard LMTO calculation of 1/1 AlMn [Figs. 1(c) and 2(c)] has an energy resolution of 100–200 meV. By including a sufficient number of empty spheres this can be improved to an estimated 50−100 meV. Neglect of the combined-correction term produces a DOS in which not even the main features are correct [compare, for example, Figs. 1(b) and 1(c)].

IV. IDEALIZED VS EQUILIBRIUM POSITIONS

Recently Krajčí *et al.*[51] have demonstrated the importance of structural relaxation for the bandgap in the case of semiconducting intermetallic compounds. In particular, it was mentioned that the relaxed structure of Al_4MnCo has a gap of 0.51 eV wide. In the idealized structure the width of this gap is only 0.15 eV. Similar results were obtained for 1/1 approximants of the hypothetical alloys *i*-AlPdIr, *i*-AlPdW, and *i*-AlAuIr.[52] The connection between relaxation and the pseudogap is the lowering of band energy via a decrease of the DOS at the Fermi level. For metallic glass alloys this connection between the pseudogap and stability was first given by Nagel and Tauc.[53]

In this section we would like to demonstrate the importance of accurate atomic positions for the electronic structure by considering α-AlMn and AlPdMn. In the first case we compared the electronic DOS of an idealized model of α-AlMn with the DOS of experimentally determined structures. In the second case we compared an idealized and a relaxed model of AlPdMn. In both cases we found that accurate atomic positions obtained via experiment or via structural relaxation of an idealized model (as opposed to strictly idealized positions) are important for an accurate description of both the pseudogap and (the absence of) fine structure in the DOS.

A. α-AlMn

The DOSs of the Elser-Henley, Cooper, and Sugiyama model for α-AlMn are plotted in Figs. 1(d)–1(f). The calculation for the Elser-Henley model was described in Sec. III. The electronic structure of the Cooper (Sugiyama) model was calculated with 68 (74) empty spheres [$O=0.148$ (0.148)]. In all three calculations we used the experimentally determined lattice parameters, viz., $a=12.68$, 12.68, and 12.64 Å, respectively. Further details of the calculation for the Sugiyama model are given in Table I. The DOS of the Cooper model [Fig. 1(e)] is markedly different from that of the Elser-Henley model [Fig. 1(d)]. In the Elser-Henley model the DOS near the Fermi level is a strongly fluctuating (spiky) function of energy. At the Fermi level it is hardly reduced with respect to the free electron result. The DOS of the Cooper model shows a wide pseudogap around E_F, indicating a lowering of the band energy. The spikiness is greatly reduced. This shows that in order to perform a reliable electronic structure calculation for α-AlMn it is necessary to use the actual (experimentally determined) positions of the atoms. An idealized model does not necessarily give the most favorable atom positions. The differences between the Cooper [Fig. 1(e)] and the Sugiyama model [Fig. 1(f)] are relatively small.

TABLE I. LMTO parameters for the Sugiyama model that give a good trade-off between maximal attainable accuracy and computational speed. For each of the 11 classes of inequivalent atoms and nine additional classes of empty spheres the table gives multiplicity, atomic coordinates (x, y, z), sphere radii *r*, and the recommended electronic basis set.

Class	Multiplicity	$x(a)$	$y(a)$	$z(a)$	r(Å)	Basis
Mn1	12	0.1978	0.3263	0.0000	1.370	*spd*
Mn2	12	0.1793	0.5000	0.3079	1.332	*spd*
Al1	6	0.0000	0.3678	0.0000	1.565	*spd*
Al2	6	0.5000	0.5000	0.1243	1.569	*spd*
Al3	6	0.2897	0.5000	0.0000	1.477	*spd*
Al4	12	0.1014	0.1655	0.0000	1.352	*spd*
Al5	12	0.3361	0.5000	0.4003	1.311	*spd*
Al6	12	0.4021	0.3314	0.0000	1.422	*spd*
Al7	12	0.1239	0.5000	0.1177	1.476	*spd*
Al8	24	0.1180	0.2991	0.1886	1.571	*spd*
Al9	24	0.3129	0.3907	0.1962	1.559	*spd*
E1	1	0.5000	0.5000	0.5000	1.475	*spd*
E2	1	0.0000	0.0000	0.0000	1.466	*spd*
E3	8	0.3559	0.3559	0.3559	0.896	*sp*
E4	12	0.0000	0.4163	0.1754	0.851	*sp*
E5	12	0.4133	0.5000	0.2690	0.841	*sp*
E6	8	0.1424	0.1424	0.1424	0.823	*sp*
E7	12	0.0000	0.2315	0.0916	0.820	*sp*
E8	8	0.2557	0.2557	0.2557	0.740	*s*
E9	12	0.0575	0.5000	0.2469	0.627	*s*

B. AlPdMn

Calculations for three models in the Al-Pd-Mn system show that our observation for α-AlMn is valid in general. It is important to calculate the electronic structure of a QC with equilibrium atomic positions. We used the models of Quandt and Elser,[35] who studied a hypothetical approximant to *i*-AlPdMn with 65 atoms per unit cell. Starting from idealized atomic positions they carried out an *ab initio* structure relaxation. We calculated the electronic DOS of both the idealized [Fig. 3(a)] and the relaxed structure [Fig. 3(b)]. Quandt and Elser[35] noted that the relaxed structure has a symmetry that is very close to that of the space group *Immm* (No. 71). We also studied the relaxed model of Quandt and Elser with the exact *Immm* symmetry. The DOS of this sym-

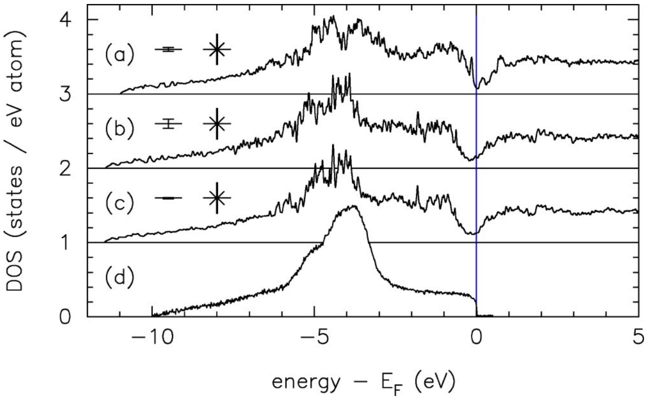

FIG. 3. (a) DOS of $Al_{70.8}Pd_{21.5}Mn_{7.7}$ (Quandt and Elser's model), using idealized, (b) relaxed, and (c) symmetrized relaxed positions. In (a)–(c) an estimate of the maximal **k**-space integration error and the resolution of 30 meV are indicated. (d) PES spectrum (Ref. 54) of i-$Al_{70}Pd_{21.5}Mn_{8.5}$. The PES spectrum is normalized such that its maximum equals 1.5.

TABLE II. Partial Si occupancies of five Al classes (defined in Table I) according to three experimental studies and one theoretical study. In the classes Al1, Al2, Al8, and Al9 there is no Si.

Ref.	Al3	Al4	Al5	Al6	Al7
Tibballs *et al.* (Ref. 55)	0.69(19)	0.55(15)	0.42(15)	0.08(10)	0.06(10)
Sugiyama *et al.* (Ref. 33)	0.99(11)	0.35(6)	0.63(6)	—	—
This paper [a]	1.00	0.42	0.58	—	—
Kirihara *et al.* (Ref. 34)	0.82(4)	0.73(3)	0.53(3)	—	—

[a] Calculation with 18 Si atoms per unit cell using the Sugiyama model.

metrized model is shown in Fig. 3(c). In the electronic structure calculations of these three models we used 30, 29, and 36 empty spheres ($O=0.149$, 0.173, and 0.169), respectively. From Fig. 3 it follows that accurate atomic positions are very important for an accurate description of the DOS near the Fermi level. In the DOS of the relaxed structure [Fig. 3(b)] there is a pseudogap (approximately 800 meV wide) near the Fermi level, which is less pronounced in the idealized structure [Fig. 3(a)]. The symmetry breaking of the relaxed structure is small: It doesn't lead to noticeable effects on the DOS [compare Figs. 3(b) and 3(c)]. Therefore the symmetrized model [Fig. 3(c)] is a useful alternative to the relaxed model [Fig. 3(b)].

The PES spectrum[54] of a single-grain *i*-AlPdMn sample at 12 K is shown in Fig. 3(d). A PES spectrum is roughly proportional to the electronic DOS, but some partial DOS contributions may be enhanced with respect to other contributions. The Pd-*d* peak in Fig. 3(d) is, for example, more pronounced than the same peak in the calculated DOS [Fig. 3(b)]. For the DOS near the Fermi energy we note that the pseudogap in the sample used for the PES is less wide (260 meV) and less deep[54] (34%) than the pseudogap of the relaxed model of Quandt and Elser (800 meV and ~75%). The theoretical DOS [Fig. 3(b)] and the experimental spectrum [Fig. 3(d)] are both smooth within their respective accuracies.

V. SILICON

In α-AlMnSi there are 11–22 Si atoms per unit cell.[29] It is usually assumed that the Si atoms substitute Al in the α-AlMn structure.[33,34,55] Although Cooper *et al.*[26] make no distinction between Al and Si, a neutron diffraction experiment by Tibballs *et al.*[55] provides partial Si occupancies for the Cooper model (Table II). In addition, Sugiyama *et al.*[33] and Kirihara *et al.*[34] report partial Si occupancies for the classes Al3–Al5 based on their structure refinements (Table II). Table II shows that there is some uncertainty in the partial Si occupancies of the Al classes of α-AlMn. Also, there is no information about possible short-range order amongst the Si atoms.

To improve our understanding of where the Si atoms are in α-AlMnSi and to investigate their effect on the electronic DOS we substituted different Al atoms in the Sugiyama model of α-AlMn (Table I) with Si. Our approach was the following. We compared the total energies of various configurations with the same number of Si atoms per unit cell. For each Si atom we used the atomic sphere radius that an Al atom with the same coordinates would have had.[65] The total energies were calculated with 27 **k** points in the Brillouin zone.[66] We arrive at an error estimate of our approach by the following consideration. Structural energy differences of close-packed systems can within the ASA be obtained within typically a few tens of meV/atom,[56–58] provided that the combined-correction term is included in the Hamiltonian. Including 74 empty spheres in each unit cell we have arrived at a description of α-AlMn as a close-packed system of atom-centered and empty spheres. In this section we compare structures with two or a few atoms interchanged, leaving the rest of the unit cell unchanged. In this case most of the systematic errors in the total energies should cancel. We therefore expect that differences in total energy can be obtained roughly within a few tens of meV/unit cell. With this error estimation most of the results presented in this section should be reliable. However, as the LMTO-ASA method can never achieve[56–58] the same accuracy as a full-potential method, it would certainly be desirable to verify some of our conclusions with more accurate methods available.

As possible Si sites we concentrated on the atom positions of the classes Al3–Al5. Of the configurations with one Si atom per unit cell the one where Si occupied a position of class Al5 had the lowest total energy. When the Si was in class Al4 (Al3) the total energy was 0.14 (0.28) eV/(unit cell) higher. When a second Si atom was added in class Al5 the total energy was 0.20 eV/(unit cell) higher when the two Si atoms were nearest neighbors than when they were at a large distance. The total energies of various configurations with one and two Si atoms per unit cell are given in Table III. We remark that it is the high energy cost associated with the Si atoms in nearest neighbor positions that leads to partial Si occupancies of more than one Al class. Without such a local rule, first the atoms in class Al5 would be substituted by Si, followed by atoms of class Al4. The partial Si occupancy of the latter class would then be determined by the Si concentration x (Sec. I).

In the α-AlMnSi sample that Sugiyama *et al.*[33] used for their structure determination there were about 18 Si atoms per unit cell. In order to study their positions we compared the total energies of various configurations with 12 and 18 Si atoms per unit cell. We minimized the total energy with respect to the lattice parameter.[67] In each configuration we kept the number of nearest neighbor Si-Si pairs as low as possible. Atoms in class Al3 are not nearest neighbors.[33] Two atoms in the classes Al3–Al5 that are both in a different class are not nearest neighbors either.[33] Therefore, it makes sense to indicate a configuration by the number of Si atoms in each

TABLE III. Comparison of the total energies of configurations with one, two, twelve, and eighteen Si atoms per unit cell substituted for Al in α-AlMn (Sugiyama model). For the cases with two Si atoms per unit cell d is the shortest distance between these atoms.

Number of Si atoms in class									d	ΔE_{tot}
Al1	Al2	Al3	Al4	Al5	Al6	Al7	Al8	Al9	(Å)	(eV/unit cell)
0	0	0	0	0	0	0	1	0		1.22
0	0	0	0	0	0	0	0	1		1.12
1	0	0	0	0	0	0	0	0		0.90
0	1	0	0	0	0	0	0	0		0.90
0	0	0	0	0	0	1	0	0		0.89
0	0	0	0	0	1	0	0	0		0.81
0	0	1	0	0	0	0	0	0		0.28
0	0	0	1	0	0	0	0	0		0.14
0	0	0	0	1	0	0	0	0		reference
0	0	0	2	0	0	0	0	0	2.56	0.48
0	0	0	2	0	0	0	0	0	2.58	0.44
0	0	0	2	0	0	0	0	0	4.17	0.31
0	0	0	2	0	0	0	0	0	4.91	0.21
0	0	0	0	2	0	0	0	0	2.52	0.20
0	0	0	0	2	0	0	0	0	2.56	0.20
0	0	0	0	2	0	0	0	0	4.12	0.06
0	0	0	0	2	0	0	0	0	4.85	reference
0	0	6	3	3	0	0	0	0		0.39
0	0	5	3	4	0	0	0	0		0.20
0	0	4	4	4	0	0	0	0		0.09
0	0	2	5	5	0	0	0	0		0.09
0	0	2	4	6	0	0	0	0		0.01
0	0	3	4	5	0	0	0	0		reference
0	0	5	6	7	0	0	0	0		0.22
0	0	6	4	8	0	0	0	0		0.14
0	0	6	6	6	0	0	0	0		0.02
0	0	6	5	7	0	0	0	0		reference

of the Al classes. Our results are summarized in Table III. In Table II the partial Si occupancies of the Al classes are given for the configuration with 18 Si atoms per unit cell that had the lowest total energy. Our values agree well with the experimental results of Sugiyama *et al.*[33] (Table II). However, it should be noted that in view of the accuracy of our calculations we cannot exclude the possibility that the configuration with the second lowest total energy in Table III is in reality the state of lowest total energy. If this were the case, this would change the partial Si occupancies of the Al classes Al4 and Al5 as listed in Table II by $+0.08$ and -0.08, respectively.

The DOSs of the lowest total energy configurations with 12 and 18 Si atoms per unit cell are plotted in Figs. 4(a) and 4(b). The specific arrangement of the Si atoms in these two configurations breaks the high symmetry of α-AlMn ($Pm\overline{3}$). Therefore some cancellation of features in the DOS of α-AlMn [Fig. 1(f)] can be expected to occur. Indeed, the DOSs of Figs. 4(a) and 4(b) show considerably less structure than Fig. 1(f). In the DOS of Fig. 4(a) there is a narrow gap at the Fermi level superimposed on the wide pseudogap that we already found in the DOS of α-AlMn [Fig. 1(f)]. In the light of the accuracy of our calculations ($\Delta E = 50-100$ meV) one cannot be sure of the existence of a real gap in this system. However, it is well known that the local density approximation underestimates the energy gap, often by a factor of 2. Hence, the possibility of an energy gap can also not be completely ruled out. In the DOS of Fig. 4(b) six additional Si atoms provide six extra electrons per unit cell. In line with a rigid-band model, the Fermi level in Fig. 4(b) lies above the narrow (pseudo)gap.

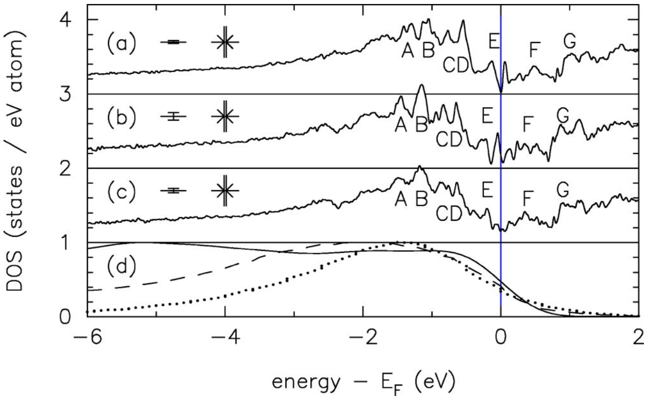

FIG. 4. (a)–(c) DOS of α-AlMnSi (Sugiyama model). (a) Configuration with 12 and (b) 18 Si atoms per unit cell. (c) Configuration with 18 Si atoms and two vacancies per unit cell. In (a)–(c) an estimate of the maximal **k**-space integration error and the resolution of 30 meV are indicated. A–G label the main peaks in the calculated DOSs. (d) SXE spectra of α-AlMnSi. Shown are the partial Al-*sd* contribution (Ref. 59) of α-$Al_{69}Mn_{21}Si_{10}$ (solid curve) and the partial Al-*p* (dashed curve) and Mn-*d* (dotted curve) contributions (Ref. 60) of α-$Al_{73}Mn_{21}Si_{6}$. Each contribution is normalized such that its maximum equals 1.

To bring the Fermi level back to the DOS minimum we considered configurations with 18 Si atoms and two vacancies substituted for Al in α-AlMn. The occurrence of vacancies is compatible with the experimentally determined mass density of α-AlMnSi, which is significantly lower than the density of the Sugiyama model.[34] The idea is that by removing two Al atoms from the structure, there are six valence electrons less per unit cell. The Fermi level thus moves back to the narrow gap in the DOS, provided that the removal of the Al atoms can be treated in a rigid-band model. We compared ten different configurations. The one with the lowest total energy had the Si atoms distributed over the Al classes in the same way as the configuration of Fig. 4(b). The vacancies were in class Al5. Like the Si atoms the vacancies preferred energetically to be at a large relative distance. The DOS [Fig. 4(c)] has less structure than the DOSs of Figs. 4(a) and 4(b). The effect of the Al removal is obviously more radical than that of the Si substitution. Figure 4(d) will be discussed in Sec. VI.

VI. SPECTRAL FINE STRUCTURE

A lot has been written about the prediction of Fujiwara[18] that the DOS of QCs consists of a dense set of spikes of width 10–20 meV.[19,39] This prediction is based on *ab initio* (LMTO) calculations for models of small cubic approximants to i-QCs, in particular α-AlMn. A model calculation for the three-dimensional Penrose tiling (also called Amman-Kramer tiling) shows that spiky features, although present in the DOSs of small cubic approximants, disappear in the DOS of the ideal QC.[61] This result is confirmed by an *ab initio* (LMTO) calculation for a realistic model in the Al-Pd-Mn system.[23] Accordingly, in PES (Refs. 2, 10 and 11) and tunneling[12–15] experiments on QCs spikes are not observed. Both theoretically and experimentally it is thus clear that the DOS of i-QCs is essentially smooth. It remains, however, an interesting question whether any fine structure can be observed in the DOS of 1/1 approximants to i-QCs. In Sec. III we concluded that an LMTO calculation for α-AlMnSi does not give reliable information on energy scales smaller than 50–100 meV. Therefore, we focus on the wider features in the DOS.

The DOSs of Figs. 4(a)–4(c) show several peaks on an energy scale of ~200 meV. We labeled the ones below the Fermi energy $A-E$ and the ones above $E_F F-G$. Figure 4(d) shows SXE spectra of α-AlMnSi.[59,60] Peaks $A-E$ are not resolved. This is not surprising since the energy resolution of the SXE technique is limited to several 100 meV. In addition, it is unclear whether peaks $A-G$ are real features of the DOS of α-AlMnSi. In our calculations the Al and Si atoms in a given class had the same nearest neighbor environments. In reality the Si atoms are expected to be slightly smaller than the Al atoms. So, there are probably local relaxations of the α-AlMnSi structure near these atoms. The same argument applies more strongly when some of the Al atoms are removed from the structure [Fig. 4(c)]. In conclusion, our calculations show that small imperfections can considerably reduce the fine structure in the DOS of an approximant to a QC. It can be expected that structural imperfections in i-QCs have the same effect. Therefore, we expect that the DOSs of both QC's and approximants to QC's do not have any observable fine structure.

VII. CHARGE DENSITY

The full charge density of α-AlMnSi has been determined experimentally[34,62] by means of the maximum entropy method (MEM). We calculated the full charge density of the configuration with 12 Si atoms per unit cell with minimal total energy (Sec. V). The results for the planes $z=0$ and $y=a/2$ are shown in Fig. 5. Most features of Fig. 5(a) are in qualitative agreement with the experimental result[62] for the plane $z=0$. One discrepancy is that the MEM analysis gives the largest charge density between the Al atoms of the classes Al1, Al6, and the Mn atoms, whereas we found the largest bonding between the Si and Mn atoms, and to a lesser extent between the Al atoms in the classes Al3–Al5 and the Mn atoms. It is known[33] that in the α-AlMn structure the shortest Al-Mn distances are found between the atoms in the classes Al3–Al5 and the Mn atoms. So, in agreement with our results, one would naively expect the strongest bonding between these atoms. Another discrepancy between our results and the MEM analysis is, that at the origin of our coordinate system we found a charge density of $0.03e/\text{Å}^3$, where the MEM analysis[34,62] gives $0.001e/\text{Å}^3$. This small value was taken as evidence that the pseudogap is due to covalent bonds rather than the Hume-Rothery effect.[34,62] Our calculations do not confirm the validity of this argument.

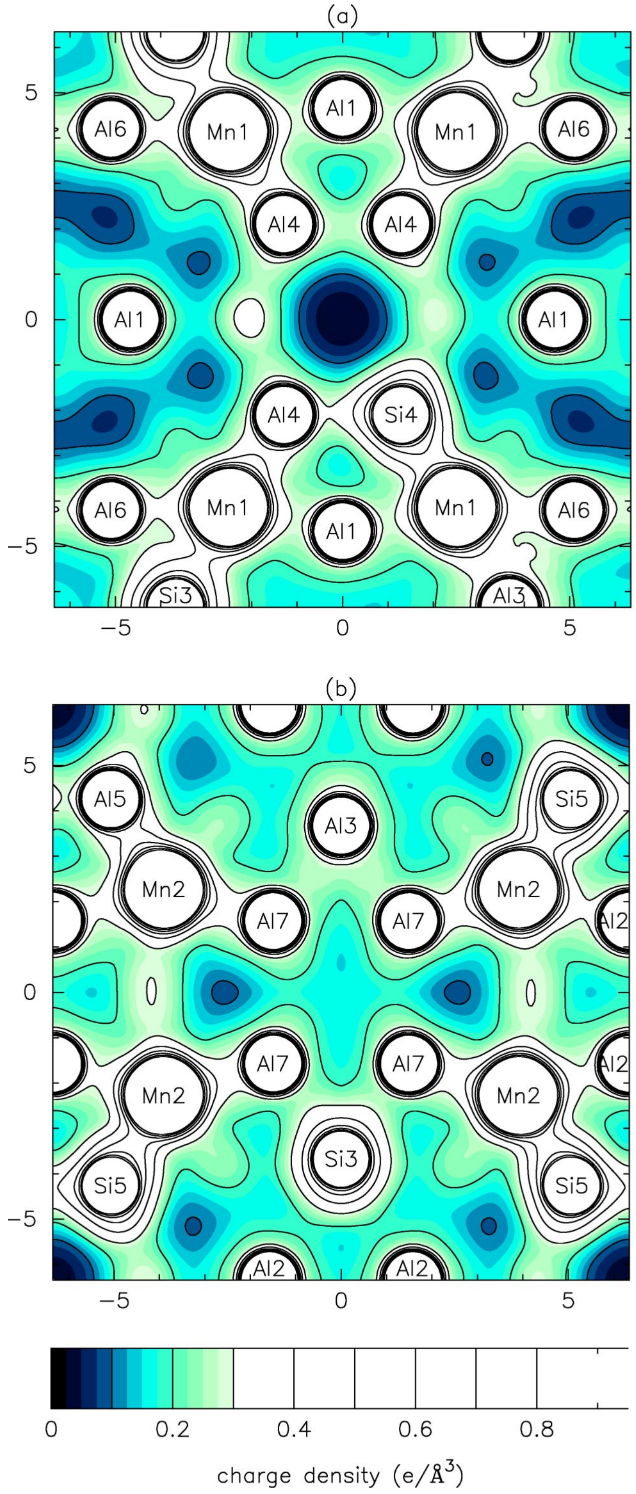

FIG. 5. (Color online) Full charge density of α-AlMnSi in the (a) $z=0$ and (b) $y=a/2$ planes.

VIII. CONCLUSIONS

We have carried out a detailed study of the electronic structure of α-AlMnSi and a hypothetical AlPdMn approximant. First we considered the effect of errors intrinsic to the LMTO method. We concluded that a good LMTO calculation of 1/1 AlMn with many empty spheres yields single-electron energies in the electronic band structure with an accuracy of 50–100 meV (the resolution). Then we demonstrated the importance of accurate atomic positions. We concluded that so-called idealized models with approximate atom positions should be regarded with caution: They may give highly inaccurate DOSs. We also studied the role of Si in α-AlMnSi. We found that the Si atoms occupy positions in the classes Al3–Al5, and that the Si atoms ‘‘prefer’’ not to be in nearest neighbor positions. This effective Si-Si repulsion is the cause of partial Si occupancies of more than one Al class. Our calculated partial Si occupancies agree well with the experimental results of Sugiyama *et al.*[33]. Finally, we calculated the charge density of α-AlMnSi in planes equivalent to $z=0$ and $a/2$, and found for many features a qualitative agreement with experimental results. In contrast to the experimental data, we found the strongest bonding between the Si and Mn atoms, and to a lesser extent between the Al atoms in the classes Al3–Al5 and the Mn atoms.

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[63] We used Löwdin downfolding (Ref. 49) for the Al-*d* states. This is the only calculation in which we used downfolding for Al-*d* states.

[64] This estimate is based on the extrapolation of the present calculations as well as interpolation of calculations for another QC, which employed a larger number of empty spheres, up to 140 (unpublished).

[65] Within the LMTO-ASA method this is the best procedure to study the effect of Al substitution by Si. Choosing the Si radii to be the same and independent of the Al atom they are replacing would increase the ASA-related error.

[66] The Γ point was included. For α-AlMn (Sugiyama model) we compared the total energy calculated with 27 and with 729 **k** points. The difference is 0.003 eV/unit cell.

[67] For the configurations with one or two Si atoms per unit cell the experimental lattice parameter $a = 12.64$ Å was used. For each configuration with 12 Si atoms per unit cell the total energy was minimized with respect to the lattice parameter, which gave $a \approx 12.60$ Å. For one configuration with 18 Si atoms per unit cell the total energy was minimized with respect to the lattice parameter, which gave $a = 12.57$ Å. This value was then used for all calculations with 18 Si atoms per unit cell. In the same way, the total energy of one configuration with 18 Si atoms and two vacancies per unit cell was minimized with respect to the lattice parameter, which gave $a = 12.55$ Å.