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Improvement of six-dimensional projection models for the atomic structure of quasicrystals

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Many six-dimensional-to-three-dimensional projection models for quasicrystals yield reasonable agreement with diffraction experiments but are still energetically unfavorable. We describe a procedure for improving the energetics of these models based upon the filling of vacant spaces, Monte Carlo chemical decoration techniques, and structural relaxations. A simplified pair-potential calculation indicates that these procedures reduce the total energy of the Ti-Mn system by more than 0.25 eV/atom.

The discovery of quasicrystals has resulted in a flourish of activity aimed at the determination of their atomic arrangements.[1] Although considerable progress has been made in understanding the diffraction properties of quasicrystals, only a few efforts[2-4] have been devoted to uncovering the energetic factors which play a role in the stability and formation of these phases. Most attempts to determine atomic arrangements have been based on matching the observed diffraction pattern, using geometrical intuition. Unfortunately, obtaining a good fit to the observed diffraction pattern does not guarantee physically reasonable atomic positions, and the energy relative to competing crystalline structures can be too high for the quasicrystal to be stable or mestastable. One missing ingredient in these modeling efforts has been the use of energy-minimization methods to refine candidate structures.

In this paper, we describe a method for generating low-energy, realistic quasicrystal models through the use of energetic analysis to determine the chemical decoration of the underlying atomic sites and the relaxed atomic positions. Our analysis includes the filling of sites vacant in usual models of Al-Mn, such as the centers of Mackay icosahedra. We consider the Ti–transition-metal (*M*) class of quasicrystals (Ti-Mn, Ti-Fe, Ti-Co, and Ti-Ni),[5] with special emphasis on the Ti-Mn system as it has received the most extensive experimental consideration. Though our methods are demonstrated here for the Ti-Mn system, we expect them to be of equal utility in other systems. The optimization of both bond lengths and chemical decorations results in a substantial reduction in the total energy. Comparable reductions would presumably be found in other systems. Further, as will be seen later, the number of vacant spaces in projection models exceeds that of related crystalline phases. We demonstrate a practical scheme for identifying and filling these vacant spaces. In a related paper,[6] we use the models devoted here to carry out total-energy calculations using a tight-binding treatment of the electronic structure.

In generating the atomic positions for the quasicrystal we exploit likely similarities between the Ti-*M* quasicrystals and the Al-Mn icosahedral phase.[7] These similarities are suggested by comparison of the α-(Al-Mn-Si) structure and its transition-metal counterpart, the Ti_2Ni structure.[8] Both of these structures consist of large icosahedral clusters [so-called Mackay icosahedra[1,7] in the α-(Al-Mn-Si) structure] and small octahedra, although the centers of the large icosahedral clusters are occupied in the Ti_2Ni structure,[9] while they are vacant in the α-(Al-Mn-Si) structure. We have used the modeling scheme of Duneau and Oguey[10] (DO) for the Al-Mn quasicrystal to generate a starting structure for the Ti-Mn quasicrystal. The DO model represents the best model of the Al-Mn system that we are aware of. It yields reasonable agreement with diffraction intensities while maintaining the correct density, and without unphysically short bond lengths. The DO method involves the projection of coordinates from a six-dimensional (6D) hypercubic lattice, with atoms or 12-atom clusters being placed at the intersections of "atomic surfaces" (which are complicated polyhedra) with the 3D space being projected upon. This results in a structure based on Mackay icosahedra with a center-to-vertex distance of roughly 5 Å and a typical center-to-center distance of 11 Å (depending upon the quasilattice constant). We have used the DO technique to generate a finite starting cluster with a radius of 17.5 Å (1538 atoms). This cluster possesses no center of icosahedral point-group symmetry.[11] It contains seventeen separate Mackay icosahedral clusters. The sites which are a part of these Mackay clusters comprise approximately $\frac{2}{3}$ of the total sites within the model; the remainder are "glue" sites. Though DO specify the occupancy of their quasilattice with Al and Mn atoms, we use their scheme only to generate the quasilattice, while the chemical decoration is obtained through Monte Carlo simulations.

The DO model serves as the starting point for a three step refinement procedure to build a model appropriate for Ti-Mn. In the first step, atoms are added to vacant spaces. The vacant spaces include the centers of the Mackay icosahedra that are present in the model, as well as additional sites to be described below. The hole-filling procedure is based on the assumption that vacant spaces in the DO model are energetically unfavorable for Ti-Mn. This is supported by examination of Ti intermetallic compounds at similar compositions. Neither the Ti_2Ni structure, nor the Ti-Mn bcc solid solution has vacant sites; in contrast, such sites are found in the α-(Al-Mn-Si) structure. Since the vacancy-formation energy of Ti exceeds that of Al,[12] it would appear that the surface energy associated with Ti bounded vacant spaces would be greater than that for ones bounded by Al. Arguments in favor of the filling of vacant spaces in the DO model also follow from a comparison of the number densities in Al-Mn and Ti-Mn. The number density in Ti-Mn (Ref. 13) is 0.069 atoms/Å^3 whereas for Al-Mn it is 0.059 atoms/Å^3.[14] The number density in Al-Mn has been scaled by the Ti-Mn quasilattice constant to eliminate effects due to the larger atomic size of Ti relative to Al. Thus we expect that the density of sites is higher in Ti-Mn than in Al-Mn. Step 2 in our refinement procedure consists of the use of a Monte Carlo simulation to decorate the fixed atomic positions with the appropriate concentration of Ti and Mn atoms. In the third and final step, the structure is relaxed using a conjugate gradient method. In the remainder of this paper we will describe each of these steps in detail.

In all three steps we use a pair-potential description of the total energy,

$$E_{\rm tot}=\tfrac{1}{2}\sum\psi(r_i,r_j) \tag{1}$$

with the effective potential $\psi(r_i,r_j)$ describing Ti-Ti, Ti-Mn, and Mn-Mn bonds. (A more accurate treatment of the total energy of the quasicrystal is the subject of a companion paper.[6]) The effective potentials, shown in Fig. 1, are derived from tight-binding theory according to a procedure described elsewhere.[15,16] The Ti-Ti and Mn-Mn potentials have been fit to yield the lattice constants and bulk moduli of these metals when in the fcc structure, while the parameters in the Ti-Mn potential are taken as the geometric mean of the Ti-Ti and Mn-Mn parameters.

It is desirable to compare the diffraction intensities obtained from the model with those obtained in experiment. Unfortunately, as yet there have been no high resolution x-ray studies of the Ti-Mn system. However, we have compared the calculated diffraction of our optimized model with TEM data[5] on the Ti-Mn system and found that all of the qualitative features are reproduced.

Filling of vacant spaces. A useful parameter which characterizes the extent to which there remain unfilled spaces within the structure is the "bond spindle."[17] This parameter measures the number of common neighbors to the two atoms forming a given bond. We define neighbors as those atoms within 3.2 Å of each other.[18] For example, in the fcc structure (cf. Table I), the nearest-neighbor bond has bond spindle 4. For icosahedrally coordinated sites, near-neighbor bonds have bond spindle 5. As seen in Table I, the DO model has a significantly lower average bond spindle than the α-(Al-Mn-Si) and Ti_2Ni structures, implying that some of its polyhedra are structurally incomplete. The presence of a larger twofold bond spindle fraction in the DO model than in the α-(Al-Mn-Si) structure suggests that the Al-based quasicrystal might also benefit energetically from the filling of vacant spaces.

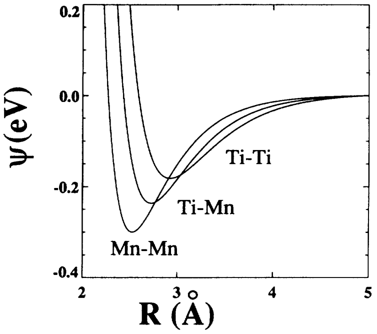

FIG. 1. Pair potentials describing Ti-Ti, Ti-Mn, and Mn-Mn bonds.

A number of threefold bond spindles can be eliminated by simply filling the centers of the Mackay icosahedra. We will label the resulting model DO2. As seen in Table I, the filing of the Mackay centers reduces the number of threefold bond spindles, while increasing the number of four- and fivefold bond spindles.

The treatment of the remaining twofold bond spindles is more difficult. In Fig. 2 we depict a twofold bond spindle. We label the atoms on the bond of interest *A* and *B*, while the neighbors of the bond are labeled 1 and 2. By constructing the vector product of the vector joining *A* and *B* with that of the vector joining 1 and 2, a direction is defined which points to the vacancy regions around the *AB* bond. Our procedure for adding an atom along this direction is as follows. An entire family of positions may be defined by

$$\mathbf{r}=\mathbf{r}_{AB}+\epsilon\mathbf{b}\ , \tag{2}$$

where $\mathbf{r}_{AB}$ defines the center of the *AB* bond, $\mathbf{b}$ is a unit vector pointing in the direction of the vector product, and ϵ is an amplitude which may be varied continuously. For each ϵ the energy of the added atom is calculated us-

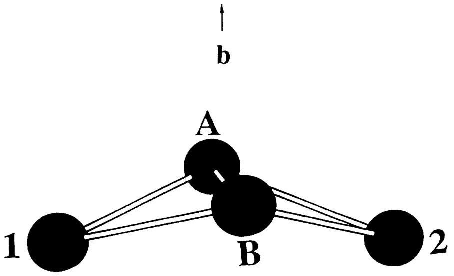

FIG. 2. Illustration of bond (*AB*) with a twofold bond spindle. Vector **b** points in direction along which atom may be added.

ing the Mn-Mn potential shown in Fig. 1. The Mn-Mn potential is used as it results in the smallest energy penalty for adding atoms in regions which result in short bonds. If the energy of addition is negative, an atom is added at that ϵ for which the energy is lowest. Those twofold bond spindles which would result in an increase of the energy if an atom were added are left untouched. By systematically carrying out this procedure on all of the twofold bond spindles in DO2, we generate an augmented DO model, which we will henceforth refer to as the ADO model. The bond spindle distribution for the ADO model is shown in Table I. The remaining twofold bond spindles correspond to sites which would not allow for the addition of new atoms without an increase in the total energy. The added sites are in the "glue" regions between the Mackay clusters. This hole-filling procedure results in the addition of 36 atoms to the region within 13.0 Å of the origin, 11 of which come from filling the centers of the Mackay icosahedra. We consider the region within 13.0 Å to avoid spurious effects due to the cluster surface.

Monte Carlo decoration. After the hole-filling procedure, the sites of the quasilattice are next assigned a chemical identity. We fix the lattice positions resulting from the previous step and perform a Monte Carlo simulation in the grand canonical ensemble, again using the pair potentials. The concentration of Ti and Mn atoms is controlled through the chemical potential difference $\Delta\mu = \mu_{\mathrm{Ti}} - \mu_{\mathrm{Mn}}$.

We start with a model all of whose sites are occupied by Ti atoms. The steps then consists of exchanging the chemical identity of the sites, with the probability of acceptance of the move given by

$$P(\text{move}) \propto \exp[-\beta(\Delta E_{\mathrm{tot}} - \mu_{\mathrm{Ti}}\Delta N_{\mathrm{Ti}} - \mu_{\mathrm{Mn}}\Delta N_{\mathrm{Mn}})] \quad (3)$$

if the change of the factor in the exponential is positive. All moves with negative energy changes are accepted. Only moves within 13.0 Å of the origin are allowed. By fixing the temperature and performing a series of runs for different values of $\Delta\mu$, a set of decorations with different concentrations are obtained. The decorations are found to be rather insensitive to a choice of Monte Carlo temperature, with the same model resulting for all temperatures less than 100 K. In Fig. 3 we show the concentration of Ti atoms within 13.0 Å of the origin of the ADO model as a function of $\Delta\mu$. The crucial point is the existence of plateau regions which signify especially stable decorations. The decorations obtained in these plateau regions exhibit a small tendency for Monte Carlo configuration changes to be accepted. For each model (DO, DO2, and ADO) we select the plateau having composition closest to that of the experimental Ti-Mn system. For the DO model, the composition is $\mathrm{Ti}_{60}\mathrm{Mn}_{40}$, for DO2 it is $\mathrm{Ti}_{59}\mathrm{Mn}_{41}$, and for ADO, $\mathrm{Ti}_{61}\mathrm{Mn}_{39}$. The ADO model displays a broad plateau at 61% Ti which compares favorably with the experimental concentration of $(63\pm2)\%$.[13].

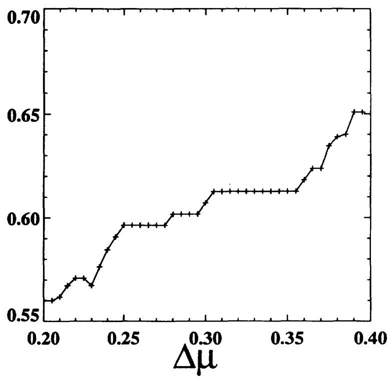

FIG. 3. Concentration of Ti atoms in ADO model as function of chemical potential difference, $\Delta\mu$.

Structural relaxation. The third and final step in our modeling procedure is to perform structural relaxations on the models in order to allow bond lengths to change. The relaxation is performed using a conjugate gradient method, with forces determined by the potentials shown in Fig. 1. As in the Monte Carlo procedure we only allow atoms within 13.0 Å of the origin to move. This corresponds to a relaxation at fixed volume.

To get a preliminary indication of the stability energy associated with filling the vacant spaces in the DO model, we have used the expression for the total energy given by Eq. (1) to compute the total energy for all atoms within 13.0 Å of the origin for all three models. These energies are compared for the fully relaxed models, all evaluated at the experimental quasilattice constant of 4.78 Å. Since the compositions of the models are slightly different, we evaluate $E(\mathrm{ADO}) - E(\mathrm{DO} + x\mathrm{Ti})$, where x is chosen to bring the composition of the DO model up to that of the ADO model. We find an energy difference of 0.04 eV/atom favoring ADO. These pair potential calculations suggest that filling holes is beneficial. The energies associated with the Monte Carlo procedure as well as the structural relaxation have also been computed. Our optimal Monte Carlo decoration has an energy 0.14 eV/atom below that of a completely disordered state.

TABLE I. Bond spindles for α-(Al-Mn-Si) structure, $\mathrm{Ti}_2\mathrm{Ni}$ structure, and three quasicrystal models described in text. We plot the distribution of bond spindles, averaged over all bonds in each structure.

Structure	Twofold	Threefold	Fourfold	Fivefold	Sixfold	Average
fcc	–	–	1.0	–	–	4.0
α-(Al-Mn-Si)	0.01	0.07	0.40	0.52	–	4.4
$\mathrm{Ti}_2\mathrm{Ni}$	–	–	0.15	0.85	–	4.8
DO	0.09	0.33	0.41	0.17	–	3.6
DO2	0.09	0.28	0.46	0.17	–	3.7
ADO	0.05	0.24	0.41	0.30	–	4.0

Similarly, the energy change associated with the structural relaxation is 0.09 eV/atom for the ADO model, comparable to the energy scale associated with the Monte Carlo decoration. For each of the steps in our procedure we have found a significant reduction in the total energy. These energy differences are analyzed via semiquantitative electronic structure calculations in a related paper.[6]

In this paper we have introduced a procedure which includes total-energy methods in quasicrystal modeling. We have shown that filling of vacant spaces, Monte Carlo decoration, and structural relaxations allow for refinements which can lower the energy of a given model by more than 0.25 eV/atom, sufficient to determine whether the model is viable or not. Though our methods have been demonstrated for the Ti-Mn system, we expect similar energy gains will be found when the same techniques are applied to other systems. These procedures have also provided a starting point for electronic structure calculations on realistic quasicrystal models.

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