

## Total Energies of Improved Quasicrystal Models

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(Received 1 November 1990; revised manuscript received 12 April 1991)

The first electronic total-energy calculations are performed on a 6D-3D projection model for the TiMn quasicrystal, as well as two refined models obtained by filling vacant spaces. The total energies correlate almost perfectly with the reduction of the vacant space, and suggest that future modeling efforts should concentrate on increasing the coordination number of Ti sites in the "glue" regions between the large icosahedral clusters which form the backbone of the structure.

PACS numbers: 61.50.Em, 61.50.Lt, 61.55.Hg

A major question raised by the study of quasicrystals is the role played by energetics in determining the free-energy balance between quasicrystals and competing crystalline phases. Though there have been a number of efforts to determine the entropy of quasicrystals [1], as yet there have been no total-energy calculations for realistic models of transition-metal quasicrystals. This Letter presents the first such calculations.

Accurate total-energy calculations necessitate an explicit treatment of the electronic structure. Because of the absence of translational periodicity in quasicrystals, conventional  $k$ -space electronic structure methods are inapplicable. For this reason, we use the real-space tight-binding recursion method [2] which does not require translational periodicity. Tight-binding treatments are especially useful in describing the bonding in transition metals (TM) [3] such as the Ti-TM class of quasicrystals we consider here.

In order to establish the important energetic factors in quasicrystalline modeling schemes, we examine a set of quasicrystal models and a few competing crystalline phases. The set of models are produced using 6D-3D projection methods developed by Duneau and Oguey [4] (DO) with various structural refinements [5]. The DO2 model is obtained from the DO model by filling the centers of all the Mackay icosahedra. The ADO model is obtained from the DO2 model by filling further vacant spaces within the "glue" regions. The decorations of these models with Ti and Mn atoms is accomplished through a Monte Carlo procedure using pair potentials. The details of our modeling procedure will be described elsewhere. The calculations are based on an analysis of all atoms in each model which are within 10 Å of the origin, which for the DO model is 268 atoms, for the DO2 model is 270 atoms, and for the ADO model is 274 atoms. The total cluster size, as described previously, is 17.5 Å in radius. We consider the inner 10 Å of these finite clusters in order to suppress surface effects.

For the purpose of comparison we have also performed calculations on alloy variants of the fcc structure, the bcc structure, and the Ti<sub>2</sub>Ni structure [6]. The bcc structure is relevant here since the equilibrium structure of Ti-rich

(e.g., less than 30% Mn) TiMn is a bcc solid solution. The Ti<sub>2</sub>Ni structure is considered since it is the equilibrium structure for Ti<sub>2</sub>Ni, Ti<sub>2</sub>Fe, and Ti<sub>2</sub>Co. The Ti<sub>2</sub>Ni structure has 96 atoms per unit cell of the fcc Bravais lattice, with three inequivalent site types. Two of these sites (one Ti and one Mn) are icosahedrally coordinated, while the remaining site has fourteen neighbors. Our calculations on the fcc structure are for the ordered CuAu and Cu<sub>3</sub>Au structures, while for the bcc structure we consider the ordered Fe<sub>3</sub>Al and CsCl structures.

We use a  $d$ -band tight-binding model Hamiltonian of the form

$$H = \sum \varepsilon_i |i, \alpha\rangle \langle i, \alpha| + \sum h_{ij}^{\alpha\beta} |i, \alpha\rangle \langle j, \beta|, \quad (1)$$

where  $i$  is a site index,  $\alpha$  labels the  $d$ -orbital symmetry,  $\varepsilon_i$  is a site diagonal energy term, and  $h_{ij}^{\alpha\beta}$  is a Slater-Koster coupling matrix element [7]. Hamiltonians of this form are standard in the analysis of transition-metal structural energies [3], and are thought to represent the dominant bonding in these systems, which comes from the  $d$  band. The tight-binding parameters are treated in the common-band approximation, which is based on the fact that the transition metals in the 3D row have nearly equal  $d$ -band widths at their respective equilibrium lattice constants [8]. The decay of the couplings has the form  $e^{-q(r-r_0)}$  with  $qr_0=3$ , and  $r_0$  adjusted suitably for the element of interest. (We have discussed elsewhere the robustness of our tight-binding model to changes in parameters [9].) The neglect of magnetic effects on the Mn atoms is justified as a result of *ab initio* calculations on Ti-rich TiMn compounds which reveal negligible Mn moments [10]. The total energy is given in terms of the density of states (DOS)  $\rho(E)$  by

$$E_{\text{tot}} = \frac{1}{2} \sum \phi(r_{ij}) + 2 \int_{-\infty}^{\varepsilon_F} dE \rho(E) E, \quad (2)$$

where  $\phi(r)$  is a repulsive pair potential. This is fitted by the equilibrium lattice constants and bulk moduli of elemental Ti and Mn in the fcc structure; the TiMn repulsive parameters are obtained as the geometric mean of the elemental parameters. The factor of 2 accounts for spin degeneracy. Our parameters are fitted by augment-

ed spherical wave [11] (ASW) band-structure results [10] for fcc Ti, fcc Mn, and  $\text{Ti}_3\text{Mn}$  in the  $\text{Cu}_3\text{Au}$  structure. The fit for Ti and Mn results from insisting upon agreement between the ASW bands and the tight-binding bands at a few high-symmetry points in the Brillouin zone. As calibration, our calculations obtain a bcc vs fcc energy difference of 0.25 eV/atom (favoring bcc) for the  $\text{Ti}_3\text{Mn}$  compound. This compares reasonably with the ASW value of 0.20 eV/atom [10]. Table I shows the interaction parameters used in our tight-binding analysis. The single site term which appears in Eq. (1) measures the splitting between the Ti and Mn  $d$  states,  $\Delta\varepsilon = \varepsilon_{\text{Ti}} - \varepsilon_{\text{Mn}} = -1.0$  eV, which fits *ab initio* results well [10]. The recursion calculations are performed to four levels, which corresponds to an exact treatment of the lowest nine moments of the DOS [2]. The validity of low-order recursion calculations in tight-binding analysis has been described elsewhere [12]. The outcome of the recursion calculation is a set of coefficients  $\{a_n, b_n\}$  which allows us to compute the Green function in the form of a continued fraction [2]. Because we terminate the recursion after a finite number of recursions, the continued fraction requires a termination procedure, for which we have chosen the standard "square-root" termination [2]. Given the DOS, the total energy then follows from Eq. (2).

The structural energies of the quasicrystal models relative to crystalline phases are shown in Fig. 1. Here, the energies are measured relative to concentration-weighted averages of isolated atoms. Although the energy of the ADO model relative to the atomic base line is higher than that for the DO and DO2 models, the only meaningful comparison is between different structures at fixed composition. Thus each structure must only be judged relative to the bcc and fcc structures at the same composition. The ADO model has the lowest energy of the three quasicrystal models. It is only 0.09 eV/atom higher in energy than the bcc structure, which has the lowest energy of all of the structures that we have treated, while the DO and DO2 energies are both more than 0.14 eV/atom higher in energy than the bcc structure. The energy difference between the ADO model and the bcc structure is remarkably low. Our calculations for other proposed models find energies 0.5 eV/atom or more above close-packed structures [9]. Similar conclusions have been reached in other work. For example, the best published structure that has been obtained using only one atom per 6D unit cell has a Madelung constant of 1.742 [13]. For Al this would

TABLE I. Tight-binding interaction parameters. The Slater-Koster matrix elements are labeled by  $\sigma$ ,  $\pi$ , and  $\delta$ .

Coupling	$\sigma$ (eV)	$\pi$ (eV)	$\delta$ (eV)	$q$ ( $\text{\AA}^{-1}$ )	$r_0$ ( $\text{\AA}$ )
Ti-Ti	-0.842	0.350	-0.030	1.027	2.922
Mn-Mn	-0.842	0.350	-0.030	1.186	2.529
Ti-Mn	-0.842	0.350	-0.030	1.101	2.726

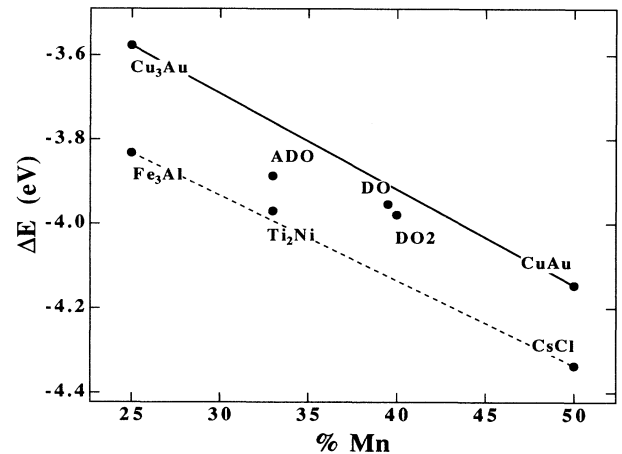


FIG. 1. Energies of various structures relative to concentration-weighted averages of the atomic constituents. Solid line is weighted average of fcc-based structures. Dashed line is weighted average of bcc-based structures.

place the electrostatic energy roughly 2 eV above that of a close-packed crystal structure. Only in very special cases can the band-structure energy in alloy systems outweigh the electrostatic energy penalty [14].

Despite its low energy, the ADO model is probably still too high in energy to be metastable. Using classical nucleation theory [15], we can estimate the nucleation rate of bcc nuclei from the quasicrystalline phase. We assume that the Gibbs free-energy difference between the bcc phase and the quasicrystal phase is 0.09 eV/atom, neglecting the entropy differences because they probably make a smaller contribution to the free energies. We further assume [16] that the interfacial energy between the two phases is less than  $0.2 \text{ J/m}^2$  (this is a typical interfacial energy for transition metals [15]), then the ADO model will be unstable to the formation of the bcc phase.

However, the total-energy trend between the DO model, the DO2 model, and the ADO model contains some important physics. The energy reductions shown in Fig. 1 are almost precisely proportional to the amount of vacant space in the structure. Thus reducing the amount of vacant space seems to be a major factor in lowering the energy of the quasicrystal. This is different from the AlMn system, in which vacant spaces are present even in equilibrium crystal structures. Our results suggest that in order to obtain more energetically favorable models for the TiMn quasicrystal, it will be necessary to find ways to eliminate more of the vacant spaces.

To obtain a local picture of these structural energies, we have carried out total-energy calculations for the ADO model and related crystalline phases on a site-by-site basis. The site-projected energy on site  $i$  is defined as

$$E_i = \frac{1}{2} \sum_j \phi(r_{ij}) + 2 \int_{-\infty}^{\varepsilon_F} dE E \rho_i(E), \quad (3)$$

where the site-projected DOS  $\rho_i(E)$  is given by

$$\rho_i(E) = \sum_n |\langle i|n\rangle|^2 \delta(E - E_n). \quad (4)$$

The total energy is the sum of the site-projected energies. These calculations provide insight into the factors favoring the “good” sites and penalizing the “bad” ones. Such analysis has been found useful in previous studies of the energetic factors favoring polytetrahedrally packed transition-metal phases [9,17]. We have considered all of the 184 inequivalent Ti sites and 90 inequivalent Mn sites within 10 Å of the origin. As above, our energies are measured relative to a concentration-weighted average of the Fe<sub>3</sub>Al and CsCl bcc structures. Analysis of the Mn sites reveals that over 80% of them have a lower site-projected energy than the site-projected energy of the Mn sites in our base-line bcc structure, with all of the energy differences bounded by  $-0.7 \text{ eV/atom} < E(\text{ADO-bcc}) < 0.4 \text{ eV/atom}$ . On the other hand, some of the Ti sites are as much as 1.5 eV/atom higher in energy than the base line. It is primarily these unfavorable Ti sites which make for the instability of the ADO model. We have found that *all* of these sites are located in the glue regions between the large icosahedral clusters. Since none of the bad sites are associated with the large icosahedral clusters, we argue that these are an energetically favorable building block for TiMn. Future modeling efforts should concentrate on the glue regions which connect them.

The origins of the high energy of some of the Ti sites may be understood through an analysis of the site-projected second moment

$$\mu_2^i = \sum_a \langle i, a | H^2 | i, a \rangle \quad (5)$$

of the electronic DOS. This is a measure of the width of the DOS, and may be interpreted as an effective coordination number [18]. In Fig. 2, we plot the site-projected energies of all 184 Ti sites (measured relative to the bcc base line) as a function of the value of  $\mu_2$  for each site. Clearly the unfavorable sites are those with small values of  $\mu_2$ . The reduction in energy which would go with increasing the second moments (e.g., increasing the coordination of these sites) of these worst sites could substantially lower the energy of the model. Experimental results [19] indicate that the formation of the TiMn quasicrystal requires the presence of small concentrations (2%–5%) of Si. An alternative approach [20] to dealing with the undercoordinated Ti sites is to replace them with Si atoms. As suggested by the open equilibrium crystal structure of Si, the reduced coordination of these sites might result in a considerably lower energy penalty than when these sites are occupied by Ti, thus leading to enhanced stability for the quasicrystal. If this scenario were correct, the role of Si in TiMn would be quite different from that predicted for AlMn. Earlier work has suggested [21] that the Si in AlMn is associated with the

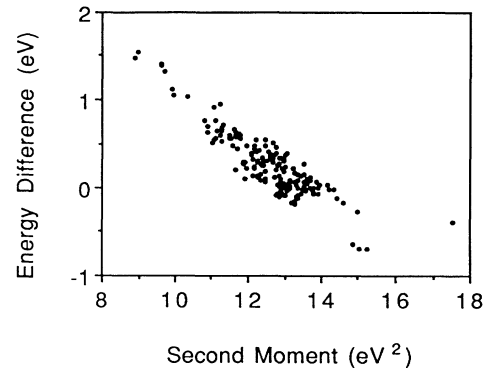


FIG. 2. Energy difference between Ti sites in the ADO model and base line given by bcc energy. The energy difference is plotted vs  $\mu_2$  for the Ti sites in the ADO model.

Mackay icosahedra, while our work suggests that in TiMn it is linked to the glue regions. Unfortunately, we cannot reliably treat TiMnSi within our tight-binding model.

In this paper we have demonstrated the feasibility of using electronic total-energy calculations to discriminate between competing atomistic models for the icosahedral phases. In addition to discriminating between competing models, these calculations also pose a challenge to the future modeling of the TiMn system. A way must be found to improve the energetics of the Ti sites within the glue regions, by either increasing their coordination number or replacing them by Si. We have also found that large icosahedral clusters (such as the Mackay icosahedron) are an energetically favorable building block for TiMn when embedded in a metallic environment. With a more effective means of joining these clusters together the energy of TiMn models could be rendered low enough for the system to be metastable.

We thank D. Chrzan, V. Elser, C. Henley, J. Holzer, D. Johnson, K. Kelton, and F. Pinski for helpful comments. This work was supported by the Department of Energy, Office of Basic Energy Sciences, and Department of Energy Grant No. DE-FG02-84ER45130.

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