Order-disorder transition in a Cd-Ca quasicrystal approximant

M. Widom and M. Mihalkovic*
Department of Physics
Carnegie Mellon University
Pittsburgh, PA 15213
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Recent experiments discovered an order-disorder transition occuring at very low temperatures in large unit cell approximants of the stable Cd-based binary alloy quasicrystals. The transition is related to correlations among orientational degrees of freedom whose separations are 12 Å. The orientational degrees of freedom represent a type of phason disorder within the unit cells of these large approximants. We analyze the interactions between the degrees of freedom using *ab-initio* calculations and derive an equivalent antiferromagnetic Ising model which shows a similar phase transition.

I. INTRODUCTION

Thermodynamically stable binary icosahedral quasicrystals occur in the alloy systems $Cd_{5.7}Yb$ and $Cd_{5.7}Ca$ [1–3]. In each case the phase diagram of the binary alloy contains a 1/1 cubic approximant of structure type Cd_6Yb at a close-by composition [4–6]. This Cd_6Yb structure can be represented in a conventional simple cubic unit cell with a lattice parameter of $a = 15.7$ Å. However, the Pearson symbol for Cd_6Yb is cI176 indicating that it is cubic, body-centered, with 176 atomic positions per simple cubic unit cell. Since 176 is not a multiple of the basic 7-atom stoichiometric unit (6 Cd and 1 Ca, Y or Yb), there must be partial occupancy. In fact, the unit cell contains 144 Cd atoms, 24 Ca or Yb atoms and 8 vacancies.

The basic structural unit is shown in Fig. 1. Vacancies concentrate in the innermost cluster, marked (a), in which 4 of a possible 8 sites are occupied. The 8 sites belong to a cube, and the 4 occupied sites belong to one out of the two tetrahedral subsets of the cube. Each simple cubic cell of Cd_6Yb contains two such basic icosahedral clusters, one centered at the vertex and the other centered at the body center. These structures are closely related to Cd_6Y.cI184, differing only in the number of partially occupied Cd sites, and the nominal orientations of the cluster center tetrahedra.

In order for the overall structure to be truly body-centered, it is necessary that the tetrahedron at each center be identically aligned or else that all body centers be randomly oriented. In each case a body-center translation leaves the structure invariant. However, recent experiments indicate order-disorder transitions in which a supercell ordering develops at low temperatures, breaking the body-centered cubic symmetry [8, 9].
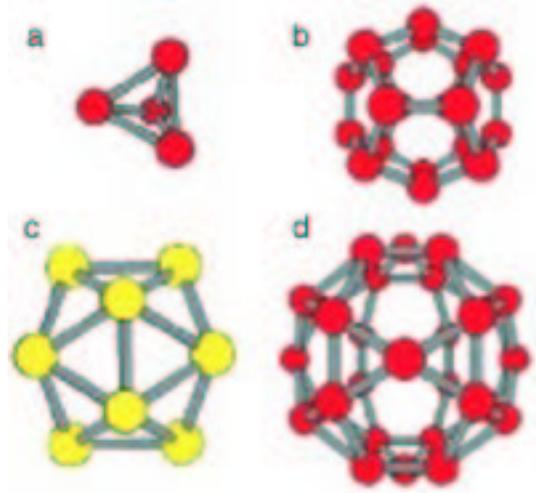
FIG. 1: The basic icosahedral cluster of the Cd_6Y structure type consists of three concentric shells of icosahedral symmetry (b-d). The internal cluster (a) is a tetrahedron. (Figure taken from Physics Today [7])

II. TOTAL ENERGY CALCULATIONS

We carry out total energy calculations to determine if the body-centered cell is energetically favorable. Because of the low transition temperature the energy difference will likely be small. Additionally, any coupling between tetrahedron orientations at cell vertex and body center must be at a distances of 10-14 Å. Interatomic pair potentials might not reliably address this subtle problem (and they are not available presently in any case).

Instead we carry out *ab-initio* calculations using the pseudopotential-based program VASP [10, 11]. This approach uses ultrasoft pseudopotentials [12, 13] or PAW potentials [14] to represent the effective interaction of valence electrons with ionic cores, and solves the many-body quantum mechanical band structure of these electrons using electronic density functional theory. This

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*Also at Slovakian address

2 Ca$_5$Cd$_3$.hP68 (-297;-17)	4 Ca$_3$Zn.oC16 (-201;1)	11 CaCu$_5$.hP6 (-184;63)
3 Ca$_3$Cd$_2$.tP20 (-323;-5)	5 Ca$_5$Zn$_3$.tI32 (-301;2)	13 CaZn$_2$.hP32 (-271;61)
7 CaCd$_2$.oI12 (-373;-12)	6 CaCd$_5$.hP12 (-362;12)	14 CaZn.oC8 (-347;45)
8 CaCd$_6$.cI184 (-224;-26)	12 Ca.hP2 (3;3)	17 Sc$_3$Zn$_{17}$.cI160 (-108;123)
9 CaCd.cP2 (-392;-45)	16 Cu.cF4 (4;4)	
10 Ca.cF4 (0;0)		
15 Cd.hP2 (-0;0)		
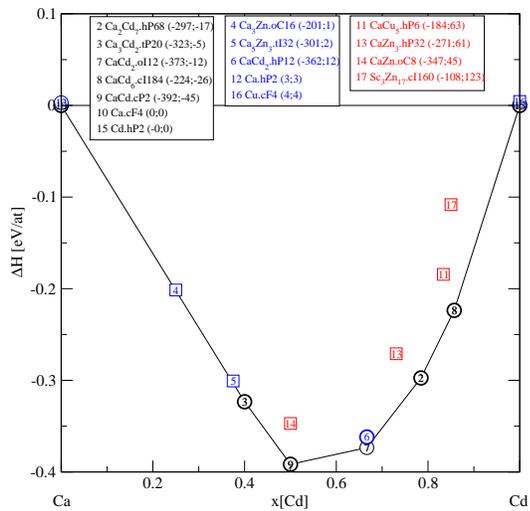
FIG. 2: This figure illustrates the enthalpy of formation of Ca-Cd compounds. Our notation is heavy circles indicate known low temperature phases, light circles indicate known high temperature phases, squares indicate either compound or structure unknown in Ca-Cd system. Line sigments connect vertices of convex hull.

approach yields reasonably accurate total energies. We choose to model Cd-Ca rather than Cd-Yb because the alkali earth element Ca is easier to treat from first principles than the rare earth element Yb.

To assess the accuracy, we use VASP to reproduce the sequence of low-temperature stable phases in the established Ca-Cd binary phase diagram [5]. To do this we calculate the cohesive energy for each known structure, and several hypothetical ones. Each structure is fully relaxed in both unit cell parameters and atomic coordinates. All energies are converged to an accuracy of 1 meV/atom or better by increasing the k-point mesh density. We then subtract each cohesive energy from the tie-line joining the pure elements in their ground states.

The result of this calculation is a plot of the enthalpy of formation (at T=0K) for all known and many hypothetical Ca-Cd structures. Agreement between our calculation and the established phase diagram requires that all known low temperature structures lie on the convex hull of enthalpy versus composition. Additionally, all hypothetical structures must lie above the convex hull, as must all known high temperature, high pressure and metastable phases.

This is shown in Fig. 2. We label each structure with its name followed by its Pearson symbol. Agreement is excellent, with most low temperature Ca-Cd compounds lying on the convex hull, high temperature structures slightly above and hypothetical structures at higher energies yet. There is one seeming difficulty with CaCd$_2$ which we now address.

The low and high temperature CaCd2 phases are reversed in energy relative to the experimental report that oI12 is stable at high temperatures and hP12 at low. However, the transition between the hP12 and oI12 variants has not been well established. Most likely, according to our findings, the presumed low temperature hP12 phase is actually a metastable phase, and the nominal high temperature phase is actually stable all the way to low temperatures.

The established phase diagram also lists the phase Ca$_3$Cd$_{17}$, which is claimed to exist from T=0K up to melting, at a composition extremely close to CaCd$_6$. The structure of this phase is unknown. Possibly this phase is actually the quasicrystal phase, whose energy we do not calculate because we do not know its structure. Note that if the phase truly is the icosahedral quasicrystal, then either the quasicrystal or the cubic CaCd$_6$.cI176 would almost surely be a high temperature phase. This is because thermodynamic rules governing alloy phase diagrams dictate that the probability is low for two distinct phases to coexist over an extended temperature range.

Another candidate for the Ca$_3$Cd$_{17}$ phase (based on atomic size ratio and chemical similarity) is Sc$_3$Zn$_{17}$.cI160. We find the energy of this structure is substantially above the convex hull and thus unfavorable. Actually, the Sc$_3$Zn$_{17}$.cI160 structure is identical to CaCd$_6$.cI176 except that the innermost tetrahedral shell (shell (a) in Fig. 1) is missing. We thus confirm that occupancy of the inner shell is energetically favorable.

III. ORIENTATIONAL CORRELATIONS

The other apparent difficulty is the "hypothetical" structure marked Cd$_6$Ca.cP176 appearing slightly below Cd$_6$Ca.cI176 in energy. Let's describe these two structures. They both contain 168 atoms in a simple cubic unit cell, and they are identical except for the orientations of the tetrahedron at cluster centers. Note that, since the tetrahedron takes two orientations, we can assign an Ising-like spin variable $\pm$ to each one. Assign a tetrahedron the $+$ sign if one of its vertices falls along the direction $(1,1,1)$, and assign it a $-$ sign if instead one of its vertices falls along the direction $(-1,-1,-1)$. In both structures the tetrahedron at the unit cell vertex takes the $+$ orientation. In the body-centered cI184 structure the cell center tetrahedron is also in the $+$ orientation, while in the simple cubic cP176 structure this tetrahedron assumes the $-$ orientation.

To guage the validity of this result it is important to check convergence in the density of the k-point mesh, the cutoff energy and the sensitivity to choice of pseudopotential and the density functional. Table I presents our
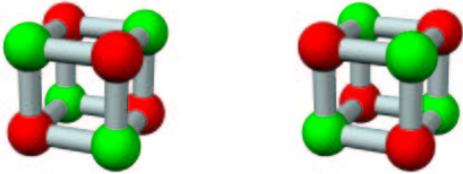
FIG. 3: This figure illustrates the Ising-like configurational degree of freedom. Red=occupied by Cd, Green=vacant. (Left) "+" configuration, (Right) "-" configuration.

TABLE I: Energy convergence studies for CaCd6.cI176 and CaCd6.cP176, and their difference $\Delta = E_{cI} - E_{cP}$. All units are eV per simple cubic cell.

Setting	E_{cI}	E_{cP}	Δ
$1 \times 1 \times 1$	-309.161	-309.260	0.099
$2 \times 2 \times 2$	-309.814	-309.975	0.161
$3 \times 3 \times 3$	-309.664	-309.754	0.090
$4 \times 4 \times 4$	-309.653	-309.780	0.127
low	-278.848	-278.956	0.108
medium	-309.161	-309.260	0.099
high	-309.662	-309.761	0.099
unrelaxed	-309.161	-309.260	0.099
partial	-311.902	-311.995	0.093
full	-312.243	-312.317	0.074

study. First we vary the k-point mesh, from $1 \times 1 \times 1$ (the Γ point) up to $4 \times 4 \times 4$ (all Monkhorst-Pack meshes). The table presents the convergence of each structure energy separately as well as the energy difference. All other computational parameters were held fixed during these calculations: medium precision (specifies cutoff energy 168 eV); ultrasoft pseudopotential; Ceperly-Alder LDA; no atomic relaxation. In the next series we hold constant the k-point density (we use Γ for speed) and test the convergence in precision going from low (cutoff 126 eV) to medium (cutoff 168 eV) to high (cutoff 210 eV). Next, continuing with medium precision and the Γ point, we compare unrelaxed energies with partial relaxation (only relaxing clusters (a) and (b) as defined in Fig. 1) and full relaxation in which all atoms can move. The maximum displacement is 0.23 Å for partial relaxation and 0.30 Å for full relaxation, always concentrated in shell (b). Specifically, those Cd atoms in shell (b) that adjoin a vacancy see the largest relaxations.

Given the Ising-like Z_2 symmetry of the order parameter (one of two orientations) it is appropriate to model the energy using an Ising-model Hamiltonian. Including sufficiently far-neighbor interactions we can surely capture the energetics accurately. However, we have only a single energy difference to work with here, so this is sufficient to extract only one coupling. Assume this is the nearest-meighbor coupling, along the cube body diagonal, and call it J_1.

TABLE II: Energies of Ising decorations in double-length structures. Units are eV per doubled cell.

Config	E_0	dE	H
+ + + +	-617.958	0	$C + 16J_1 + 12J_2$
+ + + -	-618.031	-0.072	$C + 8J_2$
+ + - -	-617.986	-0.028	$C + 4J_2$
+ - + -	-618.178	-0.219	$C + -16J_1 + 12J_2$

Each BCC lattice site has 8 nearest neighbors, each of which reverses sign when going from cI to cP. There are two lattice sites per simple cubic cell, but we must avoid over counting the bonds, since each bond is shared by two lattice sites. Hence we conclude that $\Delta = 16J_1$, or $J_1 \approx +0.004$ eV (using the fully relaxed value). Because the value of J_1 is positive the interaction is antiferromagnetic.

To determine the transition temperature for this system we wrote a simple Monte Carlo program to simulate the BCC Ising antiferromagnet. Actually, by simply reversing the sign convention for spins at body-center sites, the BCC antiferromagnet can be seen to be equivalent to the BCC ferromagnet. According to our simulations, the transition temperature should be around T=350 K.

Because this temperature is well above the reported transition temperature of T=100K, we investigated the role of further neighbor interactions. If further-neighbor couplings have appropriate signs the magnetism can become frustrated, lowering the transition temperature and leading to spatial modulation of the low temperature structure.

The next nearest neighbor lies along the cube edge, and we will call this coupling J_2. In order to extract values of J_2 we need to study a larger cell, so we doubled the cell along the x-axis, and considered the configurations denoted $\sigma_1^v \sigma_1^c \sigma_2^v \sigma_2^c$ in which the cube vertex of the first cell has spin σ_1^v, etc. Owing to the large number of atoms present we report here only the results of Γ point calculations.

Fitting these energies to a two-coupling Ising model yields values of $J_1 = +0.0068$ and $J_2 = -0.0102$ eV. Because J_2 is negative, the next-nearest interaction proves ferromagnetic, which will increase the transition temperature and also will not lead to superlattice ordering. In other words, the Ising model presented so far is rather inconsistent with the experimental findings.

IV. DISCUSSION

Given that our results disagree with experiment in both superlattice ordering and transition temperature it is clear that additional study is needed. We do not believe the basic methodology is flawed. Rather the most likely explanation is deficiency of the structural model being used. We restricted our attention to tetrahedron orientations belonging to subsets of a basic cube, in order to have a simple Ising-model description. While the cubic sets of possible tetrahedron oreintations seem ap-

propriate given the overall cubic symmetry of the cI176 structure, we must recognize that the second (b) shell is just a slightly distorted dodecahedron, so there are many more plausible tetrahedron orientations than the two we employ.

A recent study of the $M\mathrm{Cd}_6$ structure family by Gomez and Lidin [6] finds the electron density distribution of the central tetrahedra in CaCd_6 actually favor cube *edges* rather than vertices. They introduce additional partially occupied sites, proposing the new Pearson type CaCd_6.cI232. We have carried out VASP calculations for these new structures and confirm they are energetically advantageous over the original cI176/cP176 structures. If an order-disorder transition exists in this new struc-

ture, it will be at a lower temperature than found in our initial study because: (1) the energy differences among orientations are generally lower; (2) the order parameter has a higher symmetry than the Ising spins so there is a higher orientational entropy.

Acknowledgments

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