STRUCTURE AND EXCITATIONS OF ORTHORHOMBIC Al_3Co

ERIC COCKAYNE
Department of Applied Physics, Yale University, P.O. Box 208284, New Haven, CT 06520-8284 USA

MIKE WIDOM
Department of Physics, Carnegie-Mellon University, Pittsburgh, PA 15217, USA

We study the energetics of quasicrystals using a lattice gas simulation to sample atomic configurations close to the quasicrystal and its approximants. The total potential energy for each configuration is calculated by summing electronic structure based pair potentials. We apply this method to study $Al_{73}Co_{24}$ in a 14.4 Å by 12.3 Å by 8.1 Å orthorhombic cell. The structures obtained are compared with experiment. We also determine characteristic excitation energies and the associated atomic motions.

1 Introduction

The structure and excitations of alloys are governed by the interaction energies of the constituent atoms. The preferred structure at low temperatures is the structure of minimum interaction energy, and low energy structures close-by represent important excitations. A complete structural description of a quasicrystalline alloy has not yet been achieved. Furthermore, with growing interest in mechanical properties such as friction and plasticity, there is increasing need for investigation of primitive structural excitations. Total energy calculations joined with simulation of thermal fluctuations produce important information on both structure and excitations.

Energetic considerations prove useful in ordinary crystal structure refinement. In the case of quasicrystals, such considerations are particularly useful because the areas of uncertainty in "pure" diffraction structure refinements are exactly those for which energetics can make clear distinctions. For example, structure refinements on aluminum-transition metal (TM) quasicrystals typically lead to the location of atoms whose identity as Al or a TM is uncertain. While the difference between an Al and a TM atom is small as far as the effect on the total diffraction pattern, the local energy differences can be huge and can clearly decide between the two choices. Similarly, energetics suggests that partially occupied atomic positions separated by less than one atomic diameter correspond, in reality, to a single atom hopping between the sites. After a brief description of the pair potential approximation for total energies, this article describes practical aspects of the use of pair potentials in quasicrystal structure determination and results obtained on structures and structural excitations in decagonal phases.

2 Energetics for quasicrystal studies

The total energy of a configuration of atoms at temperature T, neglecting contributions due to electronic entropy, magnetic interactions, etc., is the sum of the kinetic energies of the individual atoms as a function of temperature and the temperature-independent potential energy of the configuration. Furthermore, the total configurational energy can always be expanded in a series of pair interactions, three body interactions, etc. In principle, a knowledge of the total energy as a function of microscopic configuration allows all of the thermodynamic properties to be derived.

Since an *ab initio* solution of total energies is impractical for large systems, and even cluster expansions run into practical difficulties beyond the first few terms, some form of approximation is necessary. One such approximation truncates the cluster expansion to a sum over pairs of atoms of central interatomic potentials $U_{\sigma_i\sigma_j}$

$$E = \frac{1}{2}\sum_{ij} U_{\sigma_i\sigma_j}(|\mathbf{r}_i - \mathbf{r}_j|) \tag{1}$$

where i and j label atoms, and σ denotes the chemical species. Such pair potentials have been devised for the Al-rich Al-transition metal alloys,[1] such as AlCo.[2] These pair potentials have been applied to simulate decagonal and icosahedral phases.[3,4,5,6]

In many systems, however, pair potentials are a poor approximation. Thus it is necessary to test such potentials in order to see their degree of accuracy. The Al-Co pair potentials of Phillips *et al.* were tested on a variety of AlCo phases up to 29 at. % Co.[2] The typical error, which can be estimated by comparing the predicted stable phases with the experimental ones[2], is about 5 meV per atom. While by *ab initio* standards, this might be considered only fair agreement, the speed of pair potentials compared to *ab initio* calculations (or even to models containing three body terms for that matter) is enormous, making this approach well suited to computer simulations that may explore millions of configurations.

3 Methods

In what follows we only allow atoms to occupy positions that belong to a list of discrete sites. One would like to study structures with continuous degrees of freedom, but given the present uncertainties in both structure determination and the accuracy of the pair potentials themselves, there are several advantages to using a discrete set of sites: (1) The pair potentials are perhaps not accurate enough to give reliable information about relaxation. An atom on one of the discrete sites may be closer to the true equilibrium position than an atom at equilibrium under pair potentials. (2) The effects of phonons are frozen out. Our typical simulation has a minimum site separation of 0.5 Å apart. At 1000K, the expected thermal phonon displacements are about 0.3 Å in pure Al. (3) The phason description is simplified. The discrete atomic positions chosen correspond to flat atomic surfaces as described in section 4. There is a simple correspondence between the type of atomic jump or "phason" in hyperspace and the distances that the atom moves in real space. (4) The majority of models at present use flat atomic surfaces. Our results are easy to compare with such models.

Monoclinic[7] and orthorhombic[8] Al_3Co phases are approximants to a metastable decagonal phase of approximately 8 Å periodicity along the decagonal axis that occurs near composition 26 at. % Co.[9] and likely contain similar structural elements. By the procedure described in Ref. 10, we systematically generate a set of sites that should allow any likely structure of the quasicrystal or its approximants as well as any likely phason excitations. These sites are shown in Figure 1 for the orthorhombic Al_3Co cell. The positions of most ideal sites are given by

$$(\sum_{j=1}^{4} n_j (a \cos(2\pi j/5), a \sin(2\pi j/5), cz), \qquad (2)$$

with integer coordinates n_j. Based on the monoclinic Al_3Co approximant, we estimate $a = 1.529$ Å and $c = 8.120$ Å. A small portion of the ideal sites (e.g.

those near Grin Al positions 8 in fig. 1a and 18 in fig. 1b) have half-integer coordinates.

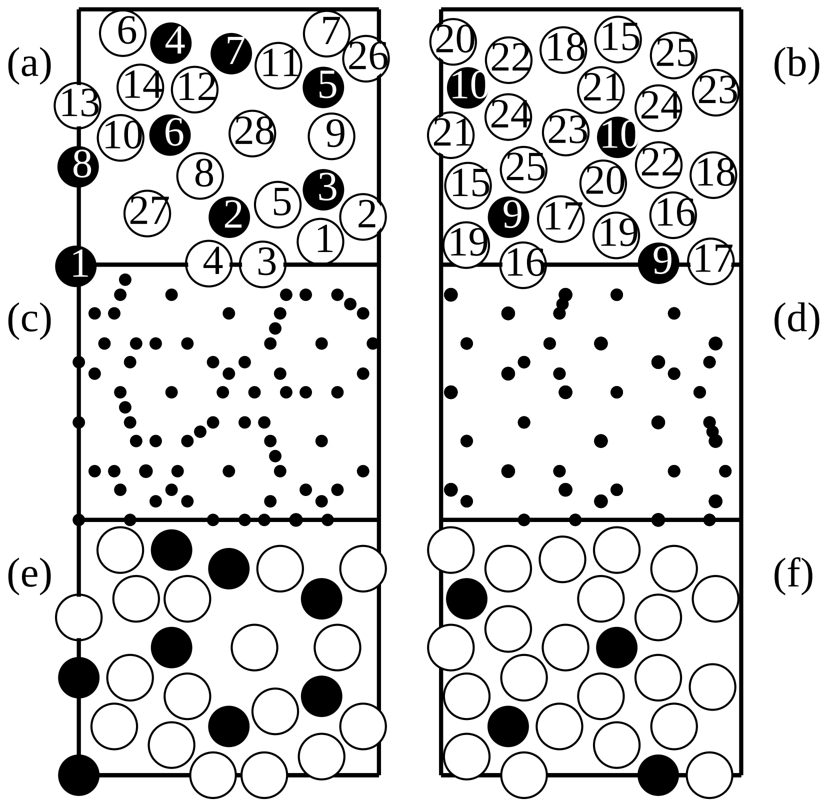

Fig. 1. Flat layers (left) and puckered layers (right) for orthorhombic Al_3Co. Top (a,b) Experimental structure with atoms labeled according to notation of Grin *et al.*. Middle (c,d) ideal sites generated according to eq. (2). Bottom (e,f) typical simulated structure at room temperature.

Having generated a list of 304 ideal sites, we then occupy subsets of sites with 73 Al and 24 Co atoms. This composition is chosen because it is close to the experimental value for the monoclinic phase and we believe it is close to the correct composition for both the orthorhombic phase and the metastable decagonal quasicrystal.

The Monte Carlo simulation is effectively a lattice gas model, moving the atoms among available sites. Details have been given elsewhere[4,5,10]. The total energy of a configuration is given by eq. (1). The individual attempted moves involve either single atoms moving to unoccupied sites or an exchange of an Al-Co pair. Detailed balance is enforced in order to obtain correct thermodynamic properties for the model.

4 Results

As a first check, we test whether the pair potentials reproduce the experimental structure. We ran the Monte Carlo simulation on the approximant shown in Figure 1 at the composition Al_{73} Co_{24} at room temperature 300K. The results for the structure obtained upon annealing are shown in Figure 1 (e,f). The x and y coordinates of the Co positions agree closely with experiment. There is a common organizing principle: the packing of pentagonal bipyramidal (PB) clusters. Each cluster has an equator of 5 Co atoms in a flat layer and a Co atom above and below the cluster centers in the puckered layer. The flat layer 4 Å away, which we call the junction layer, also contains a Co pentagon. Experimentally, the equator surrounds one central Al and the junction layer Co pentagon contains 5 interior Al, some of which we suspect may be only partially occupied. In our simulation, the junction layer Co pentagons contain on average fewer than 5 Al due to the presence of vacancies.

There are 4 PB's per unit cell in this approximant whose projected centers, when connected by edges of length 6.5 Å , form a tiling of hexagons. Each PB, however, can have its center in either flat layer, creating a variety of "PB centering patterns". We find that the total energy is similar for each PB centering pattern and that the most stable pattern appears to depend on vacancy concentration. The pattern shown in Figure 1 (e,f), with 3 of the 4 PB centers in one layer, is typical for our simulations of $Al_{73}Co_{24}$, but differs from the experimentally observed PB centering pattern.

By calculating the energies of all Monte Carlo attempts, we can find typical activation energies. We concentrate on the movements of atoms less than 2.5 Å , since these are the ones that are most likely to be physical. Figure 2 shows plots of the "energy spectra" of these short atomic jumps. Incredibly, the spectral density is nonzero in the vicinity of zero energy, and even has a tail down to negative energies. This means that, even at room temperature, very low energy structural defects are excited. Note that in our simulation technique barriers between nearly degenerate configurations may be surmounted in a single discrete atomic step.

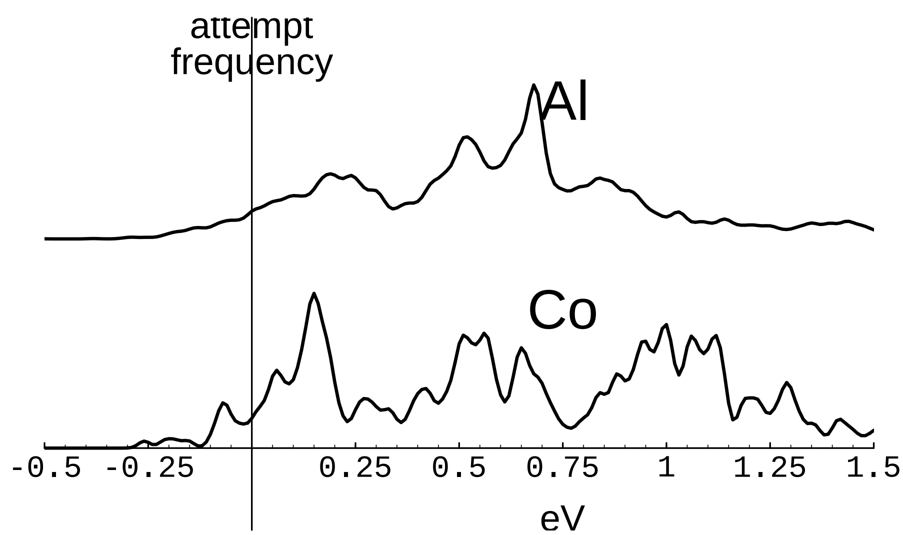

Fig. 2. "Energy spectra" for (top) short Al hops, (bottom) short Co hops. The data has been smoothed with a Gaussian broadening of 0.02 eV for each data point. Different peaks are dominated by different atomic motions, indicating typical energies of different kinds of excitations

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It is interesting that the energy spectra contain peaks. While the relative heights of the different peaks has little meaning, being an artifact of the simulation method, the existence of the peaks as well as the fact that each peak is dominated by certain types of atomic hopping has great relevance to experimentally determinable parameters such as hopping distances and activation temperatures.[11] The types of atomic motion for each jump is summarized in Table 1. The (0.52 Å) vertical motions relate to PB centering reversals. All of the other low energy excitations are phason jumps. These low energy jumps include most of the atomic motions that collectively lead to tiling rearrangements in simulations of larger approximants[5].

Table 1. Important atomic jumps in Al_3Co simulation. Ideal atomic sites in the column labeled "Example(s)" are listed according to the nearest atom in the Grin *et al.* structure. (See figure 1.)

Δr(Å)	$\Delta E(eV)$/ Atom type	Example(s)
0.52	0.15/Co, 0.2/Al	Vertical motion (puckering reversal) of Al(22) or Co(9)
0.54	0.55;0.7/Al	Al(18) motion to either side
0.76	0.2/Al	Motion of Al(7) or Al(26) to their averaged position
0.94	0.55/Al	Al(24) stepping closer to midpoint of Al(22) and Al(23)
1.08	0.7/Al	Same as above, but includes puckering reversal
1.53	0.8/Al	Off-centering motion of Al(27)
2.34	0.5;0.65/Co, 0.8/Al	Al(17) or Co(9) jumps to (necessarily vacant) Al(1) position in adjacent layer
2.47	1.0/Co	Co(4) moves in $-x$ direction to site near (necessarily vacant) Al(6) site

5 Conclusions

Our pair-potentials simulation on a 14.4 Å by 12.3 Å by 8.1 Å orthorhombic cell predict a room temperature configuration that agrees with the experimental structure in having Co pentagonal bipyramids (PB's) on a hexagon tiling, but differs in the exact pattern of the PB centering. We find characteristic energies for excitations from this structure. Many of the low energy excitations are phasons.

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