Total energies of decagonal models for quasicrystals

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Burkov proposes a plausible atomic model for the decagonal phase of Al–Cu–Co. Using pseudopotential-based pair interactions that reflect the metallic screening of the electron gas, we compute total energies for a few approximants to the decagonal phase and examine their stability through relaxation. We find some systematic atomic displacements and modifications in chemistry which bring the proposed model into closer agreement with experimental Patterson analysis, lower the energy, or both.

1. Introduction

Analysis of total energies is central to our understanding of phenomena ranging from the origins of exotic surface reconstructions to the emergence of magnetic order. Quasicrystals are no exception. A delicate free energy balance separates crystals from their quasiperiodic counterparts. The random tiling picture argues that the entropy of quasicrystals is enhanced relative to crystals because of the degrees of freedom associated with tile rearrangements [1]. These ideas gain credence from the transformations of quasicrystals to crystals at lower temperatures in both decagonal and icosahedral phases [2,3]. On the other hand, there is a growing consensus that the binding energy of quasicrystals (and related approximants) is enhanced by the formation of a pseudogap in the electronic density of states (DOS) [4].

Beyond their role in establishing the mechanisms behind quasicrystal formation, total energy studies are pivotal in our search for the atomic arrangements in these structures. Since the dis-

covery of quasicrystals, the search for realistic models with explicit atomic positions has gone on unabated. It is clear, however, that models constructed using only our knowledge of quasicrystal diffraction can have unrealistic high energies [5,6]. This paper illustrates the importance of incorporating energetic analysis into modeling efforts. We focus on the Al–Cu–Co class of decagonal quasicrystals [7].

2. Procedure

We consider the simplest description of the total energies, one based upon pair potentials. These calculations reflect in simple terms those features of a given model which are desirable and those that are unacceptable. Within the pair potential approximation, the total energies are given by

$$E_{\text{TOT}} = \tfrac{1}{2} \sum_{ij} \Phi_{\text{eff}}(r_{ij}). \tag{1}$$

The total energy as represented above ignores terms arising from the volume dependence of the energy of the electron gas which we neglect since we perform our calculations at fixed volume [8].

In this paper we treat the Al–Cu–Co system as a binary alloy composed only of Al and a single transition metal (TM) constituent, which we take

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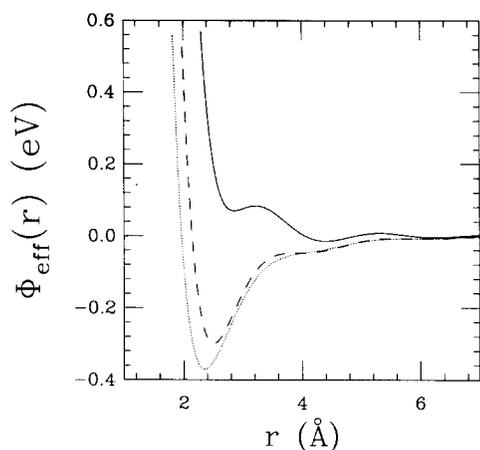
Fig. 1. Pair potentials for Al–Co system. solid line; Al–Al potential; dashed line: Al–Co potential; dotted line: Co–Co potential.

as Co. The use of only a single TM constituent may be viewed as a convenient first step in what will have to be an iterative refinement of the Al–Cu–Co decagonal structure. Experiments so far are silent on the issue of which sites are to be occupied by Cu and which sites are to be occu-

pied by Co. Further motivation for the study of Al–Co is the existence of the decagonal approximant crystal structure of $Al_{13}Co_4$ [9].

The total energy is explicitly linked to the electronic structure. In the pair-potential approximation this means that the effective potentials must reflect the metallic bounding in Al–Co. We follow the treatment of Wills and Harrison [10] in developing pair potentials for both simple metals (like Al) and transition metals (like Co). The treatment of the simple metals is standard, and involves representing the weak ion–electron interaction by an Ashcroft empty-core pseudopotential. The total energy is computed to second order in perturbation theory with self-consistent screening as described in ref. [11]. For the Co–Co pair potential, there is an additional contribution which comes from the overlap of the d-states. The Friedel model for the d-bands is used which describes the bands in terms of a single parameter related to their width [12]. Thus for the d-band metals such as Co, the total effective potential is a sum of two contributions

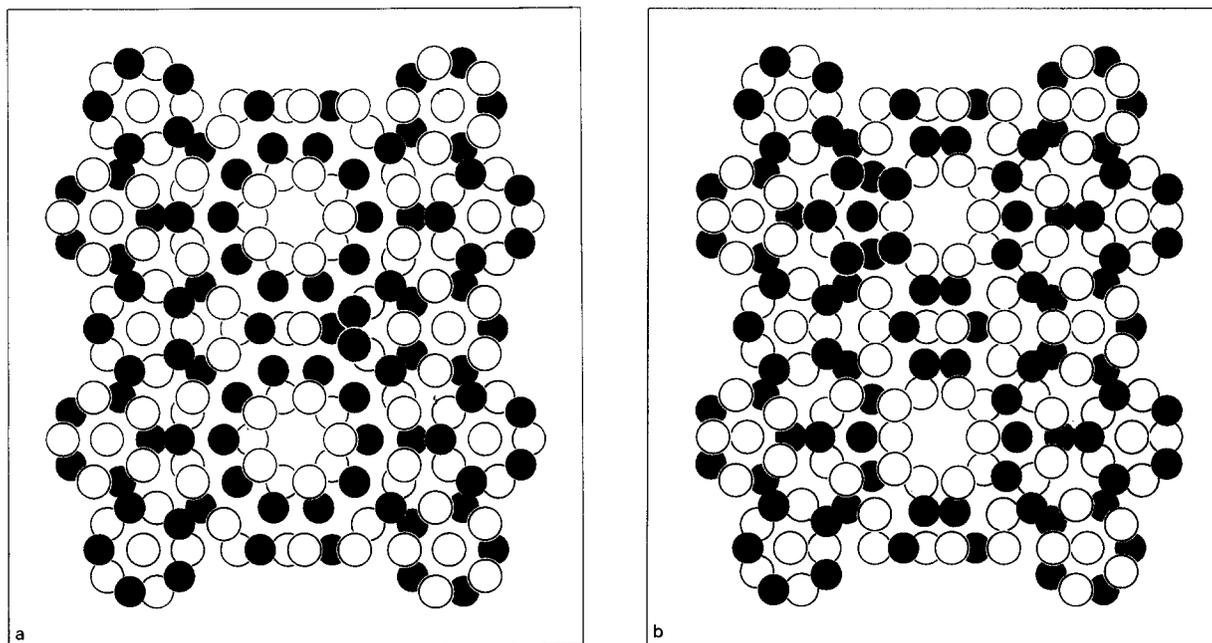$$\Phi_{eff}(r) = v_s(r) + v_d(r), \qquad (2)$$

Fig. 2. (a) Unrelaxed positions for periodic approximants built up of Burkov's decagonal clusters. Black atoms are Co, white atoms are Al. Shaded atoms separated by 1.77 Å. (b) Relaxed positions for model shown in (a).

one of which (v_s) comes from the s-band overlap, and the other of which (v_d) comes from the d-band overlap. The potentials which result from this analysis are shown in fig. 1 [13]. It is seen that the Al–Al interaction displays the usual Friedel oscillations with its first minimum at 2.86 Å. The description of the total energy embodied in these potentials is only the lowest order treatment of the structural contributions to the total energy. Though this description serves our present aim, an accurate treatment of transition-metal energetics requires higher-order terms in the energy functional that correspond to multi-ion interactions [14].

Experimentally, it is known the $Al_{65}Co_{20}Cu_{15}$ forms a stable high-temperature decagonal phase. At reduced temperatures, the decagonal phase transforms to one or more large unit cell approximants [2]. Inspection of the reconstructed electron densities resulting from a five-dimensional Patterson analysis [15] inspired Burkov [16] to invent a model for the decagonal phase that fills space with two types of decagonal clusters, one small 11 atom cluster and one large 50 atom cluster. We have carried out relaxations of crystal approximants built up of the Burkov decagons. We refer to such approximants as Burkov models. One such approximants is shown in fig. 2(a). The relaxations use the conjugate gradient method, a zero-temperature relaxation scheme which follows the energy contour to a nearby local minimum. The relaxations are continued until the energy change per step is less than about 10^{-5} eV/atom.

3. Results

These calculations yield information on a number of different fronts. First, they allow us to discriminate between competing models on the basis of the differences in their total energies. Secondly, the refinements in the structures which result from the relaxation lead to an understanding of the roles of atomic position and chemical decoration. The relaxations also reveal features of the original model which is energetically favorable to change.

In the original Burkov model, when two large decagons touch so that their outer rings share an edge, an unphysically short Al–Al bond of 1.77 Å results. The atoms in question are shaded grey in fig. 2(a). We have explored two solutions to this problem, both of which result in models which remain stable upon relaxation. One solution is to first relax only the atoms involved in such bonds, before relaxing the remainder of the structure. An alternative treatment is to replace the two atoms in the short bond by a single atom at their average position. Examination of the correspondences between structures built up of Burkov's decagonal rings of the $Al_{13}Co_4$ structure reveals that $Al_{13}Co_4$ uses both mechanisms of relaxing the short bond, one at each end of a shared large decagon edge.

The assignment of the chemical identities in the Al–Cu–Co decagonal phase is uncertain both theoretically and experimentally. In Burkov's original decagons, the innermost ring consists entirely of transition metals, while the ring with next largest radius consists solely of Al. To exam-
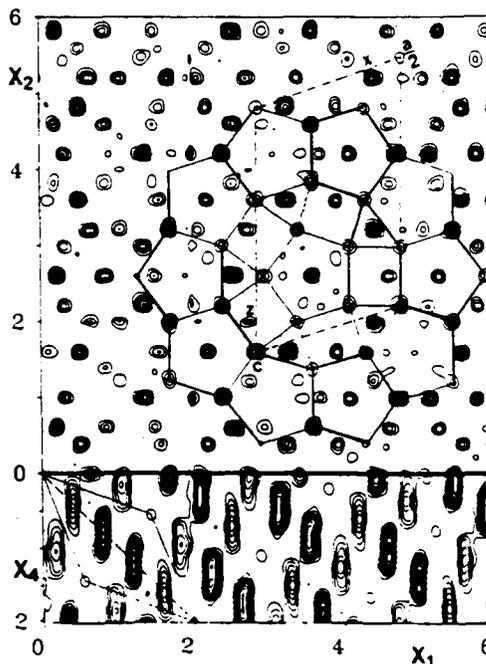

Fig. 3. Reconstructed electron density for Al–Cu–Co decagonal phase. Taken from ref. [16].

ine the energetics associated with the chemical decoration, we relaxed a model in which the chemical identity of these two innermost rings is exchanged. This exchange conserves the overall composition and the final energy is 0.04 eV/atom lower than the original relaxed model. We conjecture that for models containing open decagonal rings (like Burkov's), the inner ring should be composed of Al. Not only is this configuration lower in energy, but it is also more stable against distortions.

4. Discussion

It is especially instructive to compare the model before and after relaxation with the reconstructed densities of Steurer and Kuo [15]. A portion of the reconstructed electron density is shown in fig. 3. We find that many of the new sites obtained upon relaxation of the original Burkov model are present in the reconstructed density. One general result is the tendency of atoms in the outer rings to distort. In all of the variants of Burkov's original model that we have considered, we find that these edges break up with at least one of the atoms moving to the interior of the large cluster. Some of these new atomic positions complete prominent pentagonal clusters seen in the reconstructed electron density of Steurer and Kuo. One of these pentagons is highlighted in fig. 2(b), which shows the relaxed model with the exchanged chemical decoration. The distortions of the outer edges also arise upon carrying out a tile rearrangement ('phason flip') [17].

4. Conclusions

In conclusion, we have reviewed methods for calculating total energies and dynamical relaxations using pair potentials. These calculations are central to the effort to determine realistic atomic models for quasicrystals. Our calculations lead to some improvements in the agreement between the models and reconstructed electron densities, including positions associated with phasons.

References

[1] C.L. Henley, in: Quasicrystals: The State of the Art, eds. D.P. DiVincenzo and P.J. Steinhardt (World Scientific, Singapore, 1991).
[2] K. Hiraga, W. Sun and F.J. Lincoln, Jpn. J. Appl. Phys. 30 (1991) L302; P. Launois, M. Audier, F. Denoyer, C. Dong, J.M. Dubois and M. Lambert, Europhys. Lett. 13 (1990) 629.
[3] M. Audier and P. Guyot, in: Quasicrystals and Incommensurate Structures in Condensed Matter, eds. M. Yacaman, D. Romeu, V. Castano and A. Gomez (World Scientific, 1989); P. Bancel, in ref. [1].
[4] Electronic structure and total energies in quasicrystals are reviewed by A.E. Carlsson and R. Phillips in ref. [1].
[5] R. Phillips, H. Deng, A.E. Carlsson and M.S. Daw, Phys. Rev. Lett. 67 (1991) 3128.
[6] A.P. Smith, Phys. Rev. B42 (1990) 1189.
[7] L.X. He, Y.K. Wu, and K.H. Kuo, J. Mat. Sci. Lett. 7 (1988) 1284.
[8] Pair potentials and structural energies are described by V. Heine and D. Weaire, in: Solid State Physics: Advances in Research and Applications, vol. 24, eds. H. Ehrenreich and D. Turnbull (Academic Press, New York, 1970).
[9] R.C. Hudd and W.H. Taylor, Acta Cryst. 15 (1962) 441.
[10] J.M. Wills and W.A. Harrison, Phys. Rev. B28 (1983) 4363. The approach has been extended by C. Hausleitner and J. Hafner, J. Phys. F18 (1988) 1025.
[11] J. Hafner, From Hamiltonians to Phase Diagrams (Springer, Berlin, 1987).
[12] J. Friedel, in: The Physics of Metals, ed. J.M. Ziman (Cambridge, University Press, New York, 1969).
[13] The pair potential in alloys is discussed by Hafner in ref. [11].
[14] See the review by A.E. Carlsson, Solid State Physics: Advances in Research and Applications, Vol. 43, eds. H. Ehrenreich and D. Turnbull (Academic Press, New York, 1990).
[15] W. Steurer and K.H. Kuo, Acta Cryst. B46 (1990) 703.
[16] S. Burkov, Phys. Rev. Lett. 67 (1991) 614.
[17] See figs. 3(a) and (b) in: M. Widom and R. Phillips, J. Non-Cryst. Solids 153&154 (1993) 282.