Stable Dense Icosahedral Quasicrystals

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Using lattice sums we show that the dense, monatomic, face-centered, icosahedral quasicrystals can be stable at zero temperature. We compare the energy to other periodic crystals and find it minimal. We create phason strain in this lattice, calculate the energy, and show that this lattice is at least locally stable against such strains. We calculate the two elastic constants associated with this strain. Our calculations indicate that it is also globally stable against phason strains. We argue that it is also stable under elastic strains. We show that the energy as a function of the strain is not described by a simple quadratic expansion as implied by simple phason elastic theory.

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The problem of the stability of quasicrystals (QC) was raised by their discovery.[1] The first materials that were found were probably disordered phases because they were made by rapid quenching. There were signs of disorder in the diffraction spectra and they were metastable. Later materials with a higher degree of order were found. There is good evidence that the face-centered icosahedral phases of AlLiCu,[2] AlCuFe, and AlCuRu[3] are highly ordered and probably stable.

Landau theories[4] were used to demonstrate that icosahedral QC may be stable phases. But this approach is limited to order parameters which have no direct relevance to the real microscopic structure of the quasicrystal. (It is not even clear if discussion of one or two wave vectors is enough for those phases since obviously extremely nonstable QC can be described by the same Fourier expansions with the same dominant vectors and the parameters of any expansion are not related to microscopic theory.) Therefore, models which are related to the microscopic structure of QC are needed.

Double atomic Penrose lattices have been simulated in two-dimensional simulations.[5] It was shown that the Penrose QC is locally stable. It was also shown that structures which are very close to a Penrose lattice are reached by cooling a liquid.

In a recent[6] paper, Narasimhan and Jaric used lattice sums to calculate cohesion energies, but their results depend on a subtle difference between the distances in the simple-cubic icosahedral lattice and the cubic lattices, and stable periodic structures with higher cohesion energy can be found.[7]

In this Letter we use lattice sums to calculate zero-temperature energies of QC and compare them to other crystals. We find out that for the monatomic, face-centered icosahedral (fci) phase one can find a simple potential with a higher cohesion energy for the QC than for the other crystals, phason-strained QC's, and other QC that were compared. This situation holds over a wide range of potential parameters. This is quite interesting since the AlRuCu crystals are fci phases.

We introduce phason strains and calculate the pair distribution functions and the cohesion energies of the strained lattices. We show that the two elastic constants that define the elastic energy in small strains are positive, which means that the lattice is at least locally stable against such strains. It seems to also be stable against any other larger strains. We discuss the validity of phason elastic theory and show that it is not fully valid in our case.

Because of the high similarity between the pair distribution functions of the other monatomic icosahedral phases and the periodic cubic pair distribution functions, those QC's can be stabilized only for very small ranges of the potential parameters. Small distortions of the cubic phases cancel the preference so we do not discuss those possibilities at all.

We first discuss the icosahedral structures we use in our analysis. In our discussion we use the projection method and discuss QC which are projected from a six-dimensional cubic lattice. All the points within a strip in perpendicular space ($r^{\perp}$) are projected on the physical space ($r^{\parallel}$). There are three icosahedral Bravais lattices in 6D; the simple-cubic (sci), the face-centered (fci), and the body-centered lattice (bcl).

In Ref. 8 we discussed the dense icosahedral QC's. We showed that dense icosahedral lattices are derived from strips which are Voronoy constructions of orthogonal projections of certain lattice vectors. For the sci lattice two such kinds of Voronoy constructions exist.[8] The first is an icosahedron [defined by projection of 6D vectors of the kind (111000)]. The second strip is a truncated triacontahedron [defined by vectors of the kind (100000) and (110000)]. For the fci lattice a different QC is defined by a triacontahedron[8] [defined by (1 −1 0000)]. Their properties and their pair distribution functions are given in Ref. 8. In Table I we give the pair distribution functions of the fci dense lattice.

The statistics of the average number of neighbors for a monatomic QC (pair distribution function) is very easy to calculate; for a 6D vector $R^6=(r^{\parallel},r^{\perp})$,

$$\bar{n}(r^{\parallel})=(V_I/V_s)N_r\,, \tag{1}$$

TABLE I. The pair distribution function for a parallel distance R of the fci nonstrained lattice. We give an example of the 6D vector associated with the distances.

R	n_{av}	6D vector
1	6.465	(1 −10000)
1.41	2.226	(111100)
1.61	14.22	(110000)
1.9	1.42	(200000)
1.9	7.5	(11 −1010)
2.15	1.05	(21 −1000)

where $n(r^{\parallel})$ is the average number of neighbors at a distance $r^{\parallel}$, V_I is the volume of the intersection between the original strip and the strip moved by $r^{\perp}$, and N_r is the number of icosahedral vectors with the same length.

The cohesion energy is easily calculated, for periodic and nonperiodic crystals,

$$\bar{E} = -\tfrac{1}{2}\sum_{r^{\parallel}} \bar{n}(r^{\parallel})V(r^{\parallel}) \tag{2}$$

[for the periodic lattices $n(r^{\parallel})$ is simply the number of neighbors].

Our choice for the parameters of the potential is guided by the difference between the pair distribution functions of the periodic crystals and the dense QC's. It is very hard to stabilize the sci structures because their pair-distribution-function distances are very close to the pair distribution functions of the cubic phases. However, for the fci structure the pair distribution function is very different. As can be seen in Table I almost no atoms can be found between the minimal distance R_0 and $1.61R_0$ (only an average number of 2.2 atoms). This enables us to construct a potential which can stabilize the dense fci QC. This potential is defined in Fig. 1. Using this definition we make the following choice and compare our icosahedral QC to periodic ones, the sc, bcc, fcc and hcp lattices.

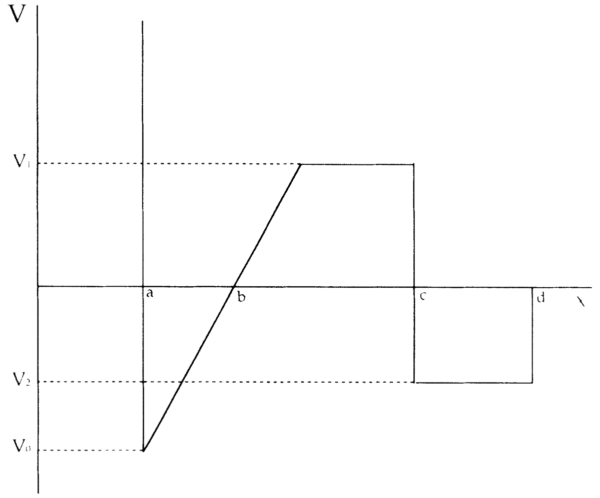

FIG. 1. The potential $V(r)$ is defined by the four distances a, b, c, and d and by the voltages V_0, V_1, and V_2: for $r<a$, $V=\infty$; for $b>r>a$, $V=-V_0+(V_1+V_0)(x-a)/(b-a)$; for $c>r>b$, $V=V_1$; for $c<r<d$, $V=-V_2$; for $d>0$, $V=0$.

We define

$$b/a < 1.1,\quad c/a = 1.5,\quad 1.618 < d/a < 1.7\,. \tag{3}$$

We analyzed the problem over the range of the parameters $\alpha = V_1/V_0$, $\beta = V_2/V_0$. We display the results in Fig. 2. The cohesion energy is quite high; for $\alpha = 0.5$, $\beta = 0.5$, the cohesion energy for the fci dense phase is $6.26V_0$. For the periodic crystals we get the following: For the sc phase the energy is 0.0, for the fcc it is $4.5V_0$, and for the bcc it is $5.5V_0$. The cohesion energy is also lower for other periodic crystals we checked (hcp, rhombohedral and hexagonal for all choices of length ratios, diamond, and others). We have not included them in Fig. 2 because they are stable, if stable, only at extreme choices of the parameters.

It is not satisfactory to compare the energy only to those periodic crystals. Obviously, we cannot compare energy with all periodic structures, but we can compare with the most relevant structures, which are the icosahedral lattices of this type with imposed phason strain. It is clear that for small strains the pair distribution functions of the strained lattices will be very close to those of the nonstrained one. Therefore, the energy will also be close and will change continuously as a function of the phason strain. Furthermore, one might naively assume that introduction of strain will introduce into the lattice a new local environment that will make the cohesion energy higher. Therefore, we construct the strained lattices and calculate the pair distribution functions and the energies.

The phason strain is described by a stress tensor T^{ij} (in the parallel direction i a strain in the orthogonal direction j is introduced). Those types of lattices can be either periodic or nonperiodic. For small strains it is possible[9] to write the difference in energy using an elastic

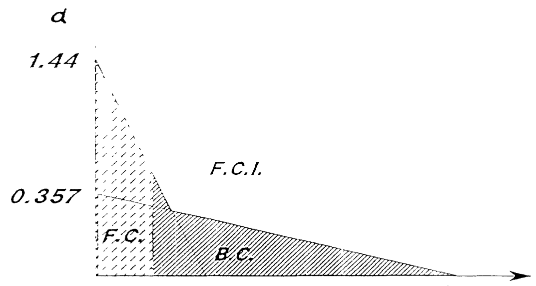

FIG. 2. A phase diagram as a function of the parameters $\alpha = V_1/V_0$ and $\beta = V_2/V_0$ of the potential given in Fig. 1. The icosahedral phase is stable over a wide range of possibilities.

expansion:

$$\Delta E = \sum \lambda_{ijkl} T^{ij} T^{kl} . \qquad (4)$$

One should notice the following remarks:

(1) Since introduction of phason strains introduces points into the lattice and takes others out the lattice, the expansion (4) is not fully defined. We are not discussing small shifts in the coordinates of the atoms, but shifts in the phason coordinate; therefore, one should define exactly how the transformation is done. The usual way of defining the lattice is to keep the strip (or the atomic surface) the same; however, in our case such a choice will not be satisfactory because it will result in the appearance of smaller distances in the lattice than allowed by our hard-core potential. Our way of defining the new lattice will be to find the icosahedral dense lattice under a certain phason strain. We will find that the lattice becomes less dense when phason strained but we still use this expansion since we want to compare the energy. Unlike the case of elastic expansions, we cannot transform one lattice to the other at all even with large translations of atoms.

(2) If the change in the phason strain is done continuously, all the average parameters of the lattice will change continuously. Therefore, it is reasonable to do a Fourier expansion of the energy. There is no general argument that the quadratic expansion (4) is a good description of the energy. We found out that it is not a good approximation even for small strains in the direction T^{11} though the energy is minimal for zero strain, so Eq. (4) is not generally valid, but we still use it to demonstrate stability.

It is well known[9] that there are only two independent elastic constants associated with phason strain in (4) (there are five elastic constants for the full elastic expansion[9]). If we introduce strains in two independent directions associated with those elastic constants, we can calculate the pair distribution functions, use them to calculate the energy, and measure those constants. As our set of coordinates we choose a set of the twofold axes of one of the tetrahedral subsets of the icosahedral group in parallel and orthogonal space. We give the same index in orthogonal and parallel space to directions associated with the same twofold operation. It is very easy to check that the elastic constants λ_{1111} and λ_{1212} are independent. We use those directions in calculating the energy.

We construct those lattices as we did in Ref. 8. We define the minimal distance, identify the vectors whose projection is smaller than a certain minimal distance, and then perform a Voronoy construction in orthogonal space to define the strip. The densest fci QC's are projected by convex strips and this is also the case for the strained ones, so this construction gives in this case the most dense lattices. The phason strain breaks the symmetry of the orthogonal vectors and therefore changes the size and the shape of the strip. Therefore, the pair distribution functions are different. We note that we still project on the original physical lattice; otherwise the cohesion energy would be lower because of a change of lattice distances.

Using this method we calculated the cohesion energies for the strained lattices. We calculated the volumes of the overlaps of strips according to Eq. (1) numerically for a set of values of phason strains (using 3.5×10^6 randomly distributed points). We found the nonstrained lattice to be the most stable one. We give an example of the results for the strain T^{12} and for the parameters $\alpha = 0.5$, $\beta = 0.5$ in Fig. 3. We find that the two elastic constants are positive. We calculated them fitting the lowest points with (4). Their values are

$$\lambda_{1111} = (1.5 \pm 0.35) V_0, \quad \lambda_{1212} = (1.2 \pm 0.2) V_0 .$$

The energy is at least a local minimum as a function of the strain as can be seen in Fig. 3 (with an accuracy of 0.01). The quadratic expansion is a good approximation for the second elastic constant and poor for the first since the energy is not symmetric under change of sign of the strain T^{11}. For the higher strains the cohesion energies are still higher. In other checks we made in other general directions the same situation exists. The energy seems to also be a global maximum though we cannot prove it in a general way.

Those results are also valid for the periodic crystals which can be defined as a projection from six-dimensional space because the parameters of each such crystal are as close as we wish to an incommensurate crystal which is defined close to it. Therefore, those calculations also give results for periodic crystals. As a further check we also calculated the energies of the rational approximations of the icosahedral crystal (where τ is approximated by rational numbers), the energy of those crystals

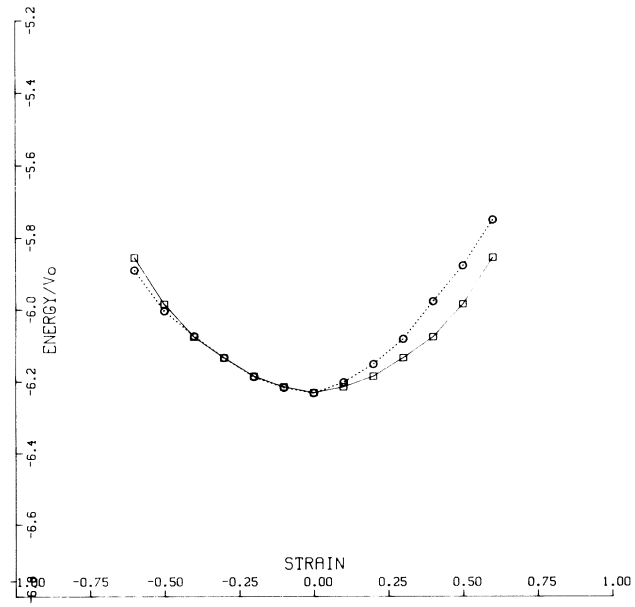

FIG. 3. The energy as a function of the strain T^{12}.

is smaller but quite close (for $\tau = \frac{2}{3}$ the energy is 6.21; for $\frac{8}{13}$ it is 6.22).

If we also introduce pressure, the lattice will be even further stabilized since we find that the density is maximal for the nonstrained QC. So, an introduction of phason strain will define a larger volume for the QC, and therefore additional mechanical energy will be added to stabilize the nonstrained lattice.

From those results it is also clear that long-wavelength fluctuations in the strain will also lower the cohesion energy. The basic disorder in the lattice will probably be related to those fluctuations since at short distances it is impossible to distinguish between different small strains.

Two short-range neighbors are enough to fix the stable position of a lattice point because of the form of the potential we defined. The dense fci lattice with this potential has a stable backbone of more than 95% of the points, which have more than one neighbor and therefore are fixed in space. Consequently, we expect that the lattice will also be stable under elastic distortions.

We have shown in this Letter that it is possible to define a potential that will stabilize an icosahedral lattice relative to other periodic crystals. We also show that the cohesion energy of this lattice is at least a local minimum and probably also a global maximum as a function of the strain. In doing so, we show for the first time how to calculate those elastic constants and discussed the validity of the phason elastic expansion.

We should note that the arguments we presented here do not fully prove that the structure we discussed is the most stable lattice. We have not checked, and it is impossible to check, all the possible lattices. We are sure that the reason for the stability of two and three atomic QC is related to the properties of two atomic potentials and two atomic icosahedral packings but this will be discussed elsewhere. But still our arguments are meaningful and we think they provide a very interesting intuition on how real QC might be stabilized. The unique properties of the pair distribution functions and properties of the dense QC's might be responsible for their stability.

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