Stable decagonal Al-Cu-Co-Si phase: A phason-perturbed quasiperiodic crystal

Z. Zhang
Beijing Laboratory of Electron Microscopy, Chinese Academy of Sciences, P.O. Box 2724, 100080 Beijing, People's Republic of China

H. L. Li and K. H. Kuo
Beijing Laboratory of Electron Microscopy, Chinese Academy of Sciences, P.O. Box 2724, 100080 Beijing, People's Republic of China and Department of Materials Physics, University of Science and Technology, Beijing, 100083 Beijing, People's Republic of China
(Received 28 April 1993)

The analysis of high-resolution electron-microscopy images of the stable $Al_{62}Cu_{20}Co_{15}Si_3$ decagonal quasicrystal shows a long-range aperiodic translation order similar to that of Penrose tiling. Thus this particular decagonal phase could be interpreted as a phason-perturbed quasiperiodic crystal.

In a previous paper Chen *et al.*[1] reported the observation of spatial quasiperiodicity in high-resolution electron microscopy images of the thermodynamically stable decagonal quasicrystal $Al_{65}Cu_{15}Co_{20}$. They concluded that the observed structure is inconsistent with conventional ideal Penrose tiling and therefore supported an entropy-stabilization mechanism in accordance with the random-tiling model. We have made a similar study and found that this quasiperiodicity, on the contrary, can possibly be interpreted as a phason-perturbed Penrose-tiling model.[2]

The recently discovered Al-Cu-Co decagonal quasicrystal[3] was found to be stable at 900 °C and can be grown into mm-size needlelike crystallites directly from the melt by slow solidification. Its x-ray[4]- and electron[3]-diffraction patterns are rather sharp, and the correlation length[5] is about 200 nm. This is a suitable decagonal quasicrystal for x-ray single-crystal diffraction[4] and scanning tunnel microscope[6] studies. Both support the Penrose tiling model of quasicrystals. However, there are also other experimental results,[7] including the previous electron-microscopy study,[1] that support the random tiling model.[8,9] Obviously, some more relevant experimental studies to clarify this point are needed.

The alloy of composition $Al_{62}Cu_{20}Co_{15}Si_3$ was prepared by melting the high-purity elements in an induction furnace under an argon atmosphere. Some Si was added to the Al-Cu-Co alloy to improve the perfection of the decagonal quasicrystal so that high-quality samples can be obtained directly from the melt.[3,10] The as-cast ingot was cut into slices from which thin foil specimens for transmission electron microscopy were prepared by mechanical thinning and subsequent ion milling. Ion milling was carried out at 3 kV to prevent ion-induced crystallization of the quasicrystalline structure on the surfaces of the specimen. High-resolution electron microscopy (HREM) was carried out in a JEOL-4000EX electron microscope.

Figure 1(a) is a HREM image of the Al-Cu-Co-Si decagonal quasicrystal taken along the tenfold axis. The most recognizable feature of this HREM image, as reported before,[1,11,12] is the wheel-like pattern. The "wheel" itself or the decagon of bright points inside it exhibits tenfold rotational symmetry. This is the fundamental subunit of the 2D decagonal quasicrystal. These wheel-like subunits packed quasiperiodically in this image, as shown by their arrangement in a row indicated by an arrow. The characteristic spacing between two such subunits is either 2.0 nm when they touch each other or 1.2 nm [or 2.0 nm/τ where $\tau=(1+\sqrt{5})/2$] and 0.77 nm (or 2.0 nm/τ^2) when they intersect each other. Five of these subunits form either a small pentagon with an edge length A of 1.2 nm or a large pentagon inflated by τ. Larger decagon of these subunits can also be seen in Fig. 1(a). Either 1.2 (Ref. 11) or 2.0 nm (Refs. 1 and 12) has been used as the characteristic length (the edge length of a pentagon, a skinny, or a fat rhombus) of the two-dimensional (2D) quasiperiodic pattern. In the following we shall use 1.2 nm as the edge length of various Penrose tiles. In this case 2.0 nm is the diagonal length of a pentagon and 0.77 nm the short diagonal length of a skinny rhombus.

If the centers of these wheel-like subunits are connected, a tiling like Fig. 1(b) is obtained. As discussed by Lück,[13] Penrose tiling has several variants or *P* sets, such as skinny and fat rhombi, dart and kite, or pentagons, boat, stars, and skinny rhombi. All such tiles can be found in Fig. 1(b). Owing to some ambiguity in making the connections, some spaces are left open. However, even these open regions have characteristic configurations, and dotted lines are drawn in some of them to show the fact that they are composed of several Penrose tiles.

Any vertex in an arbitrary tiling of Penrose tiles may be represented as a lattice point on a 5D hyperspace lattice. The procedure for defining the 5D coordinates of a vertex is as follows: An origin is chosen arbitrarily, and then a connected path is walked from the origin to the vertex of interest along the tile edges. The number of positive steps minus the number of negative steps taken along each of the five pentagonal directions is calculated and that number is assigned to the corresponding coordinate $\{n_i\}$, where $i=1,2,\ldots,5$. Following Duneau and Katz,[14] 5D space is divided into $E^5=E^{\parallel}+E^{\perp}+\Delta$, where $\Delta=(1,1,1,1,1)$ is the diagonal of 5D cubic unit cell, $E^{\parallel}$ the physical space spanned by

 ©1993 The American Physical Society

$$\mathbf{e}_i^{\parallel} = \sqrt{2}/5\{\cos[2\pi/5(i-1)], \sin[2\pi/5(i-1)]\} ,$$

and $E^{\perp}$ the perpendicular space spanned by $\mathbf{e}_i^{\perp} = \sqrt{2}/5\{\cos[4\pi/5(i-1)], \sin[4\pi/5(i-1)]\}$. In the physical space $\mathbf{e}_1^{\parallel}+\mathbf{e}_2^{\parallel}+\mathbf{e}_3^{\parallel}+\mathbf{e}_4^{\parallel}+\mathbf{e}_5^{\parallel}=0$, only four of the five basic vectors are rational independent. The use of five basic vectors is to lay emphasis on the fivefold symmetry, just as $h+k+i=0$ is used in the Miller-Bravais indices for hexagonal crystals. The projection of a 5D lattice point $n=(n_1,n_2,n_3,n_4,n_5)$ onto physical and perpendicular spaces are respectively

$$\begin{aligned} \mathbf{x}_{\parallel} &= \Sigma n_i \mathbf{e}_i^{\parallel} , \\ \mathbf{x}_{\perp} &= \Sigma n_i \mathbf{e}_i^{\perp} \quad (i=1,2,3,4,5) . \end{aligned} \tag{1}$$

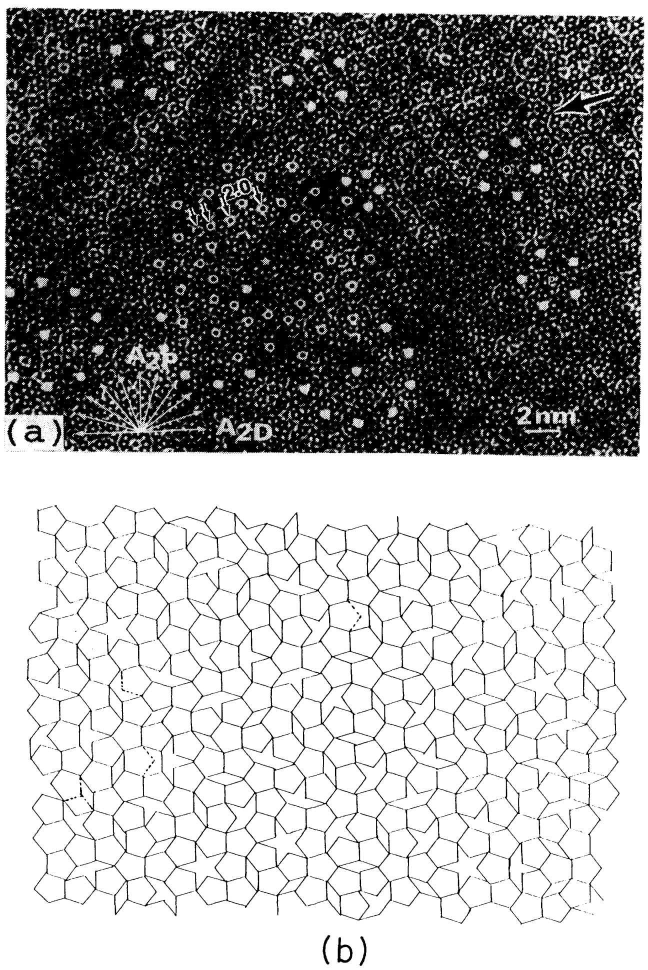


FIG. 1. (a) A portion of a HREM image of a decagonal $Al_{62}Cu_{20}Co_{15}Si_3$ quasicrystal. Wheel-like subunits displaying tenfold rotational symmetry (some are marked by white or white-black dots) form pentagons and decagons. The characteristic lengths between two centers of these subunits are 0.77, 1.2, and 2.0 nm in the τ inflation relationship, as shown in the row marked with an arrow. (b) A schematic diagram of the connection of centers of these wheel-like subunits in (a) consisting of different variants of Penrose tiles. Dotted lines show possible connections. The edge length of pentagons and rhombi is 1.2 nm.

Such a perpendicular projection of 603 vertices from an area of about 34×25 nm^2 in Fig. 1(b) is shown in Fig. 2(b). For decagonal Penrose tiling, the window is a decagon which is shown in Fig. 2(a). Comparing with Fig. 2(a), the experimentally projected vertices in the perpendicular space, Fig. 2(b), are somewhat scattered, about 12% of the points lying outside of the decagon window. However, the densely populated core, with an appearance similar to a decagon, can still be seen. The projected vertices lie on a set of pentagrids, forming pentagons and incomplete decagons. This is quite different from those reported earlier, which are divergent and extended to large regions.[1,11]

In order to further examine this point, we use Hiraga's HREM image of an Al-Cu-Co decagonal quasicrystal annealed at 800 °C followed by quenching and its schematic drawing, consisting of pentagons, stars, and other Penrose tiles.[12] Its projection in the perpendicular space is shown in Fig. 2(c). Among the 449 vertices, about 10% are lying outside of the decagon window. Its general appearance resembles Fig. 2(b), though there is less scatter.

Another important property of this projection is the mean-square fluctuation of the perpendicular projection,

$$\langle \mathbf{x}_{\perp}^2 \rangle = 1/N\Sigma(\mathbf{x}_{\perp} - 1/N\Sigma\mathbf{x}_{\perp})^2 \tag{2}$$

as a function of the number of vertices N. For an ideal Penrose tiling this value is a constant of 0.186 for large N. This is indeed the case as shown in Fig. 3(a). The random tiling theories[8,9] claim a logarithmic increase of this quantity with N: $\langle \mathbf{x}_{\perp}^2 \rangle = (2\pi K_{2D})^{-1}\ln N$ for 2D random Penrose rhombus tiling, where K is phason elastic constant (or phason stiffness). It should be emphasized that what we observed in a HREM image is the projection of slab of the real material, and for 3D quasicrystal, the observed $\mathbf{X}(\mathbf{x},\mathbf{y})$ is the integration of $\mathbf{X}(\mathbf{x},\mathbf{y},\mathbf{z})$ along the thickness direction $\mathbf{z}$ and will crossover rapidly with increase of thickness t.[15] The decagonal Al-Cu-Co-Si phase is a 2D quasicrystal. A possible method of analysis is to treat the image as if it were a 2D structure.[1,11] However, if this equilibrium phase is stabilized by entropy, one could not construct a 3D configuration by a periodic packing of 2D random tilings in the stacking direction. The entropy in such a model is obviously proportional to the layer area, whereas the entropy must be proportional to the volume. Hence there must be randomness in the stacking direction.[16] An adequate stacking random tiling model with axial symmetry was considered by Henley.[16]

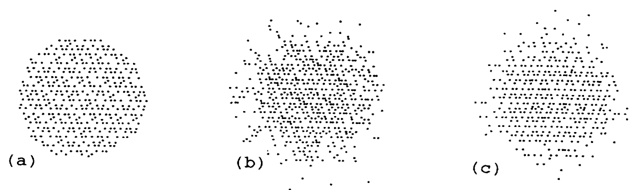


FIG. 2. Projection of the "wheel" centers onto the perpendicular space: (a) from an ideal Penrose tiling, a decagon; (b) from Fig. 1; (c) from Hiraga's Fig. 7(b) (Ref. 12). (b) and (c) are alike, with a densely populated core on a somewhat scattered background.

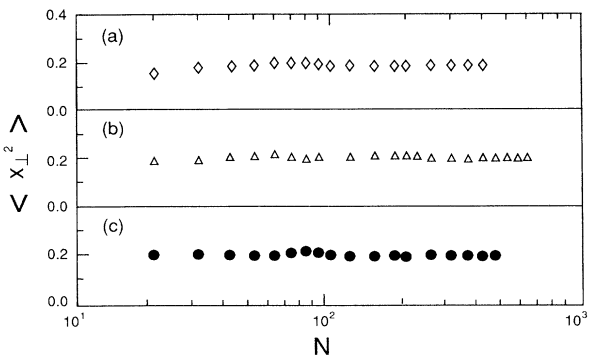


FIG. 3. Mean-square fluctuation of the perpendicular space projection vs N, number of "wheel" centers in a HREM image or vertices in a tiling. (a) Ideal Penrose tiling; (b) Fig. 1; (c) Hiraga's Fig. 7(b) (Ref. 12). The random-tiling model would predict a logarithmic increase of $\langle \mathbf{x}_\perp^2 \rangle$ with N.

He found that when $r^2 \ll z$, $\langle \mathbf{x}_\perp^2 \rangle \sim (\pi K_{2D})^{-1} \ln z$; and when $r^2 \gg z$, $\langle \mathbf{x}_\perp^2 \rangle$ has a similar logarithmically divergent rule as the 2D random tilings: $\langle \mathbf{x}_\perp^2 \rangle \sim (2\pi K_{2D})^{-1} \ln r^2$. A thin foil of about 10 nanometers is always used in HREM experiment and should fall into the latter case.

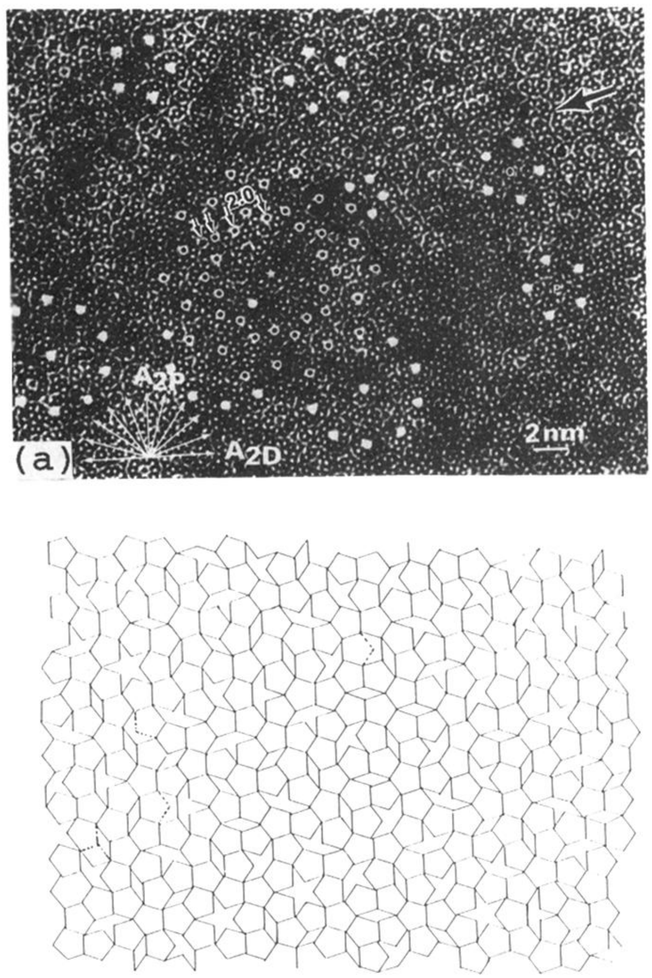
In earlier projection works of the HREM images,[1,11] a logarithmic increase of $\langle \mathbf{x}_\perp^2 \rangle$ with N was found, though the value of the phason stiffness K_{2D} is smaller than that predicted by the random-tiling models. This was considered to be a strong evidence to support the random-tiling model. However, our experimental results, Fig. 3(b), show the contrary. The $\langle \mathbf{x}_\perp^2 \rangle$ remains almost unchanged when N increases, though the average size has been raised to a level of about 0.2. The same applies to Hiraga's experimental results, Fig. 3(c).

The above results favor the Penrose quasiperiodic tiling model.[2] At least the present study shows quite different projection results from earlier HREM works[1,11] so that these authors' support of the random-tiling model of quasiperiodicity seems questionable. This is not unexpected at all if one examines their HREM images. In Fig. 2 of Ref. 1, there is periodic order in an area of 8×6 nm^2 which is a definite nanocrystalline. Even in their Fig. 1, there is also local periodic order, an obvious departure from quasiperiodicity. In other words, the sample used is not a high-quality decagonal quasicrystal. As it is known now,[17] the composition $Al_{65}Cu_{15}Co_{20}$ used by Chen *et al.*[1] is near the boundary of the stable region of the Al-Cu-Co decagonal quasicrystal at 900 °C and it might transform to a crystalline phase at low temperatures,[7] sometimes even during cooling after annealing at 800–900 °C.

Finally a few words on a HREM image. Given a HREM image is a projected image of a 3D structure in the incident beam direction and is subjected to the influence of very strong dynamical diffraction effect, it can still show the local structure down to the atomic level of a quasicrystal. If there is any phason disorder, its corresponding tiling mistakes will be qualitatively revealed in a HREM image and quantitatively in a perpendicular projection.

The authors gratefully acknowledge the National Natural Science Foundation of China and the Chinese Center for Advanced Science and Technology for financial support. Z.Z. thanks the K. C. Wong Educational Foundation, Hong Kong, for a grant.

[1] H. Chen, S. E. Burkov, Y. He, S. J. Poon, and G. J. Shiflet, Phys. Rev. Lett. **65**, 72 (1990).
[2] D. Levine and P. J. Steinhardt, Phys. Rev. Lett. **53**, 2477 (1984).
[3] L. X. He, Y. K. Wu, and K. H. Kuo, J. Mater. Sci. Lett. **7**, 128 (1988).
[4] W. Steurer and K. H. Kuo, Acta. Crystallogr. B **46**, 703 (1990).
[5] A. R. Kortan, F. A. Thiel, H. S. Chen, A. P. Tsai, A. Inoue, and T. Masumoto, Phys. Rev. B **40**, 9397 (1989).
[6] A. R. Kortan, R. S. Becker, F. A. Thiel, and H. S. Chen, Phys. Rev. Lett. **64**, 200 (1990).
[7] C. Dong, J.-M. Bubois, M. DeBoissieu, and C. Janot, J. Phys. Condens. Matter **3**, 1665 (1991).
[8] M. Widom, D. P. Deng, and C. L. Henley, Phys. Rev. Lett. **63**, 310 (1989).
[9] K. Strandburg, L. H. Tang, and M. V. Jaric, Phys. Rev. Lett. **63**, 314 (1989).
[10] L. X. He, Y. K. Wu, X. M. Meng, and K. H. Kuo, Philos. Mag. Lett. **61**, 15 (1990).
[11] Y. He, H. Chen, S. J. Poon, and G. Shiflet, Philos. Mag. Lett. **64**, 307 (1991).
[12] K. Hiraga, in *Quasicrystals,* edited by D. P. DiVincenzo and P. J. Steinhardt (World Scientific, Singapore, 1991), p. 95.
[13] R. Lück, Mater. Sci. Forum **22-24**, 231 (1987).
[14] M. Duneau and A. Katz, Phys. Rev. Lett. **54**, 2688 (1985).
[15] L. J. Shaw, V. Elser, and C. L. Henley, Phys. Rev. B **43**, 3423 (1991).
[16] C. L. Henley, in *Quasicrystals* (Ref. 12), p. 429.
[17] B. Grushko and K. Urban, J. Mater. Res. **6**, 2629 (1991).



(b)

FIG. 1. (a) A portion of a HREM image of a decagonal $Al_{62}Cu_{20}Co_{15}Si_3$ quasicrystal. Wheel-like subunits displaying tenfold rotational symmetry (some are marked by white or white-black dots) form pentagons and decagons. The characteristic lengths between two centers of these subunits are 0.77, 1.2, and 2.0 nm in the τ inflation relationship, as shown in the row marked with an arrow. (b) A schematic diagram of the connection of centers of these wheel-like subunits in (a) consisting of different variants of Penrose tiles. Dotted lines show possible connections. The edge length of pentagons and rhombi is 1.2 nm.