EUROPHYSICS LETTERS 13 October 1999

Europhys. Lett., (accepted), pp. 1-7 (2000)

Quasicrystalline gold interface with a hypo-friction property

Frédéric LANÇON[1](*), Jean-Michel PÉNISSON[1] and Ulrich DAHMEN[2]

[1] *Département de recherche fondamentale sur la matière condensée,* SP2M, CEA-*Grenoble, 38054* GRENOBLE *cedex 9, France*

[2] *National Center for Electron Microscopy,* LBNL, *University of California Berkeley, Ca 94720,* USA

(received 26 July 1999; accepted in final form 13 octobre 1999)

PACS. 61.44.Br – Quasicrystals.
PACS. 61.72.Mm– Grain and twin boundaries.
PACS. 62.20.Qp– Tribology and hardness.

Abstract. – We have studied a non symmetric and non periodic grain boundary in gold. An atomic model is presented and the atomic positions are found to be in agreement with the electron microscopy images. Using the diffraction pattern, we show that the structure is quasicrystalline and related to the irrational number $\sqrt{2}$. A complete hyperspace periodic description of the interface is given. We use this theoretical view to predict that in the case of an infinite interface of this type, two crystals should glide freely along the incommensurate x direction whereas they should be blocked along the commensurate z direction and be adhesive along the third y direction perpendicular to the boundary. A numerical test confirms this property.

Introduction. – A quasiperiodic grain boundary in gold has been observed by high resolution electron microscopy (the experimental study, as well as a part of the atomic modeling can be found in [1]). This interface between face centered cubic (FCC) grains is obtained by gold deposition onto a (001) germanium single crystal substrate surface. The gold film grows along its [011] direction, *i.e.*, the atoms at the surface of the film form rectangles with one side equal to the smallest interatomic distance r_0 and the other equal to $\sqrt{2}r_0$. There are two symmetry-equivalent epitaxial orientations, rotated 90° relative to each other around the common [011] direction. Grain boundaries tend to be normal to the film surface, and are therefore of pure tilt character. We denote the film normal as the z-direction.

Among all possible boundaries, there is a special orientation (see figure 1) in which a $(01\overline{1})$ plane in one crystal meets a (100) plane in the other crystal. We choose the y-direction normal to this boundary; hence the x-direction is the intersection of the boundary plane with the film surface. On both sides of this interface, the atomic planes perpendicular to

(*) Electronic address: FLancon@cea.fr

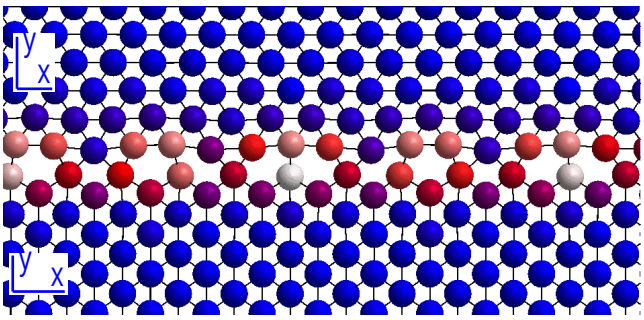

Fig. 1. – model of the $\sqrt{2}$ interface. Inter-atomic distances shorter than 0.31 nm are drawn. The atomic energy E^i_{pot} is indicated by color from dark (lowest energy) to light (highest energy). Atoms are in two layers at the altitudes 0 and $r_0/2$ along the z-direction.

$o-z$ are separated by the interatomic distance r_0. Therefore this direction (the tilt axis) is commensurate. On the other hand, the smallest distance between atomic planes perpendicular to $o-x$ is $r_0/\sqrt{2}$ in the first grain and r_0 in the second grain. Hence the structure along this direction is incommensurate. The interface could have been disordered but we show in this article that it belongs to the quasiperiodic class. More precisely it is an incommensurate composite structure[2, 3].

Using a simple and suitable inter-atomic potential for gold, we first determine atomic positions in good agreement with the experimental ones. Then using the hyperspace theory[2, 4, 5] for quasicrystals and modulated structures, we give a periodic 4D-description of this non periodic interface. As no atomic displacement occurs along the commensurate direction z, it is sufficient to use a three dimension space, (x, y, i), where $o-i$ is a virtual (or internal) direction. This hyper-space description enables us to show that an infinite interface of this type should allow the grains to glide freely along the incommensurate x direction. Such a possibility related to incommensurability was introduced using theoretical models[6, 7, 8, 9, 3] derived from the Frenkel-Kontorova harmonic chain in an external sinusoidal potential. Experimental evidence of super-lubricity has also been reported for a tungsten tip on a silicon surface [10]. This property makes this gold interface, and more generally incommensurate interfaces of this type, good candidates for hypo-friction applications in micro-technology.

Computer simulation. – Because of the strong electron-matter interaction, the precise analysis of a high resolution electron microscope image requires image simulations to interpret the observed contrast[11]. For this reason, we first construct a model to obtain atomic coordinates. This also gives the z-coordinates perpendicular to the image and information on energies.

The interaction potential is based on the second moment tight binding approximation[12]. In this case, the total potential energy of N gold atoms is:
$E_{pot} = \sum_i^N E^i_{pot}$, with $E^i_{pot} = \sum_{j\neq i}^N A \exp\left(-pr_{ij}\right) - \left(\sum_{j\neq i}^N B \exp\left(-2qr_{ij}\right)\right)^{1/2}$
where r_{ij} is the distance between atoms i and j and $\{A, B, p, q\}$ is a set of parameters that has been fitted and checked with several properties of gold[13].

To model a non periodic interface with periodic boundary conditions, we are faced with two major problems: first two semi-infinite crystals are needed, second the periodic box would be incommensurate with at least one of these semi-crystals. To overcome the first difficulty, we have introduced two interfaces perpendicular to $o-y$, *i.e.* two slabs have been simulated, with

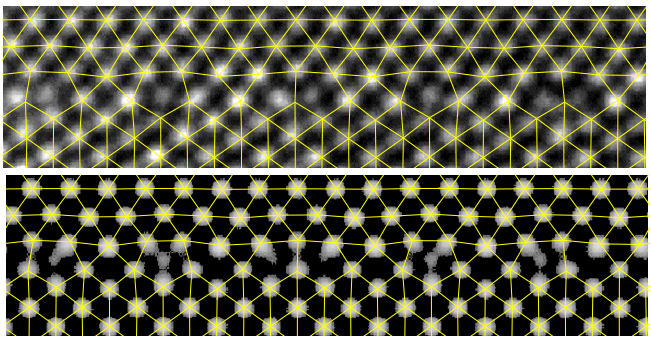

Fig. 2. – *Top*: experimental electron microscopy image superposed with atomic bonds of the model shorter than 0.32 nm. *Bottom*: simulated image calculated from the atomic positions and superposed with the same bonds (image simulation done with EMS program[11]).

a thickness large enough to get the bulk properties far from the interfaces. To overcome the second difficulty, we have used periodic approximants. Indeed the periodicity along x can be equal to n_s unit cells of width r_0 in one grain, and n_ℓ unit cells of width $r_0 \times n_s/n_\ell$ in the other grain. The following sequence tends to $\sqrt{2}$ when $i \to \infty$ (Diophantine approximations):
$n_s[i+1]/n_\ell[i+1] = (2n_\ell[i] + n_s[i])/(n_\ell[i] + n_s[i])$
with $n_s[0] = n_\ell[0] = 1$. We have mainly used two approximants corresponding to the ratio n_s/n_ℓ equal to 17/12 or 41/29. In the latter case, the relative error to $\sqrt{2}$ is less than 3×10^{-4}.

Starting from two slabs cut in a perfect crystal structure and joined together with the suitable orientation, the atomic positions are first randomly displaced with a uniform distribution of width $r_0/10$ along x, y, and z directions. This removes any symmetry of the initial configuration. Then, a relaxed structure is obtained by minimizing the energy E_{pot} with respect to the atomic coordinates as well as the size of the periodic box along the x and the y directions. One of the two interfaces of the "17:12" model is shown in figure 1. The calculated interface energy E_γ is 0.335 J/m^2.

The agreement with the experimental image is very good as shown in figure 2. We obtain the same pattern sequences, as well as the wavy appearance of the first rows due to atomic relaxations that can be observed by viewing the interface at a glancing angle. Some discrepancies in the atomic positions can be noticed. These may come mainly from the distortion of the experimental image due to the electron microscope and from the crudeness of the interactions used to build the model (in particular in the case of high energy atomic positions where the potential is less suitable). Because of the incommensurability, it cannot be expected that a piece of the material will correspond exactly to a piece of the same size of a simulated structure, but we can compare two images corresponding to almost the same relative shift of the grains.

Fourier space. – The non periodicity of the structure can be seen in the direct images of the interface, but the hallmark of quasicrystalline order is in Fourier space. Both the experimental and the computed intensities $I(q_x, q_y)$ (figure 3) contain the diffraction spots of each of the two crystalline grains. In addition, intensity lines are present as a the consequence of the planar discontinuity at this interface. But here, these streaks form a complex pattern that cannot be indexed with one integer. For the sake of simplicity let us consider the intensity restricted to $q_y = 0$, *i.e.* the x coordinates.

Figure 4 shows the diffraction pattern $I(q_x, 0)$ calculated from a "41:29" periodic approximant of the "$\sqrt{2}$" grain boundary (only the first atomic rows on each side of the grain boundary

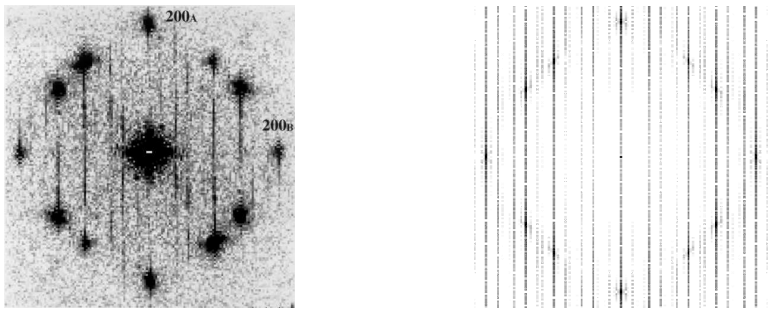

Fig. 3. – Intensity $I(q_x, q_y)$: numerical diffractogram of an experimental image (*left*); model (*right*): Fourier transform of a "41:29" approximant of the $\sqrt{2}$ interface.

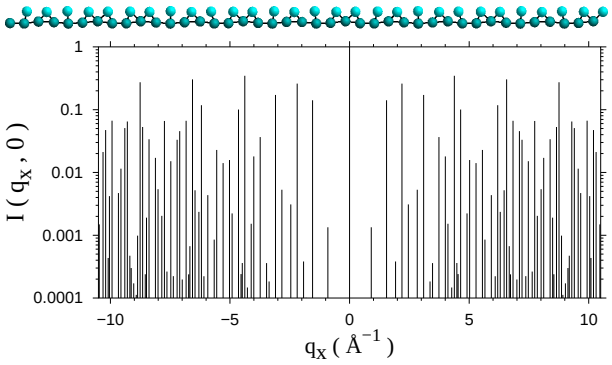

Fig. 4. – Fourier transform along the incommensurate direction of the first atomic rows (shown on top) at the $\sqrt{2}$ interface ("41:29" approximant).

have been taken into account).

Some peak positions q_x are multiples of the fundamental basis reciprocal parameter, $q_s = 2\pi/r_0$ of the first grain or $q_\ell = 2\pi/(r_0\sqrt{2})$ of the second grain. However, because of the mutual modulation of one grain by the other, some other peak positions are multiples neither of q_s nor q_ℓ, but all the q_x can be written as $n_s q_s + n_\ell q_\ell$ where n_s and n_ℓ are integers.

Because of the need of indexing these peaks with two integers, it is clearer to represent them on a square lattice of parameter $q_\ell\sqrt{3}$ in a 2D-space (figure 5). Each diffraction peak at position $q_x = n_\ell q_\ell + n_s q_s$ is set at vertex $(n_\ell q_\ell + n_s q_s,\ n_\ell q_s - n_s q_\ell)$ in the virtual space such that an orthogonal projection gives directly the diffraction pattern. If the interface were the juxtaposition of two rigid parts of a gold crystal, the non zero diffraction peaks would be restricted to the two lines of slopes $\sqrt{2}$ and $-1/\sqrt{2}$ crossing at the origin. Therefore, all the other peaks that are actually present are the result of the distortion of each grain by the other.

Hyper-space embedding. – The procedure that enables the reciprocal space to be embedded in a larger and virtual reciprocal space, can also be applied in direct space. For instance the x coordinate of an atom corresponds to a point set at $X = x\sqrt{2/3}$ and $Y = x\sqrt{1/3}$. This point is a periodic image of the point at $X \mod r_0\sqrt{2/3}$ and $Y \mod r_0\sqrt{2/3}$ inside a square elementary cell. Finally, the whole periodic structure is obtained by periodically repeating this

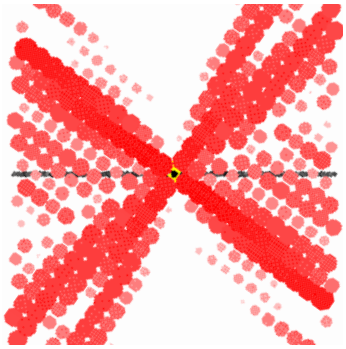

Fig. 5. – Two-dimensional view of the intensity shown in figure 4. The area and the darkness of the disks are proportional to the logarithm of the intensity. The diffraction pattern $I(q_x)$ is the projection of these spots on the horizontal line.

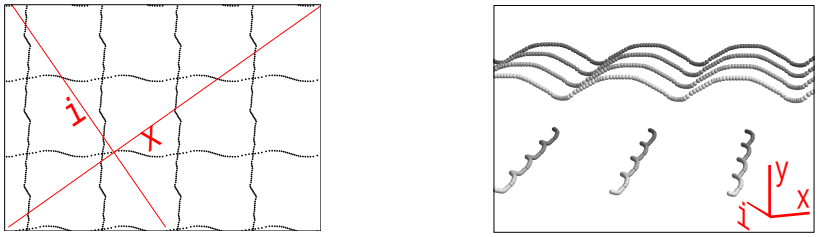

Fig. 6. – Hyperspace embedding of the $\sqrt{2}$ grain boundary: both first atomic rows on each side of the interface correspond to periodic lines in the virtual (x,i)-space (*left*) and (x,y,i)-space (*right*).

cell as in figure 6. Furthermore the coordinate y can be added to get coordinates in a (X,Y,y) or (x,y,i) hyperspace. The total information on the 3 coordinates x, y, and z of each atom implies the use of a four-dimensional space. Yet, the 3D (x,y,i)-space is enough since we have found no atomic relaxation along the commensurate direction $o-z$.

What have we gained by this hyper-space embedding of the "$\sqrt{2}$" interface? Firstly we have condensed all the information on the atomic positions along the whole infinite interface in a small square cell. For instance the range of the atomic relaxation is directly proportional to the amplitude of the lines in figure 6. Secondly, the periodic "atomic" lines in (x,y,i)-space are curved and not made of straight segments. Hence, the neighboring configuration of each atom is unique and we cannot strictly describe this grain boundary as a quasicrystalline sequence of a finite number of motifs [14, 15, 16, 17, 18] without thresholds to group the patterns in different classes. The third property, which turns out to be very important, is the continuity of the lines. This is different, for instance, from the periodic repetition of disjointed segments that corresponds to the description of the 1D Fibonacci tiling. Actually, since we have considered a finite number of particles in the model, we obtain discrete points describing these lines. But in principle, the continuity can be checked, up to any given precision, by using a large enough approximant.

Theoretical studies on simple models[6, 7, 8, 9] suggest that we would be able to get a transformation from continuous to discontinuous "atomic" lines, if we could tune the strength of the interactions between the two grains with respect to the interactions inside the grains.

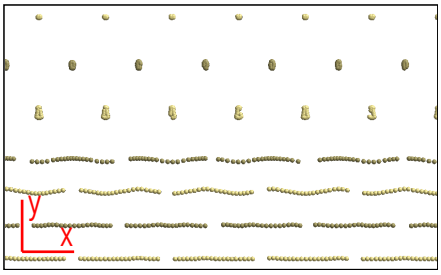

Fig. 7. – Superposition of successive snapshots showing the atomic displacements when the lower grain glides with respect to the upper one.

However here, the same material is present on both sides of the interface and it happens that the relaxations lead to continuous lines.

Hypo-friction. – By changing the position of the physical o–x line in the virtual (x,i)-space at fixed orientation (see figure 6), different intersections with the periodic set of lines are obtained, which correspond to different structures with different atomic positions. But because of the irrational orientation of $o-x$ line, these structures are locally isomorphic and would be indistinguishable from the original one[19, 20]. They are related by *phasons*. In particular, we can conclude that the energy would be conserved.

Because the "atomic" lines are continuous, figure 6 shows that a continuous translation of o–x leads to a continuous move of one grain along o–x (the intersections with vertical lines go on one side) and of the other grain in the opposite direction (the intersections with horizontal lines go on the other side). This means that the two grains are gliding against each other at *constant potential energy*. Hence there is no friction due to adhesion.

To check this property numerically, two relaxed atomic configurations were constructed as described previously, but with a different relative position of the grains along x. The relative difference of the interface energy is less than 3×10^{-6} and comes from numerical errors and from the use of $17:12$ approximants instead of a perfect incommensurate interface. Using an algorithm of the Ulitsky and Elber type[21], the minimum energy path between these two configurations was computed. Such a path follows the gradient of the energy surface in the configuration space from one local minimum to another. Thus it is perpendicular to the iso-energy surfaces and can be used to determine the saddle points, *i.e.* the energy barriers. Here the minimum energy path was found completely flat to a relative precision of 4×10^{-4}. Therefore the forces are null and the energy is minimum for all the configurations along the path.

The atomic trajectories corresponding to this path are shown on figure 7. The atoms adjust their positions during the displacement of the grains. When an atom acquires a higher energy, this is exactly balanced by other atoms lowering their energies, thus leading to a glide of the grains without friction. In fact, as can be guessed from the similarity of figures 6 and 7, the virtual direction i we have introduced to describe the interface, can be identified with time t in the case of a constant velocity glide of the grains. In this case, the "atomic" lines in the 4D hyper-space are just the atomic trajectories in the space-time.

Note that this hypo-friction property is linked to the property of the "atomic" lines being continuous in hyper-space. Indeed, during the grain displacement, the structure is always

described by a cut of the lines. Discontinuities would imply atomic jumps from one position to another during which the structure would not be locally isomorphic to the stable structures and thus would correspond to energy barriers.

Conclusions. – Computer simulations have been made to successfully model a non symmetric and non periodic interface in gold. The interface belongs to the incommensurate composite structures[2] but its unique feature is that it consists of only one type of particle, *i.e.* gold atoms. Using the theory of incommensurate structures and quasicrystals, a complete hyper-space description has been given which allows us to index the diffraction streaks.

From this description, we can deduce that the interface should have the property of hypofriction and that it corresponds to a practical realization of a Frenkel-Kontorova-Tomlinson model[9]. We have checked the frictionless glide by computer simulation. Of course, this property is clearly not limited to gold, but for other materials one should check, first, that the interface is stable and, second, that the hyper-space description corresponds to a network of continuous lines.

Besides adhesion, other sources of friction exist, as for instance defects or roughness. But the existence of this property for a simple interface is certainly important in the field of microtechnology, since two grains set with this orientation will be adherent (constant separation in the y direction); they will be fixed along z (until the plasticity domain is reached), but they will glide along the incommensurate x direction. Since this property is strictly true only for an infinite interface along x, we can deduce that the sides of real grains will limit this property. At the grain edges the atomic relaxations are different. Thus, finite interfaces of this type may be subject to friction, but this edge effect is not proportional to the contact area.

REFERENCES

[1] Pénisson J.-M., Lançon F. and Dahmen U., *9th International Conference on Intergranular and Interphase Boundaries in materials (iin98), Prague 1998*, *Materials Science Forum*, **294-296** (1999) 27–34, trans Tech Publications.

[2] Janssen T. and Janner A., *Advances in Physics*, **36** (1987) 519–624.

[3] Janssen T. and Radulescu O., *Z. Phys. B*, **104** (1997) 657–660.

[4] Janssen T., *Physics Report*, **168** (1988) 55–113.

[5] Hippert F. and Gratias D. (editors), *Lectures on quasicrystals* (Les éditions de physique, Les Ulis, France) (1994).

[6] Aubry S., in *Solitons and Condensed Matter Physics*, edited by A. R. Bishop and T. Schneider (Springer-Verlag, Berlin Heidelberg), volume 8 of *Solid-State Sciences* (1978) pages 264–277.

[7] Gyalog T. and Thomas H., *Europhysics Letters*, **37** (1997) 195–200.

[8] Kawaguchi T. and Matsukawa H., *Physical Review B*, **58** (1998) 15866–15877.

[9] Weiss M. and Elmer F. J., *Physical Review B*, **53** (1996) 7539–7549.

[10] Hirano M., Shinjo K., Kaneko R. and Murata Y., *Phys. Rev. Lett.*, **78** (1997) 1448–1451.

[11] Stadelmann P., *Ultramicroscopy*, **21** (1987) 131.

[12] Rosato V., Guillopé M. and Legrand B., *Phil. Mag. A*, **59** (1989) 321–336.

[13] Deutsch T., Bayle P., Lançon F. and Thibault J., *J. Phys. : Condens. Matter*, **7** (1995) 6407–6421.

[14] Sutton A. P., *Acta metall.*, **36** (1988) 1291–1299.

[15] Shamsuzzoha M., Smith D. J. and Deymier P. A., *Phil. Mag. A*, **64** (1991) 719–733.

[16] Deymier P. A., Shamsuzzoha M. and Weinberg J. D., *J. Mater. Res.*, **6** (1991) 1461–1468.

[17] Shamsuzzoha M., Deymier P. A. and Smith D. J., *Scripta Materialia*, **35** (1996) 327–331.

[18] Mikaelyan K. N., Ovid'ko I. A. and Romanov A. E., *Materials Science and Engineering A*, **259** (1999) 132–137.

[19] Gratias D. and Thalal A., *Phil. Mag. Lett.*, **57** (1988) 63–68.

[20] Sutton A. P., *Progress in Materials Science*, **36** (1992) 167–202.

[21] Ulitsky A. and Elber R., *J. Chem. Phys.*, **92** (1990) 1510–1511.