Quasicrystals / Quasicristaux

Prolegomena of quasicrystals

Prolégomènes des quasicristaux

Jacques Friedel

Académie des sciences, 23, quai de Conti, 75270 Paris cedex 06, France

A R T I C L E   I N F O

A B S T R A C T

The first published observations of quasicrystals in metallic alloys were in harmony with the increasing complexity of the structural description of possible solid phases, due to specific properties of the magnetic and electric charges of electrons. This led to the complex crystal phases of Frank and Kasper and Meyer's prediction of quasicrystalline structures with original diffraction properties in the reciprocal space and local symmetries not allowed for crystals. The initial works on two-dimensional tilings by Penrose and others clarified the problems involved.

© 2013 Académie des sciences. Published by Elsevier Masson SAS. All rights reserved.

R É S U M É

La première observation publiée de quasicristaux dans les alliages métalliques était en harmonie avec la complexité croissante de la description structurale de phases solides possibles, liée aux propriétés des charges magnétiques et électriques des électrons. Ceci a conduit aux phases cristallines complexes de Frank et Kasper et à la prédiction par Meyer de structures quasicristallines aux propriétés spécifiques de diffraction dans l'espace réciproque ainsi que de symétries locales dans l'espace non permises pour des cristaux. Les travaux initiaux de Penrose et d'autres sur les pavages à deux dimensions ont clarifié ces questions.

© 2013 Académie des sciences. Published by Elsevier Masson SAS. All rights reserved.

1. Introduction

I am happy that this meeting on quasicrystals takes finally place under the auspices of our Academy of Sciences. It will be opened by Denis Gratias and concluded by John Werner Cahn, two of the four signatories of the first published paper on quasicrystals in 1984. I am sorry that Dan Shechtman is not able to join us, as he is the undisputed discoverer of quasicrystals in metallic alloys and for two years toured all celebrated crystallographers such as André Guinier in our Orsay laboratory without obtaining any worthwhile suggestion!

In fact, the concept of quasicrystals was at the time slowly maturing and it would need the enthusiastic meeting of chemists and physicists with mathematicians to progress quickly to a real comprehension (see for instance [1]). Having been a spectator of some of these early steps, I thought I might try and review this prehistoric situation with you.

2. Incommensurate structures

Classical crystallography described crystals, with their triple translational symmetries in terms of atoms, point charges with masses and some ionocovalent bondings. But it was progressively realized that electrons could play a direct role in atomic structures, especially in metals, to explain, for instance, the *Hume Rothery rules* [2] followed by a number of metallic alloys in terms of average numbers of valence electrons per atom ratios,[1] Nevill Mott and Harry Jones [3] had to assume in 1936 that, in such alloys, the sphere of nearly free electrons of conduction should enter in resonance, in the reciprocal space, with the atomic structure via the Brillouin zones boundaries. It will indeed turn out that most early examples of quasicrystals follow these Hume Rothery rules; and their stability is related to a larger number of Brillouin zone boundaries than in face-centered cubic structures, the most compact crystalline ones [6,7].

Then, in 1939, Louis Néel stated that not all transitional 3*d* metals were ferromagnetic, but that some — Mn and Co — were *antiferromagnetic*, with magnetic moments of neighboring atoms antiparallel at low temperatures. This was not accepted easily by crystallographers or by quantum physicists until Shull showed after the war, by neutron scattering, that Néel merited indeed a Nobel prize. *Magnetocrystallography* then flourished, arranging magnetic moments in various ways in space. Thus, an antiferromagnetism incommensurate with the atomic lattice was observed in the 1960s and understood independently by Jacques Villain, from our Academy, and a Japanese scientist: in such metallic alloys, the interatomic magnetic couplings do produce a *helicoidal* arrangement, with a pitch usually incommensurate to the lattice.

But this kind of analysis was complicated by the somewhat slow and complex development of the possibility of *charge-* and *spin-density waves* in a gas of free electrons. Charge-density waves (CDW) were first envisaged by Rudolf Peierls in 1929 as a possible instability of a gas of nearly free electrons weakly scattered by atoms in a metal, leading to a periodic distribution of electronic charge related to the Fermi wavelength and weakly shifting the atoms. Then, after the war, Lomer would extend the concept to spin-density waves (SDW) with an antiferromagnetism of period related again to the Fermi wavelength. In both cases, this period was usually *incommensurate* with the lattice. Also in such a case, I heard Herbert Fröhlich explain, in a seminar given in Bristol in 1951, that such electronic waves should be shifted in space by an electric field. This is the Fröhlich current, that was first measured in the US by Montceau from Grenoble and then much studied, notably in Orsay, on quasi 1D organic compounds, both for CDW and SDW.

3. Quasicrystals

All this increasing complexity, often but not always related to magnetism, led mathematicians to reflect on such problems. In the 1970s, *i.e.* well before Shechtman's quasicrystals, there were two complementary efforts.

First, in a book of 1972, Yves Meyer, from our Academy, described a crystallographic system by adding to the three dimensions of the real space, three more dimensions to describe supplementary effects (such as magnetism). He remarked that, in such six dimensions, one can define crystal structures with their translational symmetries that can also have symmetries that are not observed in three-dimensional crystals, such as five-fold rotational symmetries. Then, by projecting back this six-dimensional structure to three dimensions, two cases can occur. If the projection is along a period of the six-dimensional crystal structure, one obtains a complex but crystalline structure. Such is the case of the alloys studied by Frank and Kasper in the transitional alloys with large crystal period before 1984. But if one projects the six-dimensional crystal structure along a direction incommensurate with the periods of the six-dimensional one, one obtains a *new* structure, in fact a quasicrystal as defined nowadays: it is *not* a crystal structure with usual translational symmetries, but it can have orientational symmetries among those contained in the six-dimensional crystal. Finally, as for a crystal, the Fourier transform of such a three-dimensional structure shows fine diffraction spots of various intensities; but they cover densely the reciprocal space quasi-continuously with intensities variable from spot to spot.

Then, shortly after Yves Meyers's book, mathematicians and theoretical physicists like R. Penrose and crystallographers such as A.L. Mackay, both British scientists, devised ways of covering continuously the whole two-dimensional plane using a finite number of families of paving stones (tiles), all of the same form and size in each family. Those tilings could be disordered or show specific orientational symmetries, including five-fold ones, as for the famous Penrose tilings. They were not crystals, but showed specific orientational properties and produced in the reciprocal space diffraction spots analogous to those of Yves Meyers's quasicrystals. They were indeed quasicrystals in two dimensions.

4. Conclusions

I must stop at this point, except to say that Shechtman and Blech had their own ideas about the origin of what they observed. Working with electron scattering, they were interested in the small-scale properties of their alloys. They knew that Frank and Kasper had observed structures with local five-fold symmetries, which they attributed to metallic clusters of *icosahedral* symmetry. Such arrangements had been observed for a time in free clusters, first of rare gases; they were easily

---

[1] These Hume Rothery rules initially applied to *sp* metals with nearly free electrons. They were extended by Raynor to such alloys diluted with minority *d* or *f* components, by neglecting these atoms and their electrons in the electron per atom ratio: they indeed form virtual or real bound states. André Blandin gave the first self-consistent treatment of a second-order perturbation method leading to additive long-range interatomic interactions, valid for such metals and alloys and their defects [4,5].

shown to be somewhat distorted, but denser and more stable that the closest packed face-centered cubic crystal phases. Also, as stressed by C.F. Frank, such icosahedra had been invoked by Bernal in his description of liquid metals; and they were later taken as cornerstone of a network of rotational dislocations in the model proposed by J.-F. Sadoc and M. Kleman for amorphous metals. Blech and Shechtman proposed a structure model with a number of icosahedra placed in a local order, which could indeed explain qualitatively the diffraction spots observed in their alloys. What remains true in their remarks is that Hume Rothery's rules cannot apply to compounds with a majority of *transitional* elements, either Frank and Kasper phases or quasicrystals. In such compounds, the stability must be related to the topological arrangement of atoms, as first described by F. Cyrot-Lackmann [8] and F. Ducastelle [9]. Indeed, in a structure mostly made of icosahedra, one could expect a maximum of stability for an average number of d electrons per atom somewhat larger than five, due to the number of first atomic neighbors and of triangular closed interatomic paths compared with the face-centered cubic structure.

References

[1] M. Senechal, Report on the IHES Workshop on Mathematical Crystallography, Structural Topology # 11, 1985.
[2] W. Hume Rothery, O.V. Raynor, Studies in Metals and Alloys, Institute of Metals, London, 1954.
[3] N.F. Mott, H. Jones, Metals and Alloys, Clarendon Press, Oxford, 1936.
[4] A. Blandin, J. Déplanté, J. Friedel, J. Phys. Soc. Jpn., Suppl. II 18 (1963) 1980.
[5] A. Blandin, J. Friedel, G. Saada, J. Phys. 27 (C3) (1966) 128.
[6] J. Friedel, F. Denoyer, C. R. Acad. Sci. Paris, Ser. II 305 (1987) 171.
[7] J. Friedel, Helv. Phys. Acta 61 (1968) 538.
[8] F. Cyrot-Lackmann, Adv. Phys. 16 (1967) 393.
[9] F. Ducastelle, Order and Phase Stability in Alloys, North-Holland, Amsterdam, 1991.