

# After Twenty-Five Years on Quasicrystals: where are we, where shall we go? A Personal Outlook

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#### After Twenty-Five Years on Quasicrystals: where are we, where shall we go? A Personal Outlook

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Abstract. Twenty-five years after the historical discovery of a real material exhibiting five-fold symmetry, the scientific field opened thereof is still robust and active. On the experimental side, it was strengthened in recent years by new inputs coming from studies of transport properties, surface physics, coating technology, catalysis, etc. Its future probably relies upon combining these very exotic, but now extremely well documented materials with more conventional materials in composites, or challenging the discovery of new, or more flashing, properties in a systematic screening of intermetallics compounds of un-preceded compositions. An effort towards making quasicrystals better understood outside our own community has become mandatory in view of developing the field.

Keywords:

#### Introduction

Danny Shechtman was there the whole week. To the best of my knowledge, he attended all sessions, and he asked many questions. Most probably, he was very happy to see that 25.5 years after his historical discovery of the Al-Mn icosahedral quasicrystal in his electron microscope on April 8, 1982, at about 3 pm, so many people joined the Chairman of the conference to celebrate the Silver Jubilee of his discovery. That was certainly true for me, and many others, who were involved in studies of quasicrystals and complex intermetallics for more than two decades.

Unfortunately, not all of us were there. I especially remember Marko Jaric who did so much to understand the Fourier space of aperiodic crystals. He attended the ICQ5 conference, which I organised in Avignon 12 years ago (Figure 1), the only occasion so far to have a picture of all four co-authors of the first article published on quasicrystals [1] (on this event, only D. Gratias and D. Shechtman could make the trip to Tel Aviv). Per Bak, who triggered the most intense part of our research on quasicrystals with his famous question 'where are the atoms?' cannot bring his own answers anymore. Kehsin Kuo also was not there. Last Spring, he has decided to move to a place in the Heavens where he could study in peace the reciprocal space of moons and stars. We missed him and Per and Marko very much.

The conference attracted 90 participants from 17 different countries. Time for plenary and invited lectures, oral presentations and posters was allocated to various subjects:

- Crystallography: structure determination, diffraction, tilings, ...
- Formation: growth, stability, phase transformations, ...
- Transport properties and electronic structures, dynamic properties, ...
- Surface science of quasicrystals, potential applications, ...

Three specific sessions were of special relevance: the one devoted to the memory of K.H. Kuo and his works in the past,# the two others with their outlook at soft quasicrystals # and quasiperiodic metamaterials, # which are potential highlights in future research.

My job in Tel Aviv was to summarize at the final session the experimental part of the results presented at the conference, whereas Chris Henley gave a splendid overview on theory. My own contribution in this paper hereafter shall not go in detail to the many data collected in the present Proceedings Book, which would make no sense in duplicating

information and would certainly miss any in-depth understanding of each specific area of the scientific field created by Shechtman *et al.* # Instead, I will concentrate on an overview of the trends and breakthroughs that the <u>experimental</u> discovery of a piece of matter with forbidden point group symmetry has brought us during the two last decades or so (in contrast to non-periodic tilings and patterns that were known theoretically already before Shechtman's work [2]).

#### Trends and breakthroughs

The Reader will certainly forgive me if I stress immediately at the beginning of this section that the following matter is only a question of personal taste (as was the Introduction section, I am afraid), and for sure not a material that was selected after mature discussions among the community. I can only reflect my own impressions and the achievements I feel the most promising for the future of the field, based on my own skills and involvement in quasicrystals research over the past two decades. However, listening at the beautiful review talk delivered by Marjorie Senechal entitled 'Mapping the aperiodic landscape', # I have had the clear impression that the true usefulness of quasicrystals was there, in the definite impulsion it has given to some mathematics.

Regarding quasicrystals, the remnant question for two decades or so: 'do we know where the atoms are?', was addressed at the beginning of the meeting by Denis Gratias. # Following his pretty technical, but absolutely clear talk, I felt myself convinced that, yes indeed, we know where they are. Pushing it a little bit too far, I believed for a while that we always knew! The consistency of experimental data and modelling is today so high that full confidence can be given to high dimensional crystallography models applied to an increasingly large number of systems, starting with icosahedral AlCuFe and ending in recent months with Cd-Yb shining on the front page of Nature Materials [3].

This latter system was the last one discovered in Tsai's group at NIMS, Tsukuba. **#** For the first time, a binary compound exhibited icosahedral symmetry, yet being a stable alloy. The hunt for aperiodic alloys or compounds began immediately after Shechtman's discovery and has never ended so far. Considering the tremendous efforts dedicated over several decades by the aeronautic and automotive industries to aluminium-based alloys, later to all kinds of metals and alloys, the breakthroughs of Shechtman and Tsai (*et coll.*) have a profound significance to young scientists: if you are convinced that your idea is well sounded, never give up! Like Danny Shechtman, you may discover the Graal, even in regions of knowledge that were explored several times before you. Along the same line, the remarkable electron diffraction studies by K.H. Kuo, who discovered 8-fold symmetry, were evocated at a special session dedicated to his memory. In total, judging from the efficiency of modern diffraction methods that were presented at the meeting (now that basic theoretical issues are resolved), it seemed to me that life is going easy (well, easier) to determine atomic positions in all kinds of compounds.

Major advances on the determination of physical properties were made possible when in the last decade or so quasicrystalline single grains of excellent lattice perfection were made available by few groups in the world. Essential aspects of phase selection rules for the formation of quasicrystals were presented, as well as growth and faceting, both from experimental and theoretical viewpoints. Esther Belin-Ferré and myself tried to answer another basic question (why are the atoms where they are?) regarding complexity in Al-Mg compounds. #

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A potentially important set of results by Prof. Kimura's group # concerned the occurrence of 10-fold aperiodicity in a boron-containing alloy. In my opinion, it may open a gate to finding entirely new types of quasicrystals and is therefore worth to be mentioned here. Transport properties offered the matter to two attractive sessions, from which I will remember the data by Dolinsek *et al.* # about the anisotropy of electronic transport in Al-Cr-Fe complex compounds (decagonal approximants). Phonons and phasons were subjects of intense research in the past decade, as M. de Boissieu could demonstrate in his review talk. # Coupled to phason dynamics, the notion of metadislocation, which was introduced by Urban and Feuerbacher [4], is presumably one of the key notions that quasicrystals research has introduced in condensed matter physics. It was carefully explained to the audience by one of the inventors (we missed the presence of the other who could not make the trip due to family reasons). #

Surface physics and crystallography was a major part in the conference. After a review by Ronan McGrath, **#** two sessions have addressed important points of surface structures (where are the atoms at the surface?), growth of surface layers, especially of aperiodic monolayers, and their electronic properties, adsorption of molecular layers, aperiodic surfaces as templates for new bottom-up quantum systems, etc. A small number of years after the discovery of Shechtman, surface science of quasicrystals has lead us [5] to explore the potential applications of approximants first, now of so-called CMAs (Complex Metallic Alloys, formerly SCAPs as in Ref. 4) in the frame of a European Network of Excellence bearing the same acronym. A review of potential applications of this broad family of alloys was given, **#** showing that progress is visible over the years, but with a slow kinetics. Competition with other materials on the one hand, and technical barriers like preparation of high quality thin films on the other, explain the fact.

In total, I could convince myself that the field of quasicrystals experimental research is still active, based for instance on the number of new quasicrystals compositions that were announced at the conference, e.g. by Prof. Ishimasa's group in Japan. # It must be accepted however that the number of interested scientists has declined substantially in comparison to early times (Fig. 1). In Europe, this is possibly an artefact since most of us are engaged now in the CMA network and consider quasicrystals as a specific case, but of high relevance, of complex metallic alloys. # quote K. Hoehener In Asia, the situation is more contrasted, but I was amazed by the high participation of Japanese groups. Simultaneously, the turn taken towards soft quasicrystals, towards aperiodic phononic and photonic crystals, towards metamaterials shows an appealing trend to renew the field and open it to other communities in physics (which is a minimum) and more generally to society requirements. As I could stress in my conclusion speech, maybe too abruptly, there is today quite a need for the quasicrystals community to make an effort to communicate better its results and impact on modern science to the external world. Initial difficulties raised by the great chemist Linus Pauling [6], and the absolute necessity to understand at that time "where the atoms are" have isolated the community and forced it to use a jargon that is difficult to grasp by most scientists and for sure by the layman. Twenty-five years after the discovery, this situation is behind us and there is no reason anymore not to put emphasis on "who we are" and "what we do", and not only on "where they are".

#### What I missed

Unfortunately, there was no time to address several subjects of importance in the field of quasicrystals. A fully balanced account of the inputs from all disciplines that contributed to quasicrystals sciences could therefore not be elaborated, but I actually missed some of them,

which appeared especially crucial in our field. First, I would like to mention metallurgy. Most, if not all, studies of physical properties of quasicrystals is nowadays based on the availability of single grain samples of the best quality. Such samples are grown in a very limited number of research centres (Ames, Frankfurt, Juelich, Munich, Tsukuba to quote nearly all of them), and represent a real achievement of our community, pointing out that stability and crystal perfection do not necessarily go with translation symmetry. This effort was not that much represented at the conference, nor was the tremendous work on phase diagram studies that an even smaller number of groups (especially the one of R. Lueck in Stuttgart) has supplied over the years. Along the same line, efforts were also dedicated to the supply of good quality multigrain specimens in view of an easier study of surface mechanical, catalytic, corrosion, oxidation, etc. studies. Sintering techniques able to produce large samples were pioneered in Nancy and Ames, thermal spraying was used in Korea, France, Ukraine, etc. in this respect. Development of thin film technologies adapted to the extreme sensitivity of quasicrystals compositions is currently attempted in few places because it opens the path to commercial applications in energy savings (reduced friction, protection against corrosion, lower adhesion, etc.), a topic of undisputed importance in many industries. I regretted that no expert from these domains could attend the conference, but I also understand that the most advanced ones would certainly not have accepted to divulge their results at a public meeting.

As shown above, the conference was very much oriented towards physical properties. This is a natural trend in quasicrystals science because chemical properties are determined by the (surface) composition and exhibit no correlation to the crystal structure (so far, and to the best of my knowledge). Nevertheless, oxidised or corroded quasicrystals show a great potential for technological applications, especially in the field of catalysis where Tsai *et al.* could quantify the potential of Al-based quasicrystals after leaching in alkaline solutions [7]. Proof was also brought that the performance of the catalyst is indirectly related to the underlying quasicrystal structure and composition, which slow down grain coarsening of the transition metal active element that has precipitated at the surface during leaching.

To end with, I mention that I also missed the presence of artists, who had recognized the importance of five-fold symmetry and absence of periodic order well before Penrose himself drew his famous pattern in an artistic spirit. Another example is the use of the grid method by Muslim artists in the south of Spain, by Middle Age times, that was demonstrated for the first time by Hans-Ude Nissen at an international meeting that I organised with Janusz Wolny in Krakow, Poland in July 1996 (for an illustration, see the last figure in Ref. 8). Yet, art was not absent as long as Reinhart Lueck # and Shalomo Ben Abraham # could show many of their computer-drawn patterns with so far unpublished colour symmetries. On this subject, a joint meeting of artists and mathematicians or physics theoreticians was clearly beyond the scope of the present meeting and remains to be organised in future.

#### Conclusion

The Quasicrystals Silver Jubilee was beyond doubt an excellent international meeting. The balance between experimental subjects and theory was fair. It traced clearly the many difficulties that the community has overcome in two and a half decades to transform the field in a major part of condensed matter sciences, starting from an exquisite experimental discovery due to a single man at a single point in time. Many of us contributed to this development in the months and years that followed the divulgation of the discovery in literature and, immediately afterwards, the publication in the US, France and Russia of a few theoretical articles explaining the structure of the reciprocal space of quasicrystals. The most important contribution, in my opinion, was the one by Tsai and his recurrent discovery of stable quasicrystals between 1987 and today. The existence of stable quasicrystals, which was also not foreseen before, meant immediately in my mind the possibility to secure potential applications of those materials [5]. Theory, and especially the definition of what is actually a (quasi)crystal, evolved in parallel [9, 10]. I definitely believe that this beautiful human venture gave to most of us our best moments in research. Possibly also, few of us are already looking forward to attending the Quasicrystals Mn<sub>2</sub>-Jubilee in 2032!

Till this point, nobody can ignore who was the Chairman of this very successful conference. Prof. Ron Lifshitz was not only the organiser of the event, he was his soul! He made it extremely well, owing to his careful selection of topics, organisation of by-side tours and warm welcome to each and every one. As a witness of the pre-conference time, when arguments rose to postpone the 25<sup>th</sup> anniversary of the discovery of quasicrystals on April 8<sup>th</sup>, 1982, to a later date in 2009 that would have better fitted the views of a few, I can testify that Ron behaved in an exceptional way, combining fairness to opponents and strength and will to install the conference as it had been decided in Ames by the international community at the ICQ8 conference (May 2005). It is my privilege to congratulate him, and all in his team, for making the Quasicrystal Jubilee Conference a most important and rewarding meeting.

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#### Figure caption

The international community on quasicrystals meeting in Avignon, France in 1995. The four authors of Ref. 1 are seating in the middle of the front raw. To the best of my knowledge, this was the first time they met all four. Possibly, they never met again. The young man with a pink shirt in the same raw became the Chairman of the 25<sup>th</sup> anniversary meeting.



