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# Quasicrystals: diversity and complexity

Jean-Marie Dubois[a] and Ron Lifshitz[b]*

[a]*Institut Jean Lamour (UMR 7198 CNRS, UHP, INPL, UPVM), Ecole des Mines, Parc de Saurupt, CS14234, F-54042 Nancy, France;* [b]*Raymond and Beverly Sackler School of Physics and Astronomy, Tel Aviv University, Tel Aviv 69978, Israel*

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Scientific presentations at ICQ11 — the 11th International Conference on Quasicrystals, which took place in Sapporo, Japan, in June 2010 — offered a variety of stimulating new experimental data and novel theoretical results. New aperiodic crystals were presented; new theoretical ideas were described; exciting experimental results were revealed; and potential applications of quasicrystals were reviewed, showing an unprecedented level of development. ICQ11 was a great success thanks to the high standard of its scientific content and to the efficiency of its organization. ICQ11 proved that quasicrystal research is sure to continue offering diverse challenges and profound insights into the complexity of matter.

**Keywords:** quasicrystals; aperiodic crystals; complex metallic alloys (CMA); electronic and magnetic properties; soft matter; surface science; metamaterials; applications

## 1. The 11th international conference on quasicrystals

The International Conference on Quasicrystals was convened in Sapporo, on June 13–18, 2010, for the second time in Japan, and the 11th since its inception in Les Houches, in 1985. The program was exceptional in its diversity, with 145 contributions, covering topics like formation, growth and stability; structure and modeling; mathematics; physical properties; surfaces and overlayers; applications; and metamaterials. Such a variety of subjects can be taken as a promising fingerprint for the future of the field. These notes do not provide an accurate summary of the conference, nor do they reflect an exact assessment of the current status of quasicrystal research. They are merely a selection of highlights from the conference — reflecting our own personal tastes and biases — whose purpose is to demonstrate that quasicrystals are still very interesting and challenging almost three decades after their discovery [1].

## 2. New materials, better samples, improved experimental results

It is quite common in conferences on quasicrystals to learn of newly discovered quasicrystal-forming alloy systems. ICQ11 was no exception. Only a mere decade has

*Corresponding author. Email: ronlif@tau.ac.il

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passed since the discovery of the first stable *binary* quasicrystals, CdYb and CdCa [2]. Their discovery was of great importance, not only because it demonstrated that one does not require three different metals to stabilize a quasicrystal; owing to their relative simplicity, binary quasicrystals allowed for the first essentially complete structural solution of an icosahedral quasicrystal [3]. It was therefore very exciting to hear Alan Goldman's presentation of a new binary quasicrystal—icosahedral $Sc_{12}Zn_{88}$ [4]. The new AgInYb icosahedral quasicrystal [5], which is believed to be isostructural to the *i*-CdYb quasicrystal, with Cd being replaced by AgIn, was presented by Marc de Boissieu [6], and shown to display superb crystal quality lending itself to detailed quantitative studies of phason modes. It was also the focus of state-of-the-art surface studies, presented by Hem Raj Sharma [7]. A newly discovered decagonal AlPdZn quasicrystal was presented by Patricia Thiel [8], who showed X-ray photoemission spectroscopy and STM studies of its surface, establishing that Zn is very weakly bound in this new quasicrystal.

These few examples, along with other materials like the elaborate $\gamma$-brass superstructures discussed by Stephen Lee [9], demonstrate the high degree with which the metallurgy of quasicrystals and related complex metallic alloys (CMAs) [10] is mastered today by different groups throughout the world. This is especially true for the growth of high-quality single crystals, using various techniques like the flux growth method used for the new binary *i*-$Sc_{12}Zn_{88}$ system [4]. The effort to offer excellent single-grain samples for careful studies of physical properties was very active in recent years, and received a particular boost in Europe thanks to the CMA Network of Excellence, which focused a significant effort (both in terms of funding and human resources) on disseminating such samples, as shown in Figure 1.

The increased availability of samples of excellent perfection has made a definite impact on the program of ICQ11. As a consequence, there was an increased emphasis on very careful and detailed experimental studies of physical properties. For example, in many samples these days, physical properties can readily be measured as a function of direction in real space. This was very nicely demonstrated in Ana Smontara's studies of transport properties in anisotropic complex metallic alloys [11]. Of course, better samples lead to improved understanding of the nature of quasicrystals, and the ability to make quantitative and precise experimental discoveries. For example, new insight was offered by U. Mizutani [12] on the interplay between Hume–Rothery stabilization and hybridization effects. A clear correlation was established by Roland Widmer [13] between local variations in the density of states (DOS) and the electrical resistivity in high-quality Al-based quasicrystals and CMAs. This was based on careful scanning tunneling spectroscopy (STS) measurements, showing that localized electronic states form at the bottom of the pseudo-gap, as evidenced by a spiky local DOS that varies from one position to the next. Studies of magnetic properties have seen a renewal thanks to the availability of high-quality specimens containing rare earths, as in the studies of single grains of $Cd_6R$ (R = rare earth) approximants, presented by Ryuji Tamura [14]. And as a final example we mention the exquisite studies of point-defect distributions in an ideal decagonal AlNiCo quasicrystal using aberration-corrected ultrahigh-resolution scanning transmission electron microscopy, presented by Eiji Abe [15].


Figure 1. Examples of CMA single grains grown by Czochralsky pulling out of $Al_{13}TM_4$ Taylor phases (TM = Fe, Ni, Co, (Fe,Ni), (Co, Ni), Ru) by P. Gille at the University of Munich in the framework of the CMA European Network of Excellence. The scale is indicated by a bar or by a mm-grid placed behind the specimen.



## 3. Advances in theory

Great strides have been made on the theoretical front in recent years, as demonstrated by numerous presentations at ICQ11. The increased sophistication in experimental methods, discussed above, is clearly complemented by highly advanced theoretical and numerical methods that are used for analyzing quasicrystals. Notable examples are the energetic calculations of the structural stability of AlPdMn approximants, presented by Marek Mihalkovič [16]; the calculations of the stability of $\gamma$-brass superstructures, by Stephen Lee [9]; and the *ab initio* calculations of surface catalysis, presented by Marian Krajčí [17], which we discuss further below.

Electronic properties of quasicrystals continue to be a central topic for theoretical study. Old models, like the simple Fibonacci quasicrystal, continue to provide new results [18], but more significant are the novel ideas that are constantly introduced to try to understand the behavior of electrons in quasicrystals. For example, Mikhail Chernikov [19] showed new predictions for many of the electronic properties, based on a fractional Fermi-surface model [20], whereby the interaction between the Fermi sphere and the pseudo-Brillouin zone in icosahedral quasicrystals leads to a shattering of the Fermi surface into very small electron–hole pockets. Guy Trambly de Laissardière [21] showed that, whereas medium-range quasiperiodic order is known to lead to insulating-like behavior in certain three-dimensional quasicrystals, long-range quasiperiodic order in two dimensions may lead to a metal–insulator transition. We note also that one of us has proposed to contrast the electronic properties of Al-based quasicrystals and related CMAs with their lattice complexity [22], using the information entropy attached to their unit cell as a classification index.

The mathematics of quasicrystals has also experienced major advances in recent years [23]. Aperiodic tilings are now studied and classified using advanced topological tools, as explained by Franz Gähler [24]; and new methods are being devised for the generation of icosahedral tilings, as described by Nobuhisa Fujita [25]. Traditional theories of color symmetry [26] and magnetic order [27,28] have been generalized to deal with imperfect and partial coloring, as we saw in the presentations of Peter Zeiner [29] and Louise de Las Peñas [30], and in a new model of frustrated antiferromagnetic order on the Penrose tiling that was presented by Anu Jagannathan [31]. But probably most exciting is the fact that diffraction theory has gained much progress, bringing us closer than ever to the point where we can understand what constitutes a crystal [32,33], namely, what sets of points in space give rise to Bragg peaks in their diffraction [34]. Jeong-Yup Lee [35] described a computational algorithm that can determine whether a tiling, created by substitution, is a crystal; and Michael Baake [36] took the theory beyond the crystallographic domain, describing the diffraction of various random sets of points.



## 4. Surface studies

Studies of the surfaces of quasicrystals have become a central component of quasicrystal research in the last decade or so [37,38]—a consequence of the availability of high-quality samples, discussed above, but also of the rapid development of sophisticated experimental techniques. Reports on surface studies at ICQ11 were numerous, providing important information not only on the surface structures but also, and maybe more importantly, on electronic, mechanical, tribological, and other physical properties of quasicrystals. They addressed essentially two distinct areas of surface science: the surface properties of new materials on the one hand, and the use of previously studied materials as templates for the growth of artificial structures, on the other hand.

In addition to the STS studies, mentioned above [13], crystallography was complemented by electronic structure studies, leading to the first observation, at the surface, of the underlying cluster covering in a decagonal material [39]. The surface properties of less complex metallic alloys, like $Al_{13}Co_4$, were studied numerically by Marian Krajčí [17] using *ab initio* methods, in relation to their potential for offering attractive catalytic properties. This potential was demonstrated by the group of An Pang Tsai, who studied the performance of catalysts produced from AlNiCo decagonal quasicrystals [40] and AlCuFe icosahedral quasicrystals [41] regarding methane reforming and hydrogen production, respectively. The use of quasicrystal surfaces as templates for inducing the growth of two-dimensional atomic layers with quasiperiodic order has become a very active aspect of quasicrystal research [37]. Many examples were presented at ICQ11, including the deposition of Ag, Cu, Bi, Sb, and Pb on different quasicrystals or CMAs [7,42–46], self-segregation of Zn at the surface of decagonal AlMgZn [8], and the formation of quantum dots confining electrons on quasicrystalline templates [47].

Macroscopic surface properties, especially the surface energy, are very difficult to assess experimentally. Theoretically, or numerically, they still fall beyond the power of contemporary computers and can be tackled only for simple enough CMAs as was shown at ICQ11 [48]. Practical empirical studies of surface phenomena, however, indicate that there is a great potential for further progress to understand better the origin of solid friction, using model systems based on CMA samples in relation to their crystal complexity [22].

## 5. Mesoscopic quasicrystals

Recent years have brought a surge of scientific interest in experimental systems, exhibiting quasiperiodic long-range order on a scale much greater than that of atomic quasicrystals — typically from tens of nanometers to tens of microns — collectively referred to as *mesoscopic quasicrystals*. First discovered in liquid crystals made of micelle-forming dendrimers [49], self-assembled mesoscopic quasicrystals have since appeared in other systems such as ABC-star polymers [50], and binary systems of nanoparticles [51]. They have also been created artificially in a variety of systems, such as nonlinear optical fields [52,53], and colloidal monolayers [54,55]. These newly-realized mesoscopic quasicrystals not only provide exciting platforms for the fundamental study of the physics of quasicrystals. They also hold the promise for new applications based on artificial or self-assembled nanomaterials with unique physical properties that take advantage of the quasiperiodicity, like photonic quasicrystals [56–60]. It is no surprise that mesoscopic quasicrystals took center stage at ICQ11.

Yushu Matsushita gave an exposition of the variety of intriguing phases that form in systems of block co-polymers and ABC-star polymers, including the mesoscale dodecagonal quasicrystal that was recently discovered [50]. Changhong Xiao [61] presented a newly discovered dodecagonal quasicrystal that self-assembles in mesoporous silica (Figure 2), adding yet another example to the growing number of mesoscale systems that form 12-fold quasicrystals. Theories of the growth and thermodynamic stability of these quasicrystals are only beginning to appear [62–64]. Tomonari Dotera added important insight to these theories by describing the dynamics of structural transitions in ABC-star polymeric quasicrystals [65]. An important message that emerges from these presentations — in combination with the increased number and quality of quasicrystals in the solid state, mentioned earlier — is that the growth and stability of quasicrystals is much more robust than one could have ever imagined when their discovery was first announced [1]. Michael Engel demonstrated this point very effectively at ICQ11 by showing numerically that even simple tetrahedra, acting via a hard-core potential, can self-assemble into a dodecagonal quasicrystal [66]. We also heard from Paul Steinhardt, in an engaging detective-style story, that quasicrystals also form naturally, as a natural AlCuFe quasicrystal was found embedded in a rock, which originated from Kamchatka [67].

Mesoscopic quasicrystals can also be constructed artificially, either by direct fabrication at the level of individual structural elements, or through dynamical

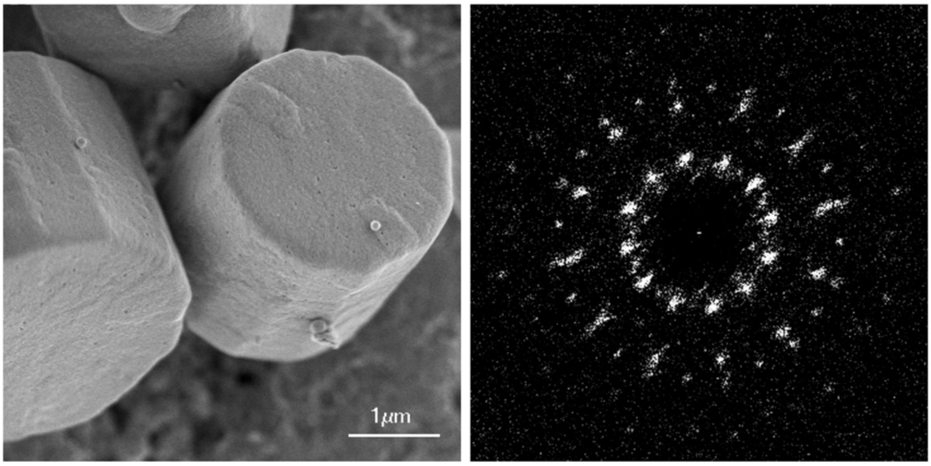


Figure 2. Dodecagonal-prism morphology of the mesoporous silica crystal (left), and an electron diffraction pattern from the central part of the sectioned crystal (right). Images courtesy of Changhong Xiao and Osamu Terasaki [61].



formation as a result of trapping or manipulation by external forces or fields. Both of these approaches were presented at ICQ11. Clemens Bechinger gave an overview of the great opportunities offered for the study of quasicrystals by colloidal particles in quasiperiodic light fields [54]. As an a example, he was able to explain why rank-4 quasicrystals (with 5-, 8-, 10-, and 12-fold symmetry) are more readily stabilized than rank-6 quasicrystals (with 7-, 9-, 14-, and 18-fold symmetry) [55]. This result may offer important insight into the current quest for the discovery of heptagonal quasicrystals in the solid state [68], which was also discussed at ICQ11 by Orsini-Rosenberg [69]. Applications based on artificial mesoscopic quasicrystals were also presented at the conference. For example, Xiangdong Zhang [70] described negative refraction metamaterials based on high-symmetry two-dimensional quasicrystals; and Vyacheslav Misko [71] showed how one could enhance the critical currents in superconductors by fabricating quasiperiodic pinning arrays at the nanoscale.

## 6. New applications

It has been traditionally considered in our community that reduced friction is a major source for potential applications of quasicrystals and CMAs [72]. This is still true, but many other potential applications were presented at ICQ11 that should inspire the true inventor. The fabrication of composites, combining reduced specific weight with enhanced mechanical resistance, is probably one of the major issues along this line. A few systems were presented: Limin Wang [73] showed the use of icosahedral Ti-Ni-Zr particles to reinforce a polymer (exactly as it was done many years ago at Ames Laboratories, but using *i*-Al-Cu-Fe powders); Hidetoshi Somekawa [74] described the management of self-precipitation to produce light Mg-Zn-Al alloys of outstanding mechanical properties; and Samuel Kenzari [75] demonstrated the direct prototyping of mechanical parts reinforced by Al-Cu-Fe powders by selective laser sintering. Since application of this latter technology has already led to the production of real parts by an industrial company, the vein of composites is presumably the one that may lead the soonest to commercialization.

Catalysts based on quasicrystalline precursors, which were pioneered in Japan by An Pang Tsai, are also fairly promising since they are supported by a home industry with the view that expensive catalysts like Pd will sooner or later be replaced by more cost-effective materials [76]. Quite a few examples were presented at ICQ11, such as a novel catalyst, made of a decagonal AlCoNi quasicrystal, for steam reforming of methane [40]. As mentioned above, this effort is combined with theoretical work based on *ab initio* numerical calculations, as was presented by Marian Krajčí [17], with the aim of showing that specific sites on the surfaces of certain CMAs may exhibit intrinsic catalytic properties of technological relevance.

Finally, a number of potential applications of CMAs and quasicrystals was presented at ICQ11, having in common the exploitation of one or other transport property of the material. Hydrogen storage was such an example, and was addressed by several posters. For example, a very careful study of the stability region in the Ti-Ni-Zr phase diagram was presented by Andraz Kocjan [77], showing how contrasted storage varies enormously with the details of the composition field. It was a delight to see how imaginative some applications may be, regarding for instance the storage of information in a Taylor approximant, using only a thermal excursion of the specimen placed in a magnetic field, presented by Janez Dolinšek [78], or how a thermal rectifier may be produced out of an ensemble of AlCuFe layers of adequately chosen conductivity, as show by Tsunehiro Takeuchi [79]. Finally, as mentioned above, mesoscopic systems like photonic quasicrystals [70] or superconductor arrays [71] may inherit interesting properties leading to an application when their internal structure is ordered quasiperiodically.



## 7. Conclusions

ICQ11 was not only a place for stimulating scientific exchange, but also an opportunity to meet again as a community. Ample time was allotted for personal interaction in the delightful social program, which was organized with as great dedication and care as the scientific program itself. ICQ11 was organized to perfection by its Chairs, Profs. Yasushi Ishii and Tsutomu Ishimasa, shown in Figure 3. We are extremely grateful to them and to their co-organizers for their great work.

For our community, ICQ11 was marked by a combination of sorrow and joy. A special session, devoted to structural studies of decagonal AlNiCo, was dedicated to the memory of the late Dr. Stefan Ritsch, who recently passed away. Reinhard Lück, who chaired the session, spoke very vividly and emotionally of Stefan Ritsch. Stefan will be forever remembered by all of us who knew him.

On the joyful side, the 3rd Jean-Marie Dubois Award was presented at ICQ11 to Marc de Boissieu in recognition of his important and pioneering work on the lattice dynamics, phasons, and atomic structure of quasicrystals. Earlier awards were given to An Pang Tsai at ICQ9 in 2005 (Ames, Iowa) in recognition of

Figure 3. Profs. T. Ishimasa (left) and Y. Ishii (center), in the company of Prof. A. Goldman (who co-organized ICQ4 some years ago) at the conference dinner.



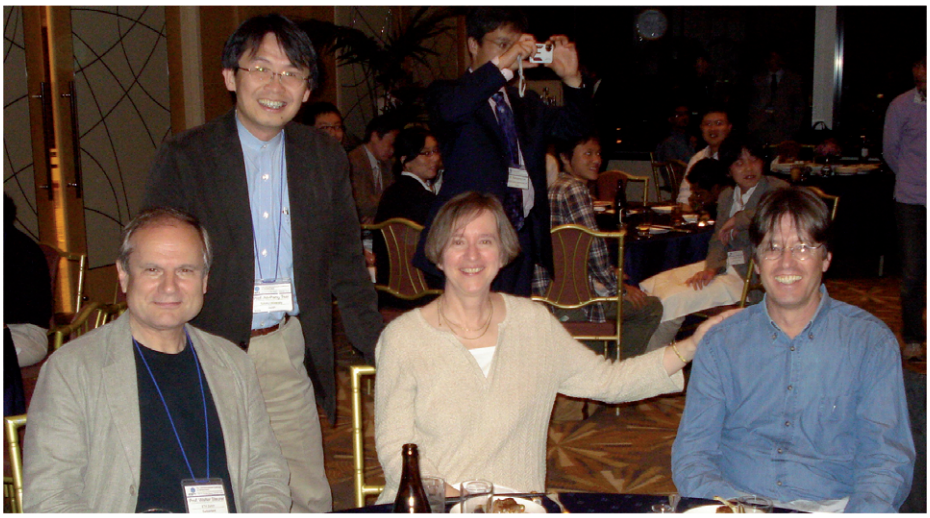

Figure 4. Patricia Thiel (in the middle) surrounded by the three recipients of the Jean-Marie Dubois Award: Walter Steurer (left), An-Pang Tsai (standing) and Marc de Boissieu (right).

fundamentally-important discoveries of new quasicrystalline phases; and to Walter Steurer at ICQ10 in 2008 (Zürich, Switzerland), in recognition of his important pioneering work on the atomic structure, formation, and stability of quasicrystals, particularly decagonal phases. All three recipients participated at ICQ11, and are shown in Figure 4 together with Patricia Thiel, the Award Secretary. The community is extremely grateful to Pat for managing the Award and to Iowa State University for sponsoring and maintaining the endowment for the Award.

As always, awards were also presented to young scientists, who were carefully selected by a special committee chaired Prof. Kaoru Kimura, for the best presentations at the conference. They were awarded to Holger Euchner (Stuttgart University) for his talk on lattice dynamics in complex ZnMg phases; to Hayato Iga

(Hokkaido University) for his poster presentation of an approximant of the dodecagonal quasicrystal in Mn-Si-(Cr,V) alloys; to Jules Mikhael (Stuttgart University) for his study of structural phase transitions in dense colloidal monolayers on quasiperiodic light potentials; and finally to Yeong-Gi So (University of Tokyo) for his poster on internal friction studies of icosahedral quasicrystals and their periodic approximants. We congratulate our young colleagues and wish them a fruitful and enriching scientific career.

At the official opening of the conference, the Chairs noted that Hokkaido University was the place where, in 1936, Dr. Ukichiro Nakaya successfully produced the world's first artificial snowflake. Accordingly, the logo of ICQ11 was designed by Cesar Pay Gómez to symbolize the past and the future — going from the snow crystal to the quasicrystal. After having produced the snowflake, Dr. Nakaya coined the famous phrase "Snow — a letter from the sky". The conference Chairs challenged us to find a proper ending to the corresponding phrase for quasicrystals. We believe that it should be "Quasicrystals — a letter from the future". It was on April 8th, 1982, that Dan Shechtman received this letter, shattering the foundations of crystallography [80]. He was clever enough not to dismiss the letter, thereby initiating a true scientific revolution, as described in John Cahn's concluding remarks of ICQ5 [81]. That future — from which the letter was received 28 years ago — is here now. Let us be sure to make the most of it, for — as in the words of Mackay and Kramer [82] — "it is too rarely that we see such a stimulating experiment as Shechtman's".



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