

Quasi-periodic Materials – Crystal Redefined

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Crystallography has been one of the mature sciences. Over the years, the modern science of crystallography that started by experimenting with x-ray diffraction from crystals in 1912 has developed a major paradigm – that all crystals are ordered and periodic. Indeed, this was the basis for the definition of “crystal” in textbooks on crystallography and x-ray diffraction. Based upon a vast number of experimental data, constantly improving research tools, and deepening theoretical understanding of the structure of crystalline materials no revolution was anticipated in our understanding the atomic order of solids.

However, such revolution did happen with the discovery of the Icosahedral phase, the first quasi-periodic crystal (QC) in 1982, and its announcement in 1984 [1,2]. The discovery created deep cracks in this paradigm, but the acceptance by the community of crystallographers of the new class of ordered crystals did not happen in one day. In fact it took almost a decade for QC order to be accepted by most of the community of crystallographers. The official stamp of approval came in a form of a new definition of “Crystal” by the International Union of Crystallographers. The last objection to the existence of quasi-periodic order in crystals faded in about 1994. The paradigm that all crystals are periodic has thus been changed. It is clear now that although most crystals are ordered and periodic, a good number of them are ordered and quasi-periodic.

While believers and nonbelievers were debating, a vast number of experimental and theoretical studies were published. This was created by a relentless effort of many groups around the world. Quasi-periodic materials have developed into an exciting interdisciplinary and international science.

The atomic order of the Icosahedral phase contains 5-fold 3-fold and 2-fold axes. The lack of periodicity is clearly observed in high resolution TEM images, and well manifested in electron diffraction and in single crystal x-ray diffraction patterns.

Soon after the discovery of the Icosahedral phase in rapidly solidified Al-Mn, the Decagonal phase was discovered in rapidly solidified Al-Cr alloys. This phase contains a 10-fold rotation axis, and periodic stacking perpendicular to it. In addition, other rotation axes observed in quasi-periodic materials are 8-fold and 12-fold

All the quasi-periodic structures observed during the first years were metastable, and transformed into periodic stable phases upon heating. This supported the false notion that quasi-periodic structures can not be the low energy phase of a given composition. The discovery of several stable quasi-periodic phases not only proved that quasi-periodic phases can be stable, but also confirmed early calculation regarding possible stability of QC structures. In addition, it enabled growing large QCs, and serious x-ray diffraction experiments. This was important to the community of crystallographers that depend mainly on precise x-ray diffraction measurements. The early QCs were discovered and studied intensively by TEM. This was necessary, since the QC grain size was only several microns. Electron diffraction in the TEM is a powerful qualitative tool for small crystals, but its precision is limited compared to x-ray diffraction. The community of

crystallographers waited until high quality x-ray diffraction patterns of large nearly perfect QCs became available, and then adopted QCs into the family of crystals.

Quasi-periodic materials have several characteristic properties. Many of them have low electrical and heat conductivity; in fact at low temperature the electrical conductivity of some of them drops to a very low value. They are hard and some of them have low friction coefficient and resist wear. These properties may indicate potential uses and several applications have been tried, and reached the markets. For example, one of the potential uses is strengthening of alloys with quasi-periodic precipitates. This has been commercialized in stainless steel, and experimented in aluminum and magnesium alloys with very good results.

This talk will outline the discovery of QCs and discuss their structure and some of their properties.

1. D. Shechtman and I. Blech, "The Microstructure of Rapidly-Solidified Al₆Mn", *Met. Trans.* **16A** (June 1985) 1005-1012.
2. D. Shechtman, I. Blech, D. Gratias and J.W. Cahn, "A Metallic Phase with Long-Ranged Orientational Order and Broken Translational Symmetry", *Phys. Rev. Letters*, Vd **53**, No. 20 (1984) 1951-1953.