

Topology and Chemistry in the Frustrated Symmetry of Quasicrystals

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Abstract. *The formation of a quasicrystalline phase, apparently displaying five-fold symmetry, was reported in rapidly solidified Al-Mn alloys for the first time back in 1984. For this discovery D. Shechtman was awarded the Nobel Prize for Chemistry in 2011. The original paper sparked immediate and lively discussion on the occurrence of five-fold symmetry axes in solids. Models and experiments confirmed the finding and are shortly reviewed here.*

The first quasicrystals were thermodynamically metastable in that they transformed to stable phase mixtures on annealing. Using a thermodynamic description of the Al-Mn system, it was shown that their free energy lies very close to that of stable compounds. Therefore, the later discovery of equilibrium quasicrystalline compounds did not come as a surprise. In all cases, stable quasicrystals are found in multicomponent systems and occur in narrow regions of the respective phase diagrams. Otherwise they coexist with other phases. This feature determines their chemical behaviour and makes difficult the main mass application envisaged so far for them: materials for coatings having low wettability which stems from a pseudogap at the Fermi level. On the other hand some appear as promising catalysts. Thus, the main impact of these materials is due to the advances they have brought in the crystallography of incommensurate phases.

1. The discovery of quasicrystals

Dan Shechtman from Haifa, Israel, discovered the quasicrystals in rapidly solidified Al-Mn alloys using electron diffraction and dark field imaging in the spring of 1982 during his sabbatical leave at the National Bureau of Standards (NBS) in the USA. In the spring of 1984 I. Blech at the Technion in Haifa made an icosahedral glass model that gave a similar diffraction pattern. This encouraged Shechtman to submit a paper with Blech to the Journal of Applied Physics that was rejected as boring metallurgy. When Shechtman returned to NBS, which meanwhile had become NIST, in 1984 the paper was revised

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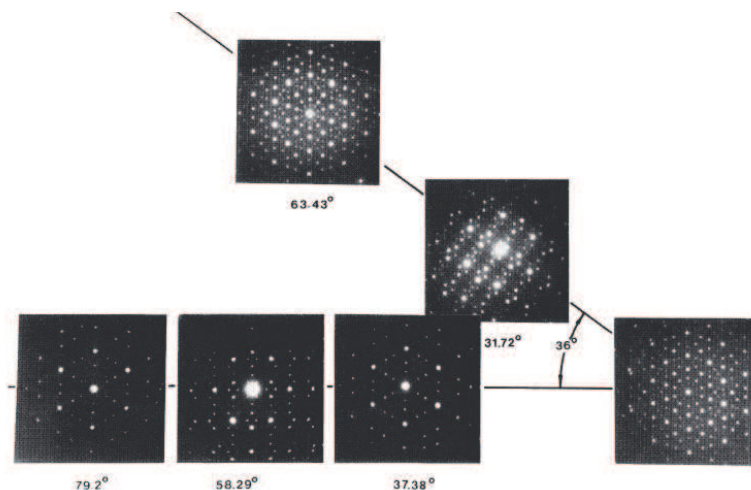


Figure 1. A series of transmission electron diffraction patterns taken from an icosahedral grain of an Al-Mn rapidly solidified alloy (reprinted from Ref. 2 with permission). The tenfold symmetry apparent in two patterns results from a combination of a twofold and a fivefold symmetry axes.

and sent to «Physical Review Letters»¹. The paper was published (Fig. 1) and sparked the interest of crystallographers, physicists and materials scientists on the new material and its structure².

A first basic question was obvious: can the atomic structure of a «phase with no translational symmetry» be understood together with its diffraction patterns of icosahedral point group, $I(235)$? Two approaches were soon tried:

- 1) to build a «quasicrystallographic» strategy specific to the icosahedral «quasicrystals» (called «the cut and projection» method) describing crystals in a high dimension space, i. e. 6D for the icosahedral phase, where the periodicity was assured and projecting the structure in a lower dimensional space to account for quasiperiodicity. This would have restored the usual tools of crystallography;

¹ D. Shechtman, I. Blech, D. Gratias and J.W. Cahn, *Metallic Phase with Long-Range Orientational Order and No Translational Symmetry*, «Phys. Rev. Lett.», 53, 1984, 1951.

² J.W. Cahn, *A celebration of the pioneering work on quasicrystals in France and the expansion of crystallography*, «Comptes Rendus de Physique», 15, 2014, e1–e5.

- 2) to take advantage of some direct observations by electron microscopy where quasicrystals co-exist, after casting, with large unit cell crystals³.

These last were called later «approximants» of icosahedral quasicrystals in the sense that their periodic structure are approximations of the quasiperiodic one. The larger the size of their unit cell, the better the approximation. Moreover, such approximants exhibit crystallographic orientation relationships with quasicrystals⁴.

As early as 1985 a first atomic model was built following the latter path⁵. This result allows to state safely that the discovery of quasicrystals as well as the determination of the atomic positions in them has been the victory of transmission electron microscopy⁶. A series of diffraction patterns convincing enough of the fact that the solid had truly definite icosahedral symmetry, was only obtainable in the electron microscope, also because the first quasicrystalline phase occurred in the form of fine grains of a few microns in size in a rapidly solidified Al-Mn alloy (Fig. 2) and could not be isolated from the matrix (an fcc solid solution)⁷.

Opposition was fierce and authoritative at the beginning. The argument was posed that the diffraction patterns were due to twinning in crystals of large unit cell⁸. However, soon more and more examples of quasicrystals appeared in the literature including stable phases (Fig. 3). In this respect the most recent discovery is that of a quasicrystalline phase of the Al-Cu-Fe system in a meteorite some thousands of years old⁹, therefore meant to be

³ P. Guyot and M. Audier, *Quasicrystals and atomic clusters*, «Comptes Rendus de Physique», 15, 2014, pp. 12-17.

⁴ P. Guyot, M. Audier and M. de Boissieu, *Quasicrystals and Incommensurate Structures in Condensed Matter*, in J. Yacaman, et al. (Eds.), Proc. 3rd Int. Conf. on Quasicrystals, WorldScientific, 1990, p. 251.

⁵ P. Guyot and M. Audier, *A quasicrystal structure model for Al-Mn*, «Philos. Mag.», B, 52, 1985, L15.

⁶ E. Abe, *Electron microscopy of quasicrystals – where are the atoms?*, «Chem. Soc. Rev.», 41, 2012, pp. 6787-6798.

⁷ D. Shechtman and I. Blech, *The Microstructure of Rapidly Solidified Al₆Mn*, «Metall. Trans.» A, 16A, 1985, 2005.

⁸ L. Pauling, *Apparent Icosahedral Symmetry is due to directed Multiple Twinning of Cubic Crystals*, «Nature», 317, 1986, p. 512.

⁹ L. Bindi, P.J. Steinhardt, N. Yao and P.J. Lu, *First discovery of a natural quasicrystal*, «Science», 324, 2009, p. 1306.

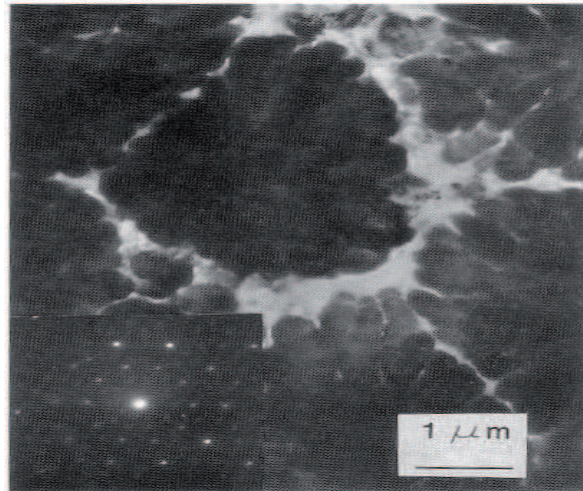


Figure 2. Transmission electron microscopy image of icosahedral grains embedded in an Al matrix in an $\text{Al}_{81}\text{Mn}_{14}\text{Si}_5$ rapidly solidified alloy. The dark dendritic grain at the centre is a quasicrystal oriented along the fivefold axis. Its Selected Area Diffraction Pattern is also shown. (from Ref. 23).

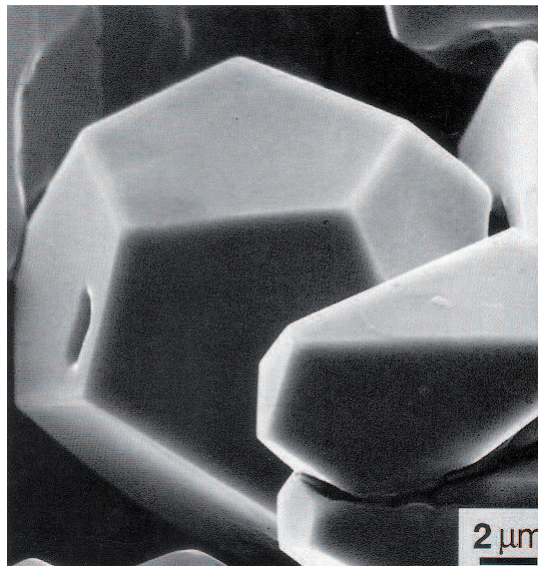


Figure 3. A stable quasicrystal of the $\text{Al}_{65}\text{Cu}_{20}\text{Fe}_{15}$ compound as grown from the melt displaying pentagonal faces (from H.U. Nissen, C. Beeli, «Period. Mineral.», 59, 1990, pp. 31-67).

an equilibrium phase, which confirms the findings on synthetic alloys of the same composition¹⁰.

2. The structure of quasicrystals. Where do atoms sit?

Crystal structures can be described as resulting from a compromise between short-range order and long-range order. In principle, every single atom tries to achieve the energetically most favourable atomic environment. Since all atomic environments must occur at the same time, not only the formation of the preferred neighbourhood of atom X with atom Y occurs, but also all these individual clusters must be packed in a space-filling crystal structure. This can be geometrically very unfavourable. The simplest cases, where every atom has exactly the same neighbourhood, are the cubic and hexagonal close-packed structures. They have the highest possible coordination of equal spheres as well as the maximum filling of space. However, only a number of metallic elements crystallize in such structures. The reason are multiple: the occurrence of anisotropic interaction potentials due to covalent bonding contributions, specific electronic (e. g. magnetic) interactions and phononic contributions to lattice stability¹¹.

Chemical interactions and geometrical constraints due to atomic size ratios determine the compound stoichiometry in the formation of the crystal structure. They can be quite complex and determine the number of different compounds that are possible in a given intermetallic system. The more complex the stoichiometry of an intermetallic compound is, the larger the number of different environments becomes and the more difficult their packing. This often leads to phase mixtures. Very often rapid solidification helps in obtaining new phases, possibly metastable. They nucleate from the melt at high temperature and therefore are simpler in their crystal structure than equilibrium compounds. However, the difficulty in atom packing may hinder crystal formation to produce metastable metallic glasses (amorphous metals) representing the extreme case for the so-called *confusion principle*¹². It has been supposed that quasicrystals were an intermediate case between crystals and glasses, however, it is now

¹⁰ A.P. Tsai, A. Inoue and T. Masumoto, *A Stable Quasicrystal in Al-Cu-Fe System*, «Jpn. J. Appl. Phys.», 26, 1987, p. 1505.

¹¹ W. Steurer, *Why are quasicrystals quasiperiodic?*, «Chem. Soc. Rev. », 41, 2012, pp. 6719-6729.

¹² M. Baricco, E. Bosco, E. Olivetti, M. Palumbo, P. Rizzi, A. Stantero and L. Battezzati, *Rapid Solidification of Alloys*, «Int. J. Mater. Products Technology», 20, 2004, pp. 358-376.

clear they are much closer to the former¹³. Thermal equilibration by annealing leads to the decomposition of quasicrystals into more simple equilibrium structures in most instances¹⁴. The stable quasicrystals, e. g. Al_6CuLi_3 and $\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$, appear long lived as other intermetallic compound. Calculations show they actually correspond to a local energy minimum¹⁵.

It should be recalled that there are numerous examples of complex structures in intermetallic phases containing structural subunits ('clusters') having local icosahedral symmetry. However, these are packed together with other atoms/clusters into periodic lattices¹⁶.

Basically, there are two ways of describing the structure of quasicrystals and their rational approximants. The tiling – or 'quasilattice' – approach, on one hand, is similar to the description of periodic structures with lattices decorated with atoms. In contrast to lattices, quasilattices have at least two different 'unit cells' that can be decorated by atoms or clusters. The higher-dimensional or nD approach, mentioned above, describes quasiperiodic structures based on periodic nD hyperspace structures with n corresponding to the rank of the Fourier module of the quasicrystal, i.e., the number of reciprocal basis vectors needed to index the reflections of a diffraction pattern with integers only.

In early studies of the structure of quasicrystals high-resolution phase-contrast TEM imaging provided evidence that they are made of a combination of clusters and the corresponding quasilattices. Still information on the local atomic configurations of quasicrystals was lacking since the projected atomic positions are imaged as a dark region. The question then remains: how elements are arranged in the quasiperiodic structure? In other words, which are the chemical configurations in the structure? Since most stable quasicrystalline phases of high-structural quality are multicomponent systems, it was expected they displayed chemical order. The coming of scanning transmission electron microscopy (STEM) has allowed significant progress in determining the chemical structure of quasicrystals¹⁷ because the contrast in this technique (Z-contrast) is atomic-number dependent.

¹³ E. Abe, *Electron microscopy of quasicrystals – where are the atoms?*, cit.

¹⁴ L. Battezzati, C. Antonione and F. Marino, *Quasicrystals and stable phases in $\text{Al}_{81}\text{Mn}_{14}\text{Si}_3$* , «Scripta Metallurgica», 22, 1988, pp. 623-626.

¹⁵ J.M. Dubois, *Properties and applications of quasicrystals and complex metallic alloys*, «Chem. Soc. Rev. », 41, 2012, pp. 6760–6777.

¹⁶ R. Ferro and A. Saccone, *Structure of intermetallic compounds and phases*, in «Physical Metallurgy», R.W Cahn and P. Haasen (Eds), North Holland, Amsterdam 1996, p. 205.

¹⁷ E. Abe, Y. Yan and S.J. Pennycook, *Quasicrystals as cluster aggregates*, «Nat. Mater.», 3, 2004, p. 759.

STEM combined with an annular-detector results in atomic-resolution images when atomic columns are scanned one-by-one with a finely focused electron probe (size less than 2 Å), therefore, the Z-contrast selectively shows up the atomic positions, more evidently those of heavy elements. As a consequence, new models for the atomic structure of quasicrystals were developed. All previous models making use of evidence provided by high-resolution phase-contrast TEM observations, assumed either tenfold or fivefold atomic configurations in the clusters. It was then assumed the symmetry of clusters should directly reflect the entire symmetry seen in the diffraction pattern. Some decagonal quasicrystalline samples were found to

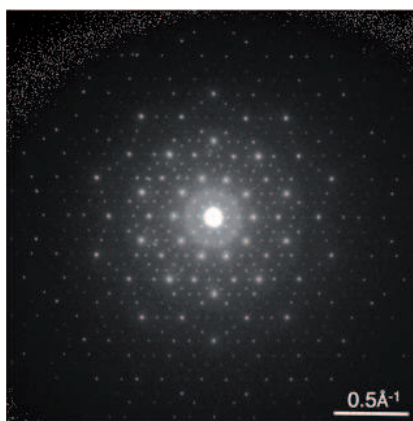


Figure 4. Electron diffraction pattern taken along the tenfold symmetry axis of the $\text{Al}_{72}\text{Ni}_{20}\text{Co}_8$ decagonal quasicrystal. Note sharp reflections similar to perfect periodic crystals. This pattern can no longer be explained according to the early framework of incommensurate crystals. (reprinted from Ref. 6 with permission).

have a cluster arrangement similar to a Penrose pattern, i. e. planar tiling of two different rhombic tiles with matching rules which assured space filling¹⁸. This view is purely mathematical and does not provide information on why the atoms should pack into such complex structures. As noted at variance in E. Abe¹⁹, the structure of Al-Cu-Co was represented as a random packing of decagonal clusters having tenfold symmetry which are allowed to overlap with their neighbours, partially sharing atoms. The immediate deduction from this is that configurational entropy might be relevant for the stability of quasicrystals with respect to competing crystalline phases.

A step forward occurred in the study of decagonal $\text{Al}_{72}\text{Ni}_{20}\text{Co}_8$, a quasicrystal having high degree of structural

perfection (Fig. 4). It appeared that the local tenfold symmetry within the 2 nm decagonal cluster was broken. The atomic sites for Ni and Co are not arranged with ten-fold symmetry, but with mirror symmetry (Fig. 5). However, this local arrangement in decagons is not found to be random but occurs in a perfect quasiperiodic pattern. Again mathematics helped with the Gummelt

¹⁸ R. Penrose, *The role of aesthetics in pure and applied mathematical research*, «Bull. Inst. Math. Applic.», 10, 1974, p. 266.

¹⁹E. Abe, *Electron microscopy of quasicrystals – where are the atoms?*, cit.

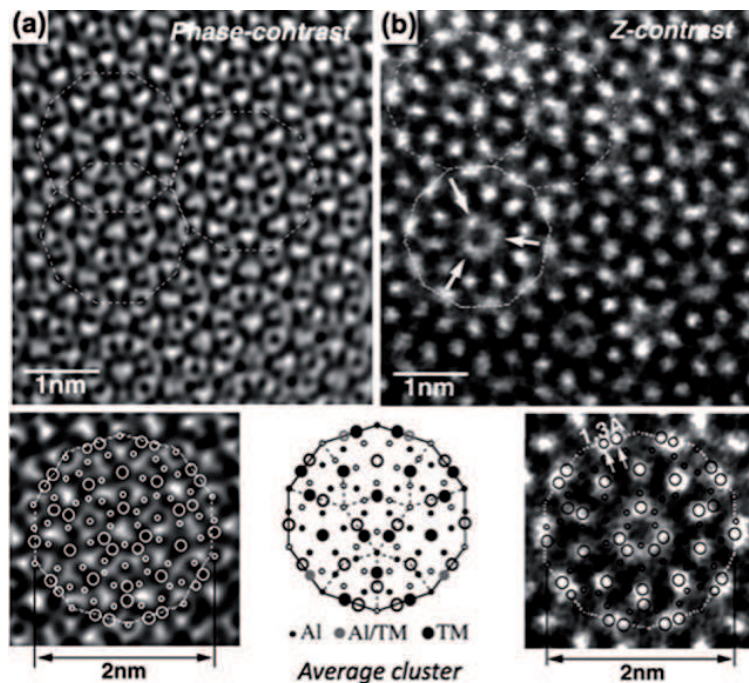


Figure 5. Images showing atomic-resolution of the $\text{Al}_{72}\text{Ni}_{20}\text{Co}_8$ decagonal quasicrystal. (a) phase-contrast TEM and (b) Z-contrast STEM images, taken along the tenfold symmetry axis. Decagonal clusters of 2 nm across are shown by dashed lines in both images and are reproduced below each pattern with superimposed atomic position of Al and Transition Metals according to a model of the structure reported in the middle. Note that in image (a) the atoms occupy dark regions of the pattern whereas in image (b) they occupy bright region, more evident are those of heavy elements.

construction of decagons overlapping with their neighbours according to a well-defined rule²⁰ forcing the decagons into a perfect quasiperiodic arrangement as in the Penrose tiling. First principle calculations have then shown this arrangement corresponds to maximizing the alloy density and to a local energy minimum²¹. Therefore, the quasicrystals occur in this highly ordered compound as a consequence of energy minimization.

²⁰ P. Gummelt, *Penrose Tilings as Coverings of Congruent Decagons*, «Geom. Dedicata», 62, 1996, 1.

²¹ M. Mihalkovic, I. Al-Lehyani, E. Cockayne, C.L. Henley, N. Moghadam, J.A. Moriarty, Y. Wang and M. Widom, *Total-energy-based structure prediction for decagonal Al-Ni-Co*, «Phys. Rev. B: Condens. Matter Mater. Phys.», 2002, 65, 104205.

The structures of the less-ordered quasicrystals which have constituted a large part of the literature, may well differ from this picture and be described by random-packing of clusters with their high-symmetry resulting from averaging over the local random disorder, as discussed in early models. Another kind of disorder is caused by phason fluctuations, i.e., low-energy excitations that lead to atomic jumps at short distance in double-well potentials²². These appear to be common at high temperature where entropic contributions to the free energy of the phases are relevant.

3. Approximants

The stability range of quasicrystalline phases is rather narrow as a function of composition, e. g. the $\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$ one mentioned above. Even more when the temperature decreases down to room temperature. The regions in the phase diagram in the near vicinity of these compounds contain approximant crystals with nearly identical composition and very similar atomic order as the quasicrystal²³. Approximant compounds display periodic lattices that are very close to neighbouring quasicrystals because they can be referred to the same high dimensional periodic lattice, but according to a projection scheme based on rational numbers approximating the golden mean. These numbers are equal to the ratio between two successive members of the Fibonacci series 1/1, 3/2, 5/3, etc., and accordingly the unit cell contains more and more atoms, i. e. increasingly large lattices. Note that only the first members in the series were found so far²⁴. The largest unit cell size discovered experimentally is that of the $\text{Al}_{60.3}\text{Cu}_{30.9}\text{Fe}_{9.7}$ compound with lattice parameters $a = 3.21$ nm; $b = 11.63$ nm; and $c = 1.98$ nm, having nearly 5000 atoms per unit cell.

4. Stability of quasicrystals

A number of quasicrystals are known to occur in phase diagrams as equilibrium phases. Their free energy must then correspond to a minimum in the composition space. They are surrounded by approximant compounds often having similar short range order. It is, therefore, envisaged that the difference

²² A.P.Tsai, A. Inoue and T. Masumoto, *A Stable Quasicrystal in Al-Cu-Fe System*, cit.

²³ J.M. Dubois, *Properties and applications of quasicrystals and complex metallic alloys*, cit.

²⁴ J.M. Dubois, *Properties and applications of quasicrystals and complex metallic alloys*, cit.

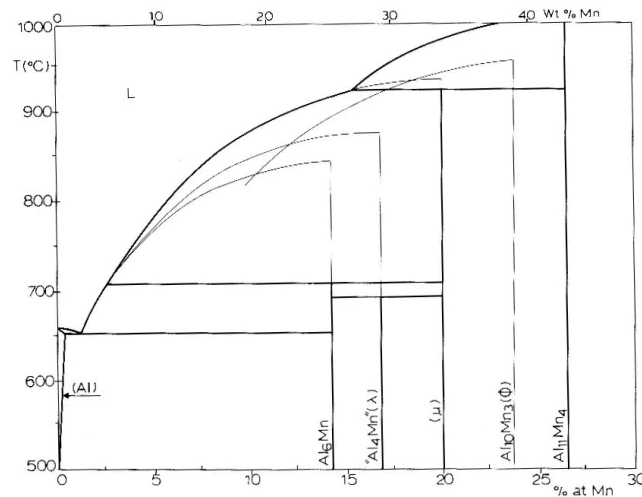


Figure 6. The Al-Mn phase diagram computed by means of the Calphad approach. The thin lines show metastable liquid-crystal equilibria for the compounds which melt with a peritectic reaction. The Al_6Mn and Al_4Mn are approximants.

in free energy between all these is small. In general, the stabilization of compounds is enthalpic in origin being their structures highly ordered. There are examples also of compounds having negative entropy of formation, i. e. their entropy is lower than the average of that of the constituents²⁵. Quasicrystalline phases may then be stabilized by small entropy contributions due to mixing of clusters, elemental substitution, phason flips.

On the other hand, a large number of quasicrystalline phases, especially those obtained by non-equilibrium processing, e. g. rapid solidification and thin film deposition, are metastable in that they transform into more stable phases on annealing²⁶. The Al-Mn system has been the subject of early investigations in which the thermodynamic stability of the quasicrystalline phase was evaluated. The melting point was established to occur a few tens of degrees below that of the equilibrium compounds, Al_6Mn and Al_4Mn ²⁷.

²⁵ C.B. Alcock and O. Kubaschewski, *Metallurgical Thermochemistry*, Fifth Edition (International Series on Materials Science and Technology), Pergamon Press, Amsterdam 1979.

²⁶ L. Battezzati, C. Antonione and F. Marino, *Quasicrystals and stable phases in $\text{Al}_{81}\text{Mn}_{14}\text{Si}_5$* , cit.

²⁷ D.M. Follstaedt and J.A. Knapp, *Metastable phase boundaries of quasicrystalline phases*, «Mater. Sci. Eng.», 99, 1988, p. 367.

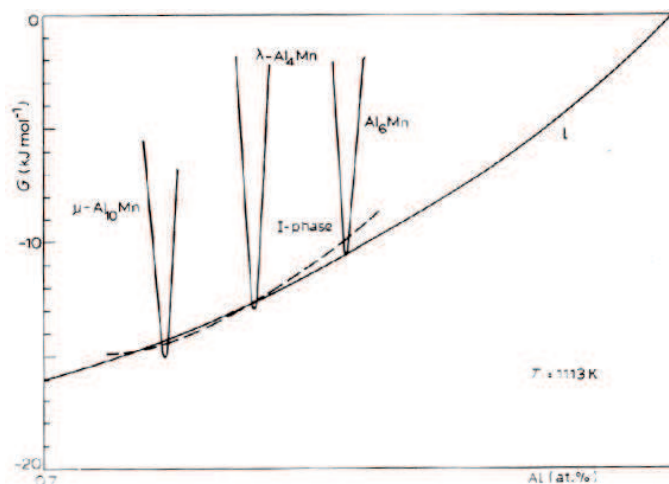


Figure 7. A free energy scheme at the melting point of Al_6Mn . The curves represent the free energy of phases as a function of Al content (l stands for liquid, the curve for the icosahedral phase is dashed). Note that the free energy of the icosahedral phase lies above that of the other solid phases (or of their mixtures), therefore it is not a stable phase in this system. Note also the small difference in free energy between the icosahedral phase and the other compounds. The icosahedral phase becomes kinetically favoured on rapid quenching.

Their entropy content was estimated to be around 1 J/molK above that of the corresponding compounds²⁸. Furthermore, the entropy of fusion was found to respect rather closely the Trouton law being exactly of the order of the gas constant. It was, then, deduced that the melt should have a degree of order, possibly icosahedral. This has two consequences: the interfacial tension between liquid and quasicrystal should be lower than that of other phases and, as a corollary, the nucleation of the quasicrystals must be easier than that of competing periodic compounds. This was proven with a model calculation explaining the need of non-equilibrium techniques to hinder the formation of stable compounds in favour of the quasicrystalline phase²⁹.

²⁸ L. Battezzati, C. Antonione and F. Marino, *On some thermodynamic and kinetic aspects of icosahedral phase nucleation in Al-Mn.*, «J. Mater. Sci.», 24, 1989, pp. 2324-2330.

²⁹ C. Antonione, L. Battezzati, M. Calleri and F. Marino, *Formation and Transformations of Quasicrystals: Some Chemical and Metallurgical Aspects*, «Period. Mineral.», 59, 1990, pp. 121-147.

5. Impact and Applications

It is undoubted that the main impact of the discovery and study of quasicrystals has been a change in paradigm for crystallography. The International Union of Crystallography in 1992 redefined the word crystal:

By crystal we mean any solid having an essentially discrete diffraction diagram, and by aperiodic crystal we mean any crystal in which three-dimensional lattice periodicity can be considered to be absent.

This favoured the development of experimental techniques, e. g. STEM, and models of structure. The attention of researchers has been re-directed to the study of complex intermetallic phases and their properties³⁰.

Various applications have been realised so far, or envisaged, according to the type of property of interest³¹. The following transport properties were found exploitable: infra-red absorption for heating devices, reduced adhesion and friction (because of low work of adhesion due to low density of states at the Fermi level) for surface functions, heat insulation, and data storage based on contactless thermal cells. The main mechanical property is hardness for: mechanical reinforcement of alloys by precipitates grown *in situ*, or addition of reinforcement particles in metal or polymer matrices. For chemical properties the main applications has been in producing corrosion resistant surfaces and low cost catalysts or hydrogen storage media. At the moment none has gained a substantial share of the respective market, although progress in processing suggests some should be close to commercialization such as catalysts for methane reforming and anti-adhesive coatings.

It is finally mentioned that, after the awarding of the Nobel Prize to D. Shechtman, conferences were organized on the topic of quasicrystals and review papers given at them appeared very recently in the «Chemical Society Reviews» (vol. 41, 2012) and the «Comptes Rendus de Physique» (vol. 15, 2014) to which the interested reader is addressed for more in depth discussions.

³⁰ «Book Series on Complex Metallic Alloys», E. Belin-Ferré ed., World Scientific, Singapore 2008-2010.

³¹J.M. Dubois, *Properties and applications of quasicrystals and complex metallic alloys*, cit.