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QUASICRYSTALS: A PRECIOUS MATERIAL

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Abstract

The paper discusses about a class of crystals identified in nature that depict an orderliness in their structure but lack periodicity, thus giving birth to the term quasiperiodic crystals or simply quasicrystals. Being relatively poor conductors of heat and electricity, quasicrystalline alloys, most of which contain about 70 percent of aluminium, do not behave as one might expect. Other interesting properties involving, for instance, adhesion, corrosion, friction and hardness, suggest that the industrial future of quasicrystals is promising as it projects hydrogen storage compatibility while the present is already bearing its fruits, notably in lubricants and coating applications.

Keywords: Quasicrystals, Hydrogen Storage, Lubricants, Coating Applications

1. INTRODUCTION

Atomic structures of pure solids have been divided into two classes: crystal structures and glassy structures. Crystal structures are highly ordered: (a) They have long ranged translational order characterized by a periodic spacing of unit cells; (b) They have long range (near-neighbor bond) oriental order with a symmetry corresponding to special crystallographic discrete subgroups of the rotation group; (c) They have a rotational point symmetry. An

amorphous structure by contrast, has none of the long-range correlations of the crystal. Recently, a notion of a new kind was introduced of an ordered atomic structure – one which would represent a new phase of solid matter if found in nature. The new structure is like a crystal which has long-range translational order and long-range orientational order. However, the translational order is not periodic and structure does not have a rotational point symmetry. Instead, the new structure is quasiperiodic, a well-defined but more subtle kind of translational order. Because the new structures have many of the properties of crystals, with notable exception that they are quasiperiodic rather than periodic, we termed them as quasiperiodic crystals or quasicrystals.

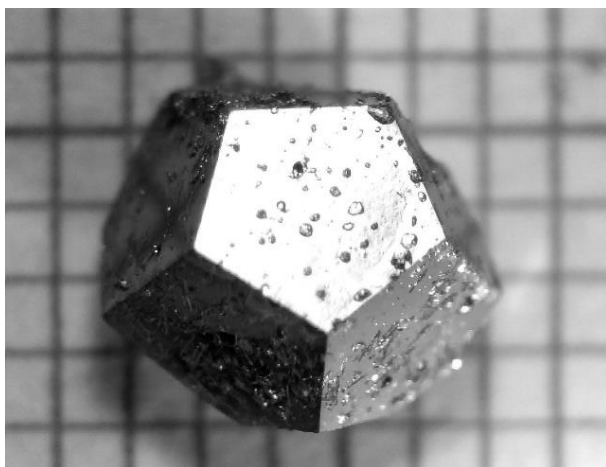


Fig 1 : Single-grain sample of a quasicrystalline compound AlPdRe

An ideal quasicrystal is constructed by the infinite repetition in space of two or more distinct (atomic or molecular) structural units, called ‘unit cells’, packed in a lattice that has a long range quasiperiodic translational order and long range orientational order. By a quasicrystal unit cell, we mean only a repeating motif, but unlike crystals the motif is not repeated periodically. We will refer to the structure obtained by a packing of unit cells as a packing in general while the underlying lattice will be referred to as a quasilattice. Their diffraction patterns show Bragg reflections revealing symmetries which are incompatible with periodicity. Quasicrystals are found most often in aluminium alloys (AlLiCu, AlMnSi, AlNiCo, AlPdMn, AlCuFe, etc.), but numerous other compositions are also known (CdYb, TiZrNi, ZnMgHo, ZnMgSc, InAgYb, PdUSi, etc.)[1].

2. CHARACTERISTICS AND CLASSIFICATION

Quasicrystals are structural forms that are both ordered and nonperiodic. They form patterns that fill all the space but lack translational symmetry. Classical theory of crystals allows only 2, 3, 4 and 6-fold rotational symmetries, but quasicrystals display symmetry of other orders (folds). Just like crystals, quasicrystals produce Bragg diffraction, but where crystals have a simple repeating structure, quasicrystals are more complex.

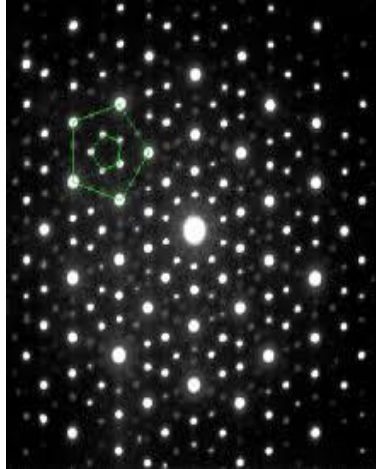


Fig 2 : Electron diffraction patterns of the icosahedral ZnMgHo quasicrystals – 10 fold symmetry

Quasicrystals can be classified based on their structure in the following groups:

Quasiperiodic in two dimensions (polygonal or dihedral quasicrystals) - There is one periodic direction perpendicular to the quasiperiodic layers.

- octagonal quasicrystals with local 8-fold symmetry [primitive & body-centered lattices]
- decagonal quasicrystals with local 10-fold symmetry [primitive lattice]
- dodecagonal quasicrystals with local 12-fold symmetry [primitive lattice]

Quasiperiodic in three dimensions – There is no periodic direction to the quasiperiodic layers

- icosahedral quasicrystals with 5-fold [primitive, body-centered & face-centered lattice]
- icosahedral quasicrystal with broken symmetry (stable binary Cd₅Yb)

Regarding thermal stability, three types of quasicrystals are distinguished:

- Stable quasicrystals grown by slow cooling or casting with subsequent annealing
- Metastable quasicrystals prepared by melt-spinning, and
- Metastable quasicrystals formed by the crystallization of the amorphous phase.

Except for the AlLiCu system, all the stable quasicrystals are almost free of defects and disorder, as evidenced by x-ray and electron diffraction revealing peak widths as sharp as those of perfect crystals such as Si. Diffraction patterns exhibit fivefold, threefold and twofold symmetries, and reflections are arranged quasiperiodically in three dimensions [1][3].

3. PROPERTIES

3.1. Electrical and Thermal Properties

The electrical behavior leads to class of related properties involving the Hall effect, thermoelectric power, magnetic susceptibility, and optical conductivity. The negative value of the Hall coefficient (RH) for the most perfect QC brings evidence that the majority of free carriers is made up of electrons. Since the coefficient at room temperature is more than 10 times larger than for pure aluminium, there is a reduced density of free carriers. The hierarchical packing of clusters in the structure along with the strong Coulomb interaction lead to repeated (so-called recurrent) localization of the bonding electrons. Phonon-assisted hopping conductivity may then generate “antipairing” in much the same way as the inverse (i.e., pairing) produces superconductivity.

The thermal conductivity values $K(T)$ are indeed very small - much smaller than those expected for purely metallic compounds. For instance, at room temperature, $K(T)$ for quasicrystalline AlFeCu and AlPdMn is more than two orders of magnitude smaller than for aluminium, more than one order of magnitude smaller than for steel, and about one-half that for zircon which is currently considered to be one of the best thermal insulators (indeed, it is widely used because of its insulator properties). The phonon saturation effect is also observed as plateau in the $K(T)$ curves covering a temperature range from about 25K to 100K. The unexpected feature is that at higher temperature, $K(T)$ resumes an increasing trend as illustrated in Fig 3.

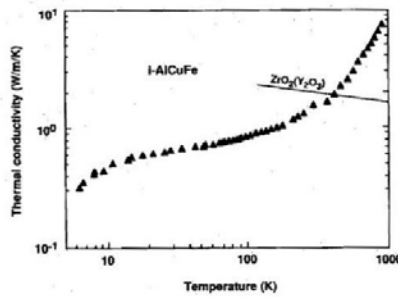


Fig 3 : The temperature dependence of the experimentally determined thermal conductivity of AlFeCu icosahedral quasicrystal compared with that of zircon. This may be understood in terms of nonlinearity effects which allow vibration modes to interact. The temperature dependence is quite different from classical metal samples for example Lithium.

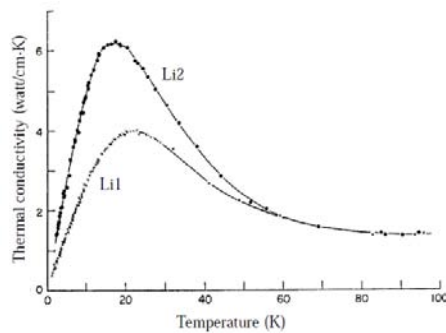


Fig 4 : The temperature dependence of the experimentally determined thermal conductivity of Li metal sample

Application of this temperature dependent conductivity in thermometry and heat flow detection is straightforward, and the development of devices is underway at the present time. The coating of QC on bulk metallic parts as an efficient thermal barrier layer for engines and the like is taken up in the next section.

3.2. Magnetic Properties

Magnetism also presents some curious features in QC. The presence of transition metals such as iron or manganese would normally introduce unpaired electron spins into the material, and paramagnetism, if not ferro- or antiferromagnetism, should be observed. This is not at all the case: strictly stoichiometric QC is diamagnetic, with a negative susceptibility of about $-5 \cdot 10^3$ emu/g. However, a transition from dia- to para-magnetism is observed at about 50° below the

melting point⁹, and the susceptibility continues to increase with temperature in the liquid state. Diamagnetism occurs only when spins are exactly balanced. This happens for exactly saturated electronic states, as may be expected for stability of the recurrent localization in QC. Interestingly, QC exhibit some spin tenability via temperature or composition shifts which may be useful in electronic and computing devices. The frequency dependence $\sigma(\omega)$ of the electrical (or so-called optical) conductivity also deviates strongly from that for metallic behavior. In agreement with direct-current measurements, $\sigma(\omega)$ remains small for most of the frequency range, especially towards low-energy values.

However, a rather strong resonance shows up as shown in Fig. 5 at around 10^4 or 290THz (corresponding to infrared radiation with a wavelength of about 1 mm). Assuming this resonance comes from electron-plasma oscillation a mean-free amplitude of about 22 Å for majority carrier can be deduced. Such a value is very close to the distance between two elementary clusters in the structure of AlPdMn QC, something that would be expected if a hopping mechanism is relevant for conductivity in QC. Fig. 6 shows that sandwiches of QC between oxide layers such as SiO₂ or Al₂O₃ have reflectivity (R) gap centered on the visible wavelength range¹⁰. A straightforward application of such a property involves energy coating for solar cells, insulator screens or window glass [2][3].

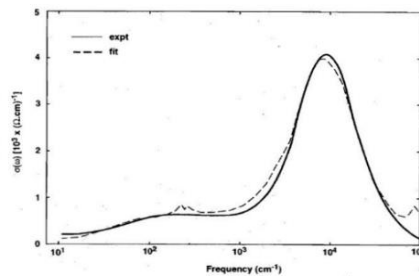


Fig 5 : The experimentally determined and curve-fitted optical conductivity $\sigma(\omega)$ of icosahedral AlPdMn quasicrystals at room temperature as a function of the frequency

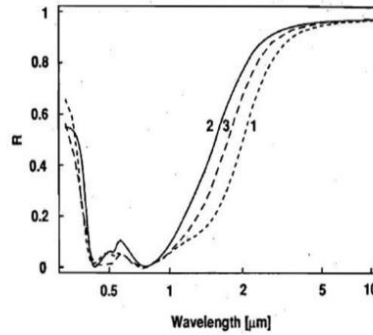


Fig 6 : The reflectivity of quasicrystal layer sandwiched between two layers of three different types of oxide insulators

3.3. Other Properties

A second class of QC properties are less well understood but interesting and useful nonetheless, especially when some of them can be applied in combination. The class includes reduced wetting, a low friction coefficient, high hardness, elevated corrosion resistance, a ductile, brittle transition, and superplasticity above 700°C (for most practical QC). High hardness is actually one of the strong points of QC. Values up to 10GPa have been measured, comparing favorably with the hardness levels for heat treated, tribological steel (so-called high-speed steels and steels used for ball bearings).

The wetting behavior of QC surfaces lies at the origin of two very important properties, namely anti-adhesion and low friction coefficients in tribological applications. But as has been well known for a long time, there is no such thing as an intrinsically good friction behavior because the friction partner, the third body (lubricant, wear debris, transfer layer, etc.) and testing conditions make their own contributions to the overall friction response. Published data remain scarce and correspond mainly to dry scratch testing using indenters with spherical tips.

The friction coefficient with diamond remains as low as 0.05 under cnt-load operations, for loading both below and above the critical value for transverse cracks to form. Friction coefficients for cemented carbide, hardened steel and alumina tips are of the order of 0.20. QC friction on QC is being tested and seems to give coefficient almost as low as that obtained with diamond indenters.

Regarding corrosion resistance, QC compare quite well with stainless steel: their performance is ranked between austenitic and ferritic steels. Surface analyses seem to demonstrate that

oxygen adsorbed on the surface of QC single crystals destroys quasiperiodicity within a layer of less than 20\AA thick which passivates the material. A special, and highly interesting, aspect of corrosion resistance of QC is their biocompatibility. Measurements of samples implanted in living animals demonstrate the absence of chemical and immune reactions along with a long-duration tolerance [3][4].

4. APPLICATIONS

4.1. Quasicrystals as a Coating Material

Most of these properties combine effectively to give technologically interesting applications which have been protected recently by several patents. For instance, the combination of nonsticking, hardness, corrosion resistance, and low thermal conductivity gives almost ideal material for coating frying pans or other cookware: cooked food does not stick to the pan, which can be cleaned vigorously without damage; the food is not spoiled by chemical reaction and the liquid calefaction layer does not form thus improving greatly the cooking.

Quasicrystalline coatings, usually $10\mu\text{m}$ to 1mm in thickness, are made by plasma spraying powders produced by gas atomization of a melt. Cost largely depends on the alloy composition, with coatings based on AlFeCu costing about 40ECU/kg. Quasicrystalline powders are presently manufactured under the trade-name CRISTOME for coating cooking utensils. Nearly 9 MECU is being investigated in the development with the aim of coating 10 million frying pans each year using about 500 tonnes of powder.

The same set of associated properties (hardness, low friction, corrosive resistance) combined with biocompatibility is also very promising for introducing quasicrystals in surgical applications as a coating on metallic parts used for bone repair and prostheses.

4.2. Quasicrystals as a Lubricant

As a second example, combining the low friction coefficient and the high hardness and corrosion resistance is obviously very efficient in reducing both surface damage and energy dissipation in the moving contact between two solids. Quasicrystalline cylinder liners and piston coatings in motor-car engines would undoubtedly result in reduced air pollution and increased engine lifetimes. Finally, low thermal conductivity and corrosion resistance become especially useful at high temperatures when quasicrystalline coatings are superplastic. They constitute thermal screens that can easily accommodate thermal constraints and the thermal

expansion of the protected bulk material, features that cannot be realized with today's best insulators such as zircon. Rocket motors and aero-engine turbine would benefit from this technology.

4.3. Quasicrystals for Hydrogen Storage

The depletion of the world's petroleum reserves and the increased environmental impact of conventional combustion-engine-powered automobiles are leading to renewed interest in hydrogen storage materials. Hydrogen contains three times the energy of conventional hydrocarbon fuels, and since the byproduct of hydrogen combustion with oxygen is water, the environmental impact is greatly reduced. Hydrogen storage is a key issue preventing the development of hydrogenpowered automobiles. Hydrogen atoms can be absorbed into either interstitial sites or on surfaces of materials. The recovery of the hydrogen, however, typically requires heating the material to high temperatures, also above 400C, which severely limits the technological application of these materials. Lightweight carbon-based storage materials, such as carbon nanotubes provide potential alternatives, but studies of these materials have only recently started and their properties are not yet optimised. In the mid 1990s, TiZrHf-based quasicrystals were demonstrated to store more hydrogen than competing crystal intermetallic phases. The numerous tetrahedral interstitial sites in icosahedral quasicrystals, structurally favourable sites for hydrogen absorption, give these novel phases potential technological importance. Since hydrogen atoms favour Ti, Zr or Hf alloys, TiZrHf based quasicrystals are most promising (to a weight percent of 2.5%). As an added benefit, the constituent materials are low-cost. Recent advances have improved prospects, revealing a relatively flat plateau at high pressures (100–200 psi) for hydrogen concentrations to 3 hydrogen atoms per metal atom in the $\text{Ti}_{41.5}\text{Zr}_{41.5}\text{Ni}_{17}$ quasicrystal [3][5].

Table 1 -: A selection of some of the most commonly used materials used for hydrogen storage with hydrogen per metal atom ratio, weight percentage and most notable features

Material	H/M	Weight % H	Comments
LaNi ₅	1.1	1.5	Negative electrode in Ni-metal-hydride batteries.
TiFe	0.9	1.6	Best material for stationary applications; requires high pressure or surface activation
Mg	2.0	7.7	Light, expensive; volumetric density too large; unloading temperature higher than typical exhaust from internal combustion engine.
V	2.0	3.8	Expensive
Ti ₄₅ Zr ₃₈ Ni ₁₇	1.7	2.5	Reasonably inexpensive; high loading capacity; requires surface activation.

5. CONCLUSIONS

Quasicrystals are clearly fascinating materials: crystal structures, with their five-fold symmetry, are unconventional and properties are surprising and could be remarkably useful for hydrogen storage. Of course, there are still many problems we must face. For instance, producing industrial quantities of good quality quasicrystals is not that simple, although not impossible. Material cost is another challenge, and traditionalism in industry has to be taken seriously. But the future is promising and the present is already bearing its fruits.

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