The Properties and Applications of Quasicrystals

Seminar II

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Abstract

Being relatively poor conductors of heat and electricity, quasicrystalline alloys, most of which contain about 70 atomic 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 while the present is already bearing its fruits, notably in coating applications.
Contents

1 Introduction........................................................................................................................................2

2 Basic Characteristics and History......................................................................................................2

3 Very Different Structures................................................................................................................5

4 Electrical and Thermal Conductivity.............................................................................................8

5 Other Properties and Applications................................................................................................10

6 Conclusion......................................................................................................................................14

7 References......................................................................................................................................14
1. Introduction

Quasicrystals are materials having a new type of long-range order such that their diffraction patterns show Bragg reflections revealing symmetries which are incompatible with periodicity [1]. However, they are highly ordered systems [2] with correlation lengths of several tenths of a micrometer [3]. Large single crystals can be grown [4] whose quality is such that dynamical diffraction has been observed [3]. The atomic structure of quasicrystals can be reasonably well described in terms of a self-similar packing of atomic clusters using techniques of high-dimensional crystallography [5, 6]. Aside from the peculiar structures, quasicrystals also exhibit very unexpected properties [7]. Perhaps their most intriguing feature is a very high electrical and thermal resistivity. Its value, which almost equals that of an insulator [8], is unexpected for a material containing about 70 atomic percent of aluminium. Fundamental physical characteristics of this type combined with other unusual properties mean that quasicrystals have emerged in a surprisingly short period of time since their discovery as rather useful materials having valuable existing and potential application.

![Figure 1: Single-grain sample of a quasicrystalline compound AlPdRe [9].](image)

2. Basic Characteristics and History

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.

Aperiodic tilings \(^1\) were discovered by mathematicians in the early 1960s, but some twenty years later they were found to apply to the study of quasicrystals. The discovery of these aperiodic forms in nature has produced a paradigm shift in the fields of crystallography and solid state physics. Quasicrystals had been investigated and observed earlier but until the 80s they were disregarded in favor of the prevailing views about the atomic structure of matter.

\(^1\) A proposed formal definition of the term aperiodic tiling: “A tiling of the plane is aperiodic if and only if it consists of copies of a finite set of tiles, that themselves only admit non-periodic tilings.”
Roughly, an ordering is non-periodic if it lacks translational symmetry, which means that a shifted copy will never match exactly with its original. The more precise mathematical definition is that there is never translational symmetry in more than \( n - 1 \) linearly independent directions, where \( n \) is the dimension of the space filled; i.e. the three-dimensional tiling displayed in a quasicrystal may have translational symmetry in two dimensions. The ability to diffract comes from the existence of an indefinitely large number of elements with a regular spacing, a property loosely described as long-range order. Experimentally the aperiodicity is revealed in the unusual symmetry of the diffraction pattern, that is, symmetry of orders other than 2, 3, 4, or 6.

![Figure 2: Electron diffraction patterns of the icosahedral ZnMgHo quasicrystals – 10 fold symmetry [10].](image)

The history of quasicrystals begins with the paper titled "Metallic Phase with Long-Range Orientational Order and No Translational Symmetry" published by D. Shechtman and others in 1984. The discovery was made nearly two years before, but their work was met with resistance inside the professional community. Shechtman and coworkers demonstrated a clear-cut diffraction picture with an unusual fivefold symmetry produced by samples from an Al-Mn alloy which has been rapidly cooled after melting. The same year Ishimasa and coauthors sent for publishing a paper titled "New ordered state between crystalline and amorphous in Ni-Cr particles" in which a case twelvefold symmetry was reported. Soon another equally challenging case presented a sample which gave a sharp eightfold diffraction picture. Over the years hundreds of quasicrystals with various compositions and different symmetries have been discovered. The first quasicrystalline materials were thermodynamically unstable. When heated, they formed regular crystals. But in 1987, the first of many stable quasicrystals were discovered, making it possible to produce large samples for study and opening the door to potential applications. In 1972 de Wolf and van Aalst reported in print that the diffraction pattern produced by a crystal of sodium carbonate cannot be labeled with three indexes but needed one more, which implied that the underlying structure had four dimensions in reciprocal space. Other puzzling cases have been reported, but until the concept of quasicrystal came to be established they were explained away or simply denied. However at the end of the 1980s the idea became acceptable and in 1991 the International Union of Crystallography amended its definition of crystal, reducing it to the ability to produce a clear-cut diffraction pattern and acknowledging the possibility of the ordering to be either periodic or aperiodic. Now the symmetries
The Properties and Applications of Quasicrystals

compatible with translations are defined as "crystallographic"\(^2\), leaving room for other "non-crystallographic" symmetries\(^3\). Thus aperiodic or quasiperiodic structures can be divided into two main classes: those with crystallographic point-group symmetry, to which the incommensurately modulated structures and composite structures belong, and those with non-crystallographic point-group symmetry, to which quasicrystal structures belong.

![Figure 3: New Ames Laboratory Logo, showing two decagonal and one icosahedral single-grain quasicrystals](image)

Since the original discovery of Shechtman hundreds of quasicrystals have been reported and confirmed. Undoubtedly, the quasicrystals are no longer a unique form of solid; they exist universally in many metallic alloys and some polymers. Quasicrystals are found most often in aluminium alloys (AlLiCu, AlMnSi, AlNiCo, AlPdMn, AlCuFe, AlCuV, etc.), but numerous other compositions are also known (CdYb, TiZrNi, ZnMgHo, ZnMgSc, InAgYb, PdUSi, etc.).

![Figure 4: Quasicrystal of an alloy of aluminium, copper and iron, displaying an external form consistent with their icosahedral symmetry](image)

\(^2\) all periodic crystals

\(^3\)For example: icosahedral quasicrystals (5-fold symmetry: Al-Pd-Mn, Al-Cu-Fe, Ag-In-Yb), dodecagonal quasicrystals (12-fold symmetry: V\(_2\)Ni\(_2\), Cr\(_{70.6}\)Ni\(_{29.4}\)), decagonal quasicrystals (10-fold symmetry: Al-Co-Ni, Al\(_5\)Ir), octagonal quasicrystals (8-fold symmetry: Mn\(_4\)Si, Cr\(_5\)Ni\(_3\)Si\(_2\)).
We can classify the quasicrystals, regarding 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** - *no periodic direction*

- **icosahedral** quasicrystals with 5-fold [primitive, body-centered & face-centered lattices]
- **icosahedral** quasicrystal with **broken symmetry** (stable binary Cd$_{5.7}$Yb)

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,
- 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 [13].

### 3. Very Different Structures

Differences between the crystallography of periodic crystals (PC) and quasicrystals (QC) can be examined in either real or reciprocal space. Both viewpoints are useful for understanding some of the properties of quasicrystals. To illustrate schematically the real-space models of PC and WC, consider linear (one dimensional) chains built up with sequences of two segments, one large (L) and one short (S). PC can be obtained via addition rules. For instance, adding strips LS over and over again gives the periodic chain LS LS LS LS LS... To obtain a QC chain, substitution rules must be used instead. For instance, any given strip of LS segments can be grown by substituting L by LS and S by L in sequence; this results in the following successively grown strips:

<table>
<thead>
<tr>
<th>Initial strip</th>
<th>LS</th>
<th>LL</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plus 1 substitution</td>
<td>LSL</td>
<td>LSL</td>
</tr>
<tr>
<td>Plus 2 substitutions</td>
<td>LSLLS</td>
<td>LSLLSL</td>
</tr>
<tr>
<td>Plus 3 substitutions</td>
<td>LSLLSLSL</td>
<td>LSLLSLSLSL</td>
</tr>
<tr>
<td>Plus 4 substitutions</td>
<td>LSLLSLSLSLSLSL</td>
<td>LSLLSLSLSLSLSLSL</td>
</tr>
<tr>
<td>Plus 5 substitutions</td>
<td>LSLLSLSLSLSLSLSLSLSLSLSL</td>
<td>LSLLSLSLSLSLSLSLSLSLSLSLSL</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Initial strip</th>
<th>SS</th>
<th>SL</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plus 1 substitution</td>
<td>LL</td>
<td>LLS</td>
</tr>
<tr>
<td>Plus 2 substitutions</td>
<td>LSL</td>
<td>LSL</td>
</tr>
<tr>
<td>Plus 3 substitutions</td>
<td>LSLLS</td>
<td>LSLLS</td>
</tr>
</tbody>
</table>

5
The result is a perfectly ordered, deterministic sequence of L and S segments without any indication of periodicity. For one dimensional structures, it may be difficult to imagine why this awkward substitutional operation should be preferred instead of a straightforward periodic packing. Indeed, one-dimensional QC are expected to be unstable with respect to PC. But in two and three dimensions, substitution may be the only way to grow a structure. This is the situation, for instance, with pentagonal and icosahedral structural tiles (patterns of atoms), whose fivefold symmetries cannot be accommodated by periodicity. QC consequently become the stable structures as long as pentagonal or icosahedral atomic blocks can form.

In a monoatomic PC such as a metal crystal, all atomic sites are strictly equivalent. If some electrons are loosely bonded to atoms they have no reason to locate on a particular site and can travel essentially freely through the bulk of the metal. The result is a high conductivity and isotropy, with all the well-known consequences for properties and their applications.

Conversely, in QC structures strictly equivalent sites cannot be found in the fully extended surroundings of the sites are considered. The “free” electrons, if there are any, are forced to “locate” preferably at low-energy sites within the constraints of the Coulomb interaction, although in reality this model must be somewhat smoothed out. QC structures are such that identical atomic clusters of any size can be found at distances apart of about twice the cluster size (Fig. 6). Conductivity is therefore reduced to hopping or/and tunneling communication between hierarchy of almost identical sites, with bonding isotropy reduced to the preferred direction for hopping [14].

Which atoms form a quasicrystalline alloy depends on the electronic structure and the size of the atoms. Why the previously mentioned atoms form a quasicrystal and others don’t is a very complicated and not yet well understood process that furthermore exceeds the topic discussed in this seminar.

Figure 5: Scanning electron microscopy image of quasicrystal icosahedra (20-faced regular polyhedral displaying five-fold rotational symmetry) formed from composite silica spheres (not shown) about 30nm across (scale: bar = 2μm) [15].
The Properties and Applications of Quasicrystals

Figure 6: A planar section, perpendicular to a fivefold direction, through the structure of an icosahedral AlPdMn quasicrystal. Small rings of 10 atomic sites are visible. These correspond to the equatorial plane of the basic clusters. The rings are arranged in a self similar ring of rings which, in turn, combine in the second inflation step to form a large decagon, and so on [16].

The reciprocal space description of QC adds to our understanding and supports similar conclusions. Both PC and QC structures can be analyzed in terms of their Fourier components in that the space dependence of their density can be expressed as a sum of density waves, i.e.,

$$\rho (r) = \frac{1}{V} \sum_{\mathbf{G}} \rho (\mathbf{G}) e^{i \mathbf{G} \cdot \mathbf{r}}$$  \hspace{1cm} (1)$$

For PC, the set of \( \mathbf{G} \) vectors define a discrete reciprocal lattice in which each wave vector can be written as an integer linear combination of three basis vectors \( \mathbf{a}_i \):

$$\mathbf{G} = h \mathbf{a}_1 + k \mathbf{a}_2 + l \mathbf{a}_3$$

For QC, the number of integer linearly independent vectors required to span the reciprocal space exceeds the spatial dimension. For instance, six basis vectors are required to span the reciprocal space of three-dimensional icosahedral QC, i.e., Eq. (1) must be replaced by:

$$\mathbf{G} = c_1 \mathbf{a}_1^* + c_2 \mathbf{a}_2^* + c_3 \mathbf{a}_3^* + c_4 \mathbf{a}_4^* + c_5 \mathbf{a}_5^* + c_6 \mathbf{a}_6^*$$

Many direct consequences follow:

- It is confirmed that the point symmetry is incompatible with periodic translational order in three-dimensions;
- The wave vectors \( \mathbf{G} \) define a set of points which fill the space densely;
- There is a periodic image of the structure in a higher dimensional space (six dimensions for icosahedral structures) which can be used in quasicrystallography approaches [5, 17].

The inferred differences between the properties of PC and QC are basically contained in the analysis of wave propagation of the two types of structures. Plane waves with any wave vector \( \mathbf{k} \) except for \( \mathbf{k} \) vectors which satisfy the diffraction condition,

$$2\mathbf{G} \cdot \mathbf{k} \pm |\mathbf{G}|^2 = 0$$  \hspace{1cm} (2)$$
propagate easily in a periodic structure. The states that are excluded correspond to two-component standing waves; they remain extended but do not contribute to the propagation or transport of energy.

In QC, the exception becomes the rule since the $G$-vectors form a dense set. In this case, any $k$-vector can comply with Eq. (2). And thus be diffracted. Moreover, it is readily demonstrated that multiple diffractions occur generally and that the number of individual plane waves contributing to the resulting steady state increases with $|k|$. This comes from a simple geometrical derivation based on the Ewald sphere.

One is therefore tempted to ask if all propagation phenomena are excluded in QC. The basic question may be not this simple. Let us consider the particle (electron or phonon) associated with the plane wave of energy $\omega$ and wave vector $k$. In PC, the dispersion curve $\omega(k)$ shows a gap opening $\Delta \omega$ when $k$ obeys Bragg’s law (Eq. 2) and has its extremity on the Brillouin zone limit. The lifetime of the particle is consequently reduced to $\Delta t \approx \frac{1}{\Delta \omega}$. Gap openings are in the THz range, i.e., $\Delta \omega \approx 10^{12} \text{Hz}$, for the phonon dispersion curve. For lifetimes about $10^{-12} \text{s}$ and group velocities below $10^3 \text{m/s}$, the corresponding free path is less than 10 Å. In a QC structure, the dispersion curve is actually a dense hierarchy of gaps; but most of the gaps are very narrow. With a typical value of $10^9 \text{Hz}$ ($10^{-4} \text{THz}$) for $\Delta \omega$, the particle can propagate up to several micrometers. So propagative states can coexist with nonpropagative states in QC, the latter being much numerous and the former less effective than in crystals.

4. Electrical and Thermal Conductivity

In agreement with the analyses of the previous section, inelastic neutron-scattering measurements [15, 18] show that extended real phonons are observed only in the vicinity of strong Bragg reflections for wave vectors smaller than 0.35 Å$^{-1}$ and energies below 1.5 THz (equivalent to 6 MeV or about 70K). At higher energies, plane-wave models are no longer relevant for describing atomic vibrations in QC. Energy scans at constant wave vector at points well removed from strong Bragg peaks result in a broad distribution of excitations (Fig. 7) which is very similar to the total “phonon” density of states (Fig. 8) [19]. Wave vector scans at constant high energy (e.g., at 3 and 5 THz) give flat dispersion curves — evidence for a lack of effective propagation. Interestingly, the minimum wavelength (or maximum wave vector) at which true unbroadened acoustic modes can be observed corresponds roughly to the largest standing wave that can settle into a cavity having the same size as the basic atomic unit in the structure ($\approx 9$ Å).

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4 This holds as long as the size of the crystal doesn’t reach nano scale (as long as the size of the crystal is much greater than the free path of electrons and phonons). Quasicrystalline structure is perfect (no dislocations and other effects — except the point defects) on the coherent length of about 100nm.
The Properties and Applications of Quasicrystals

Figure 7: Energy dispersion of the inelastic neutron scattering signal of AlPdMn quasicrystals measured at two different values of the wave vectors at points in reciprocal space located away from any strong Bragg peak. Note the broad distribution of excitations [14].

Figure 8: The vibrational density of states for the icosahedral AlPdMn quasicrystal [14].

Such a reduced range of real extended phonons should result in very poor thermal conductivity, reaching a maximum value around 70K when all possible phonons are fully excited (The Dulong-Petite regime) [15]. Most of these predictions are observed experimentally. 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 [20] (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 [21, 22]. The unexpected feature is that at higher temperature, \( K(T) \) resumes an increasing trend (Fig. 9.1). This may be understood in terms of nonlinearity effects [15] which allow vibration modes to interact. The temperature dependence is quite different from classical metal samples for example Lithium (Fig. 9.2).
The Properties and Applications of Quasicrystals

Figure 9.1: The temperature dependence of the experimentally determined thermal conductivity of AlFeCu icosahedral quasicrystals compared with that of zircon [14].

Figure 9.2: The temperature dependence of the experimentally determined thermal conductivity of Li metal sample [22].

For similar reasons, most of the electronic transport is expected to come from phonon-assisted collective electron hopping between equivalent sites in the structure, and QC must behave in almost the same way as insulators at low temperature, with recovery of some conductivity as the temperature increases. Such behavior, based on a recurring hierarchical localization of the bonding electrons, is in fact in good agreement with what has been observed in resistivity data for the highest quality AlPdRe QC alloys [22]. At around 0.5K, the electrical resistivity of this QC can exceed 30Ωcm, a value which is $10^9$ to $10^{10}$ times larger than that of pure aluminium (Fig. 10.1). The conductivity

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5 This holds also for other classical metallic systems.
The Properties and Applications of Quasicrystals

increases almost linearly upon heating\(^6\), reaching a value at room temperature that is a factor of some 200-times larger than its value at the temperature of liquid helium. Chemical composition and quasicrystalline perfection are critical: defects and slight departures from ideal stoichiometry give a fairly dramatic recovery of the conductivity.

\[
\sigma(T) \propto T
\]

This behaviour is quite unexpected since the behaviour of all the components is quite different as can be seen in Fig. 10.2

\[\rho(T) \propto T^{1/2}\]

The same law applies to elements such as Pd, Re, which are present in the previously mentioned quasicrystal.
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.

QC alloys obviously do not belong to the conductor family; nor are they typical insulators since conductivity is significantly restored upon heating. Semiconductors or semi-metals cannot be considered as being closer to QC in as much as the electron density at the Fermi level in QC is smaller than in metals by a factor of only 3-10. QC definitely represent something quite different. 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.

5. Other Properties and Applications

The electrical behavior analyzed in the previous section leads to class of related properties involving the Hall effect, thermoelectric power, magnetic susceptibility, and optical conductivity. The negative value of the Hall coefficient $R_H$ for the most perfect QC brings evidence that the majority of free carriers is made up of electrons [24]. Since the coefficient at room temperature is more than 10-times larger than for pure aluminium, there is a reduced density of free carriers. But as already stated the reduction is not proportional to the amount expected on the basis of the low conductivity of QC. At liquid-helium temperature of 4.2K the negative $R_H$ has decreased from about $-10^{-9}$ to $-10^{-8}$ which is again quantitatively, consistent with the temperature dependence of the conductivity.

Thermoelectric power coefficients $S(T)$ for QC show an interesting behavior [25]. They can be quite large, up to several tens of μV/K, are mostly negative in value and decrease down to a minimum at around 100K. Above room temperature they become increasingly positive. Tuning the temperature of the minimum seems to be possible using a small shift in composition and/or appropriate annealing treatments. This effect can be used to accurately monitor a temperature setting without the help of sophisticated electronic devices.

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 soichiometric QC is diamagnetic, with a negative susceptibility of about $-5 \cdot 10^9$ emu/g. However, a transition from dia- to para-magnetism is observe at about 50° below the melting point, and the susceptibility continues to increase with temperature in the liquid state [26] (Fig. 11). 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 [27, 28]. 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 (Fig. 12) at around $12$ GHz.

8 The reason is very similar to that in semiconductors – it is a pseudogap in the electronic density of state at Fermi energy. Increasing temperature gives rise to the electronic (the same goes for gaps) excitations via pseudogaps from the valence to the conducting band. If one part of the metal is located at a higher temperature, there are more charge carriers in the conducting band. This leads to the fact that the density of conducting electrons is higher in that part, which furthermore leads to larger electrical voltage across the sample (thermoelectric voltage).

9 This is expected due to the transition of the quasicrystal from solid to liquid state.
$10^4\text{cm}^{-1}$ 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 (Fig. 6), something that would be expected if a hopping mechanism is relevant for conductivity in QC. Practical consequences should be very interesting, one of which is illustrated in Fig. 13 [29] showing that sandwiches of QC between oxide layers such as SiO$_2$ or Al$_2$O$_3$ have reflectivity (R) gap centered on the visible wavelength range$^{10}$. A straightforward application of such a property involves energy coating for solar cells, insulator screens or window glass.

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$^{10}$ The gap is of course dependent on the thickness of the oxide layer and is due to negative interference (because of the complex structure of the QC this phenomenon is expected, but the position of the minimum cannot be so easily explained)
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). Unfortunately, QC are very brittle at room temperature, with fracture strains as small as 0.35%, i.e., fracture at strains that are only just above the value of 0.2% that is usually taken to be the engineering yield strain. This restricts mechanical applications to coating situations, even though superplasticity shows up at high temperature with strains reaching up to 10% prior to fracture.

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 various indenters with spherical tips. The friction coefficient with diamond remains as low as 0.05 under constant-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. Brittliness is attenuated with the scratch and in all cases repeated passes reduced the friction coefficient down to a limit. 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 20Å 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.

The reason for high hardness is the nonperiodic structure. In classical periodic metals the atomic planes or layers slide past one another when under strain (movement of the dislocations). But in the nonperiodic structures there are no atomic planes so such sliding is not possible. Hence the material has elevated hardness.
Most of these properties combine effectively to give technologically interesting applications which have been protected recently by several patents [38]. For instance, the combination of non-sticking, 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\textsuperscript{12}.

Quasicrystalline coatings, usually 10\textmu 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 tones of powder.

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

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.

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 hydrogen-powered automobiles. Hydrogen atoms can be absorbed into either interstitial sites or on surfaces of materials. The recovery of the hydrogen\textsuperscript{13}, however, typically requires heating the material to high temperatures, also above 400\textdegree C, which severely limits the technological application of these materials. Lightweight carbon-based storage materials, such as carbon nano-tubes 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 Ti41.5Zr41.5Ni17 quasicrystal, exceeding 4 wt.% (figure 13) [39, 40].

\textsuperscript{12} It is very important to carefully spray the quasicrystaline coating on cookware (it has to remain glued to the surface while withstanding constantly strain, friction and heating proceses), because most of the quasicrystaline compounds can be poisonous if consumed.

\textsuperscript{13} The unloading procedure or the recovery of hydrogen is managed with temperature regulation – increasing the temperature causes the hydrogen molecules to exit the quasicrystaline lattice.
Figure 13: Equilibrium hydrogen vapour pressure for icosahedral phase (Ti45Zr38Ni17) and 3/2 rational approximant phase (Ti40Hf40Ni20) samples produced by rapid quenching, measured as a function of hydrogen concentration during absorption at 300°C. [39].

<table>
<thead>
<tr>
<th>Material</th>
<th>H/M</th>
<th>Weight % H</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaNi5</td>
<td>1.1</td>
<td>1.5</td>
<td>Negative electrode in Ni-metal-hydride batteries.</td>
</tr>
<tr>
<td>TiFe</td>
<td>0.9</td>
<td>1.6</td>
<td>Best material for stationary applications; requires high pressure or surface activation</td>
</tr>
<tr>
<td>Mg</td>
<td>2.0</td>
<td>7.7</td>
<td>Light, expensive; volumetric density too large; unloading temperature higher than typical exhaust from internal combustion engine.</td>
</tr>
<tr>
<td>V</td>
<td>2.0</td>
<td>3.8</td>
<td>Expensive</td>
</tr>
<tr>
<td>Ti45Zr38Ni17</td>
<td>1.7</td>
<td>2.5</td>
<td>Reasonably inexpensive; high loading capacity; requires surface activation.</td>
</tr>
</tbody>
</table>

Table 1: A selection of some of the most commonly used materials used for hydrogen storage with the hydrogen per metal atom ratio, weight percentage and most notable features. [40].

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14 Other materials such as Na etc. can also be used, due to high weight percentage ratio.
6. Conclusion

Quasicrystals are clearly fascinating materials: crystal structures, with their five-fold symmetry, are unconventional and properties are surprising and could be remarkably useful. 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.

7. References

The Properties and Applications of Quasicrystals

[38] http://www.nature.com/nature/journal/v461/n7266/fig_tab/461892a_F2.html (05.12.09)
[40] http://people.ccmr.cornell.edu/~rhennig/publications/PhilMag86.957.pdf (06.12.09)