Quasicrystals

A new kind of symmetry

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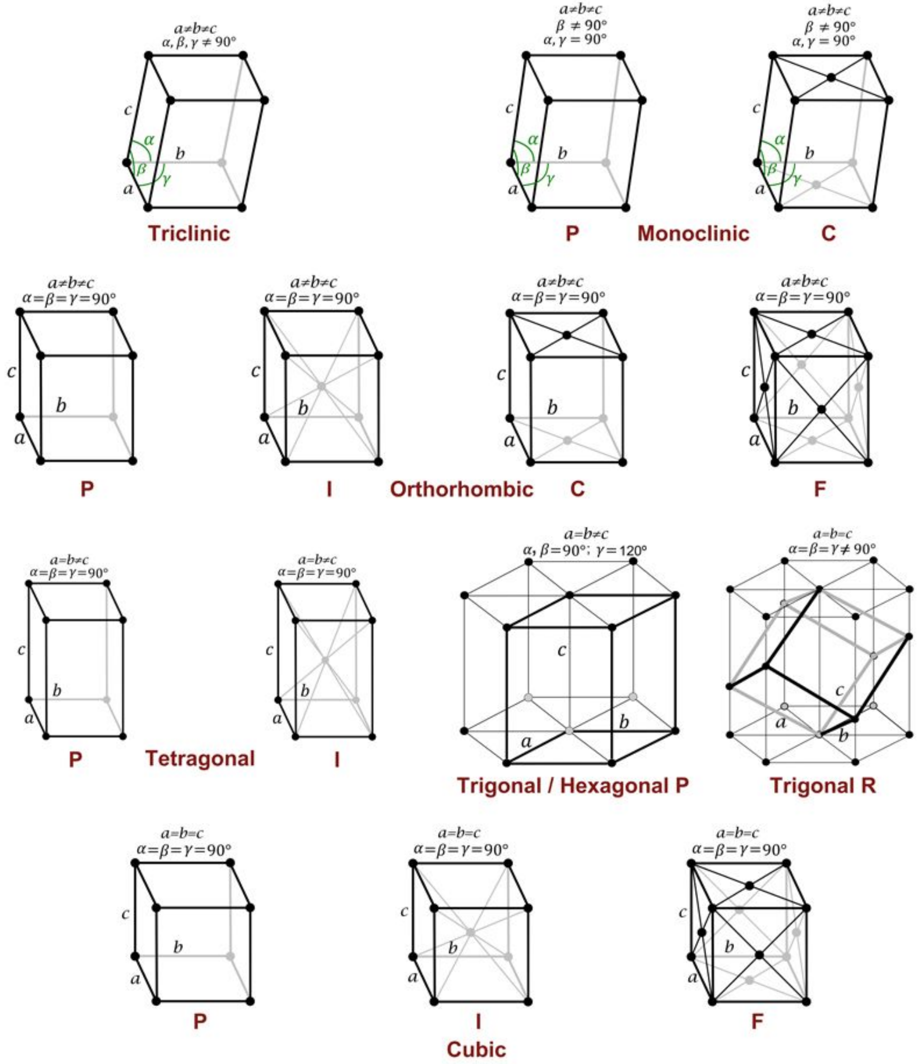
First, definitions

- A **lattice** is a *poset* in which every element has a unique infimum and supremum. For example, the set of natural numbers with the notion of ordering by magnitude (1<2). For our purposes, we can think of an array of atoms/molecules with a clear sense of assignment.
- A **Bravais lattice** is a discrete infinite array of points generated by linear integer combinations of 3 independent *primitive* vectors: $\{n1a1 + n2a2 + n3a3 \mid n1, n2, n3 \in Z\}$.
- Crystal structures = info of lattice points + info of the basis (primitive) vectors.
- Upto isomorphism of point groups (group of isometries leaving at least 1 fixed point), 14 different Bravais lattice structures possible in 3D.

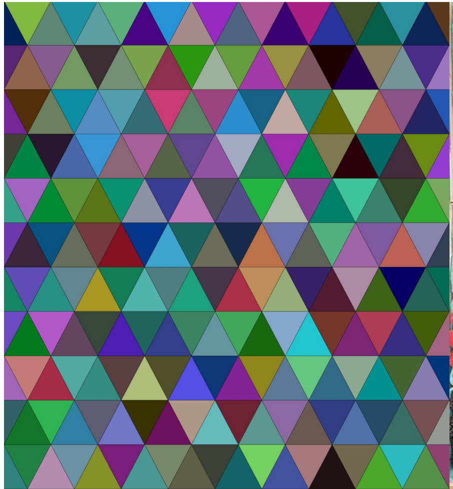

a≠b≠c
α, β, γ ≠ 90°
c
α
β
γ
b
a
Triclinic
a≠b≠c
β ≠ 90°
α, γ = 90°
P
Monoclinic
C
a≠b≠c
α=β=γ=90°
P
I
Orthorhombic
C
F
a=b≠c
α=β=γ=90°
P
Tetragonal
I
a=b≠c
α, β=90°; γ=120°
Trigonal / Hexagonal P
a=b=c
α=β=γ≠90°
Trigonal R
a=b=c
α=β=γ=90°
P
I
Cubic
F

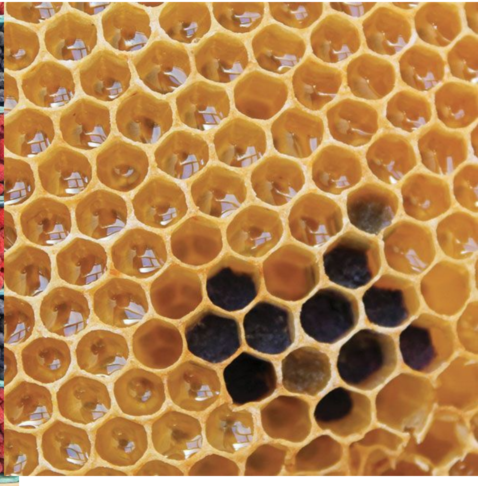
Now, crystals...

- Loosely speaking, crystals are molecular arrangements built out of multiple **unit cells** of one (or more) Bravais lattice structures.
- **Crystallographic restriction theorem**: The rotational symmetries of a discrete lattice are limited to 2-, 3-, 4-, and 6-fold.
- This leads us to propose a “functional” definition: A crystal is a material that has a discrete diffraction pattern, displaying rotational symmetries of orders 2, 3, 4 and 6.
- Note: Order 5 is a strictly *forbidden* symmetry → important for us.

Tessellations aka tilings

Now that we have diffraction patterns to work with, we consider the question of whether a lattice structure **tiles** or **tessellates** the plane. This is where the order of the symmetry plays a role. The crystals are special, as they display **translational symmetries**. As such, the tiling of their lattice structures (which we could see thanks to diffraction patterns) are **periodic**- they repeat at regular intervals.

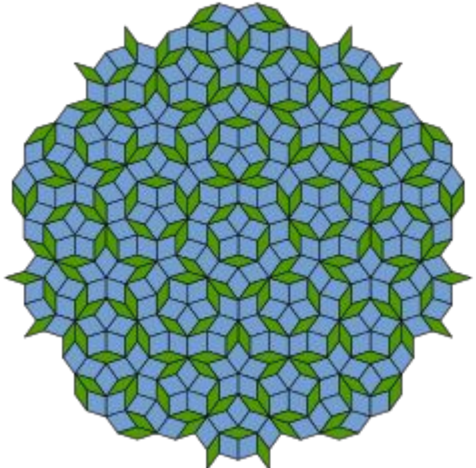




Tilings continued

A tiling is **non-periodic** if it admits no translations. A set of tiles is **aperiodic** if it admits only non-periodic tilings. Classic example: **Penrose tilings**. This particular example exhibits *reflection symmetry* and ***five-fold rotational symmetry***, as well as *self-similarity* common in fractals. It appears locally periodic, hence the term **quasiperiodicity** of tiling, which still exhibits long range order. This is the feature that distinguishes a **quasicrystal** from a crystal.

Medieval Islamic artists used them extensively.



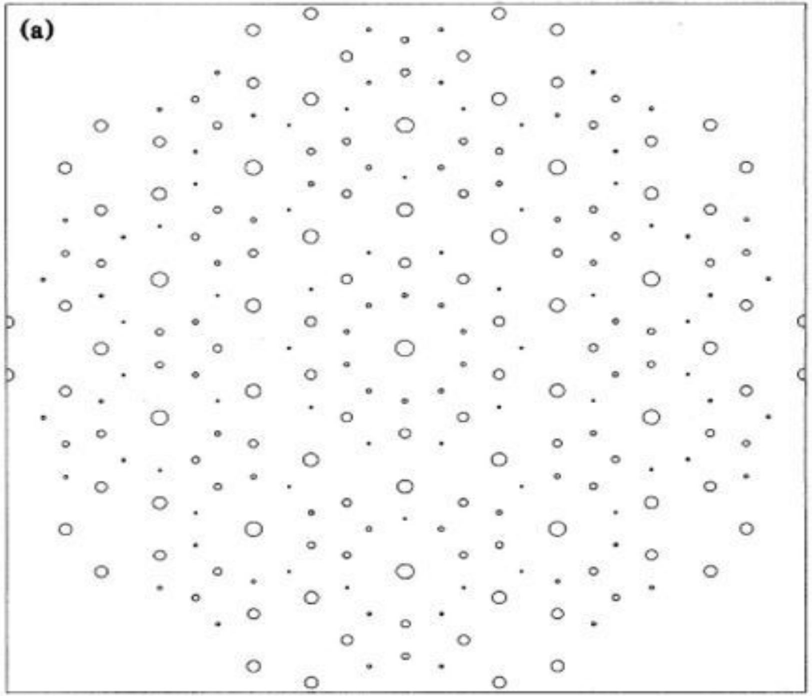
History of the not-a-crystal

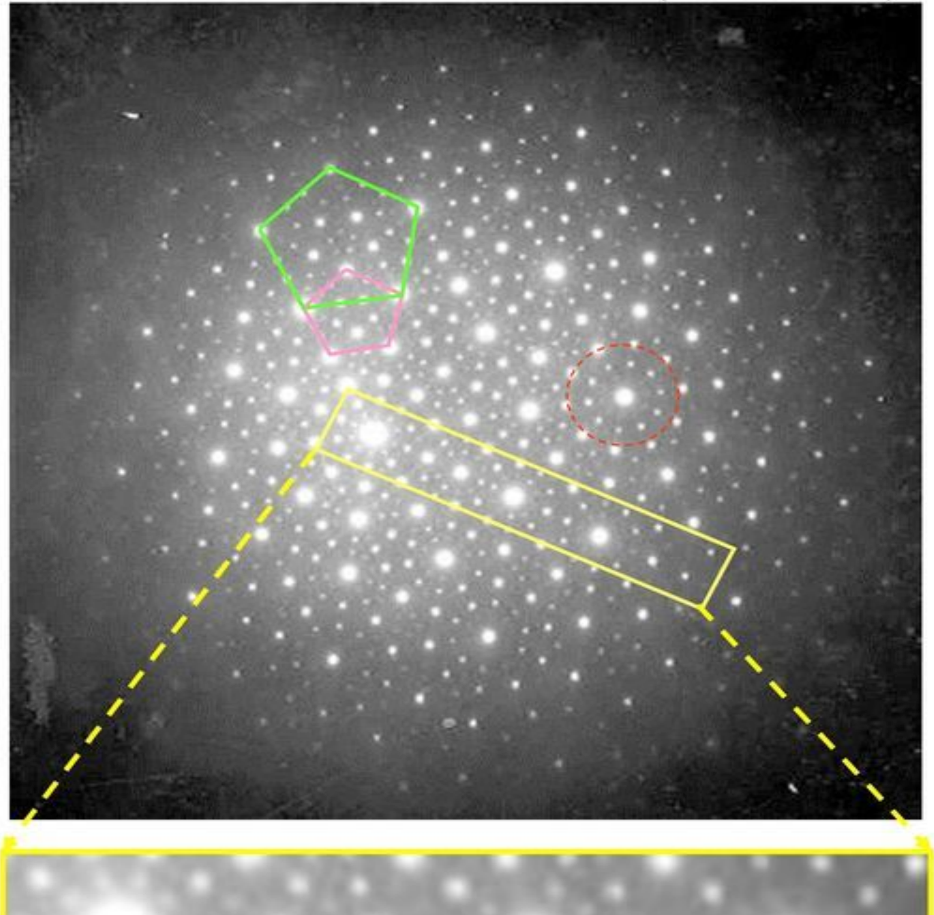
In 1982, **Dov Levine** and **Paul J. Steinhardt** analytically computed the diffraction pattern of an ideal quasicrystal, following their mathematical discovery by Penrose, who had generalized the notion of a crystal to structures with quasiperiodic translational order. Upon classification of two- and three-dimensional quasicrystals by their symmetry under rotation, it was seen that many disallowed crystal symmetries are allowed quasicrystal symmetries, as we previously saw with the Penrose tiling. Their motivation was powered by physics- **Daniel Schechtman's** discovery of the strange electron diffraction pattern exhibited by a rapidly cooled **alloy of Al** (86%) **and Mn** (14%), which exhibited the hitherto forbidden 5-fold symmetry.

DIFFRACTION PATTERN

Indication of long range rotational order

5-fold diffraction pattern from $Mg_{23}Zn_{68}Y_9$ alloy (icosahedral)





Computed diffraction pattern for an ideal icosahedral quasicrystal (in a plane

Approach of Original Calculations

1) Find lattice positions of each point in a simple k-QC, where k is the number of linearly independent (incommensurate) lattice spacings along each lattice vector direction.
2) Obtain diffraction pattern by taking Fourier transform of delta functions summed over each lattice position.
3) Compare with actual diffraction pattern obtained by Schechtman.

Remark: In fact, strange diffraction patterns were observed as early as 1930’s, but the language of quasiperiodicity wasn’t available to describe the results.

Lattice positions of 2D (3D) (i) $\vec{x}\cdot\vec{e}_i = x_{in}$, $\vec{x}\cdot\vec{e}_j = \vec{x}_{jn'}$, $(\vec{x}\cdot\vec{e}_k = x_{kn''})$

· Diffraction pattern = F.T. of $\sum_{\vec{x}'} \delta(\vec{x}-\vec{x}')$

$\vec{x}' \longrightarrow$ from (i)

3D :-

$$F(\vec{k}) = \sum_{\vec{i}>\vec{j}>\vec{k}} F_1(\vec{k}\cdot\vec{u}_{ijk})\, F_1(\vec{k}\cdot\vec{u}_{jki})\, F_1\, \vec{k}\cdot\vec{u}_{kij}).$$

where $\vec{u}_{ijk} = (\vec{e}_j\times\vec{e}_k)/[\vec{e}_i\cdot(\vec{e}_j\times\vec{e}_k)]$

$\{\vec{e}_i\}$ are unit vectors along the axes of a regular polygon (hedron)

w/ $i>j\ (>k)$ w/ partial order.

Important results

- For all disallowed crystalline symmetries in 2D constructed from a *regular* polygon with E edges, a quasicrystal is possible for E=8, p, or 2p, where p is a prime number greater than 3; then k = [E/2] for E odd and [E/4] for E even, where [n] is the greatest integer less than n.
- A similar argument can be used for 3D to show that icosahedral, tetrahedral, and octahedral quasicrystals are possible with k = 2.
- As for the computed case, the predicted diffraction pattern is composed of Bragg peaks which densely fill reciprocal space in a self-similar pattern.
- Operations of periodicity 5 in the icosahedral quasicrystals generate the golden ratio. (Not making this up!)
- <u>Conjecture</u>: Atomic arrangement with quasicrystal symmetries should be less dense than a dense-random-packed solid, with confined vacant volumes distributed quasiperiodically throughout the structure.

Relation to root lattices

- Finite reflection groups can be classified into crystallographic and non-crystallographic reflection groups. In the crystallographic reflection groups, as per the restriction theorem, we can have orders 2, 3, 4, and 6.
- The crystallographic point group of a root lattice coincides with the automorphism group of the corresponding root system, where each reflecting hyperplane is specified by a vector (root) perpendicular to it.
- As one might expect, the symmetries exhibited by the roots systems has a direct counterpart in physical (quasi)crystalline structures.
- M Baake, et al. showed that root lattices and their reciprocals might serve as the right pool for the construction of quasicrystalline structure models. All non-crystallographic symmetries observed so far are covered in minimal embedding with maximal symmetry.

Classification of QC’s

Structural classification:-

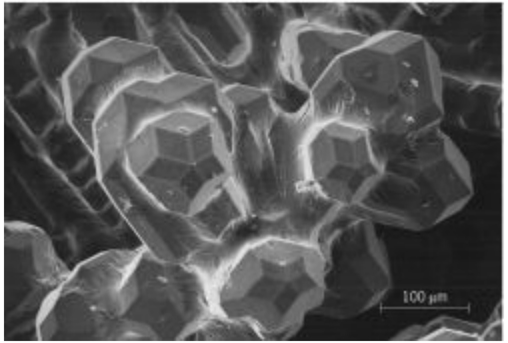
1) *Quasiperiodic in two dimensions (polygonal or dihedral quasicrystals)* - There is one periodic direction perpendicular to the quasiperiodic layers.

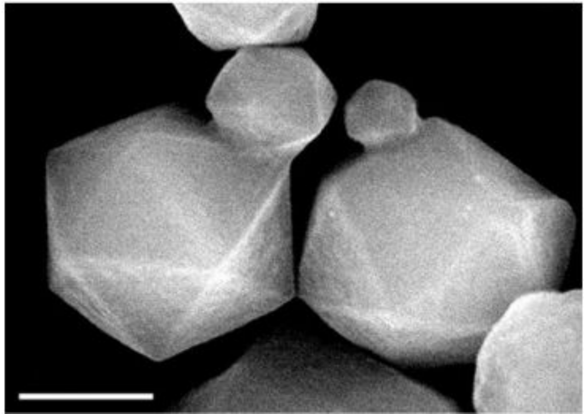
- **Octagonal** quasicrystals with local 8-fold symmetry [primitive & body-centered lattices] e.g. Mn4Si, Cr5Ni3Si2
- **Decagonal** quasicrystals with local 10-fold symmetry [primitive lattice] e.g. Al-Co-Ni, Al5Ir
- **Dodecagonal** quasicrystals with local 12-fold symmetry [primitive lattice] e.g. V3Ni2, Cr70.6Ni29.4

2) *Quasiperiodic in three dimensions* - no periodic direction

- **Icosahedral** quasicrystals with 5-fold [primitive, body-centered & face-centered lattices] e.g. Al-Pd-Mn, Al-Cu-Fe, Ag-In-Yb
- **Icosahedral** quasicrystal with **broken symmetry** e.g. stable binary Cd5.7Yb

Quasicrystal of an alloy of aluminium, copper and iron, displaying icosahedral symmetry.



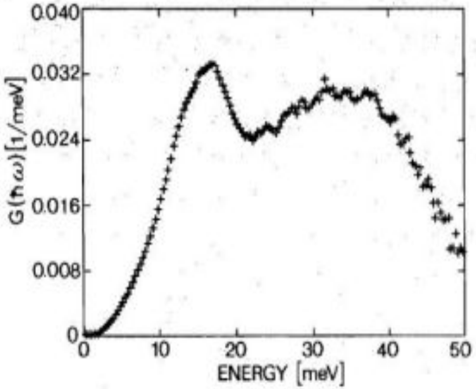


Thermal classification:-

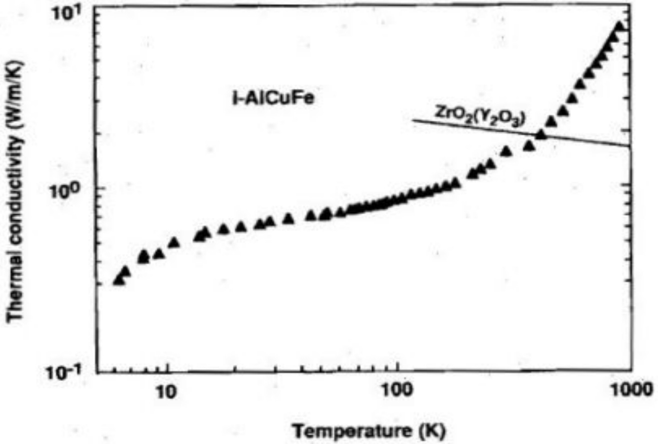
- **Stable** quasicrystals grown by slow cooling or casting with subsequent annealing
- **Metastable** quasicrystals prepared by **melt-spinning**.
- **Metastable** quasicrystals formed by the crystallization of the **amorphous phase**.

Electrical properties

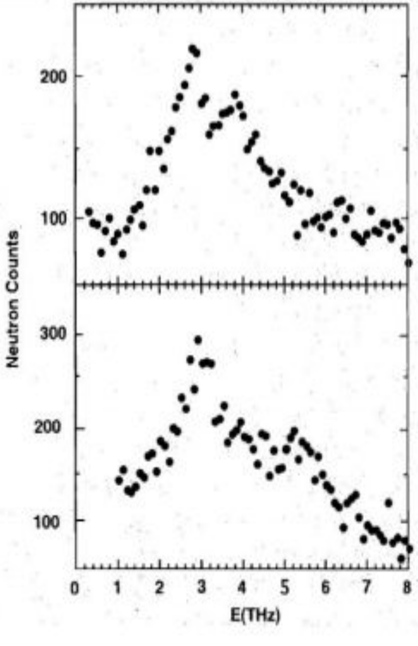
- QC alloys do not belong to the conductor or insulator family. Conductivity restored upon heating.
- Electron density at the Fermi level in QC is smaller than in metals by a factor of only 3-10. So, QC's cannot be classified as semiconductors.
- The hierarchical packing of clusters in the structure 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.



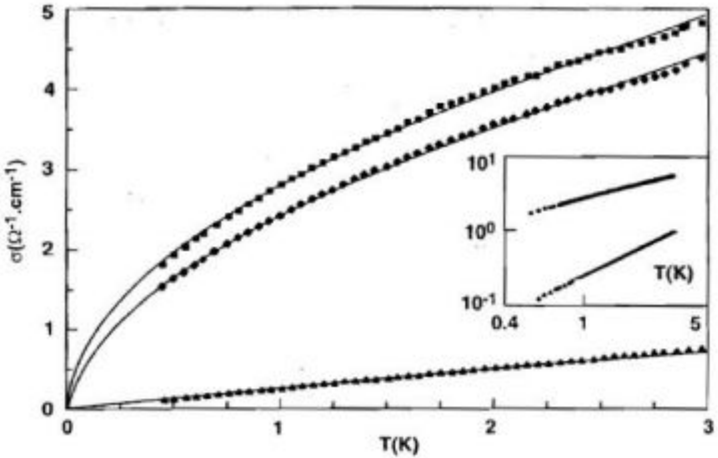
The vibrational density of states for the icosahedral AlPdMn quasicrystal [14].



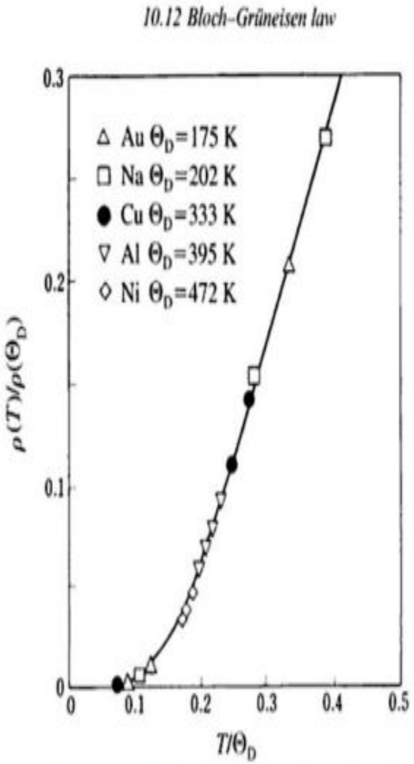
1: The temperature dependence of the experimentally determined thermal conductivity of AlFeCu icosahedral quasicrystals compared with that of zircon [14].



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].



The electrical conductivity $\sigma(T)$ at low temperatures of AlPdRe quasicrystals showing the $\sigma \sim T$ behavior for a prefect icosahedral phase (lower curves) as well as the $\sigma \sim T^{1/2}$ law for a slightly less good sample (two uppermost curves). A log-log plot is shown in the insert for the uppermost and lower curves [23].



Temperature dependence of the electrical resistivity ρ (which equals $\frac{1}{\sigma(T)}$) showing the $\rho \sim T$ behavior for various pure metal samples (Au, Na, Cu, Al, Ni)[7], where Θ_D is the Debye temperature of the metal. This is known as the Bloch-Grüneisen law.

Practical applications in day-to-day lives

- *Non-sticking+hardness+corrosion resistance+low thermal conductivity* = almost ideal material for coating frying pans or other cookware.
- *Low friction coefficient +high hardness+corrosion resistance* = reduction in surface damage and energy dissipation in the moving contact between two solids. Quasicrystalline cylinder liners and piston coatings in motor-car engines results in reduced air pollution and increased engine lifetimes. When combined with biocompatibility, QC has a promising future in surgical applications as a coating on metallic parts used for bone repair and prostheses.
- At high temperatures, QC's become *superplastic*. Rocket motors and aero-engine turbines would greatly benefit, since QC's can accommodate thermal constraints and the thermal expansion of the protected bulk material.

QC as an assistant to H-fuel

- 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 requires heating the material to high temperatures above 400C.
- 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.

References

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