Quasicrystals as cluster aggregates

Quasicrystals are solids that exhibit symmetries long thought forbidden in nature. Since their discovery in a rapidly solidified Al–Mn alloy in 1984, the central issue in the field has been to understand why they form. Are they energetically stable compounds or stabilized by entropy? In recent years, major strides have been made in determining atomic structure, largely by direct imaging using advanced electron microscopy. One system is now known to be energetically stabilized, and quasicrystals are therefore firmly established as a new physical state of matter. They represent a unique packing of atomic clusters some tens of atoms in size, with substantial localized fluctuations, referred to as phasons. Understanding phasons may in future allow their unique macroscopic properties to be tailored for useful materials applications.

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Quasicrystals are aperiodic solids that exhibit rotational symmetries incompatible with conventional periodic lattice order, for example, icosahedral symmetry in three dimensions and tenfold symmetry in the plane. The first example[1] was obtained as a metastable icosahedral configuration in a rapidly solidified Al–Mn alloy (Fig. 1a). Soon after this discovery, thermodynamically stable quasicrystals were found in several other alloys[2–4]. At present both metastable and stable quasicrystalline phases can be formed in a variety of metallic alloys[5], and certain stable phases can be grown into a single grain several millimetres (Fig. 1b) or even centimetres in size. It would appear obvious, therefore, that quasicrystals can represent a free-energy minimum state at a given temperature. Such highly perfect quasicrystalline materials exhibit a striking diffraction pattern (see Fig. 2); namely, (i) a large number of diffraction peaks, (ii) peak sharpness comparable to that from nearly perfect crystals such as silicon, and (iii) all peaks are located at their ideal positions, consistent with the quasicrystalline symmetry within the limits of instrumental resolution.

These diffraction features, in particular the sharp diffraction peaks (represented by delta-functions)
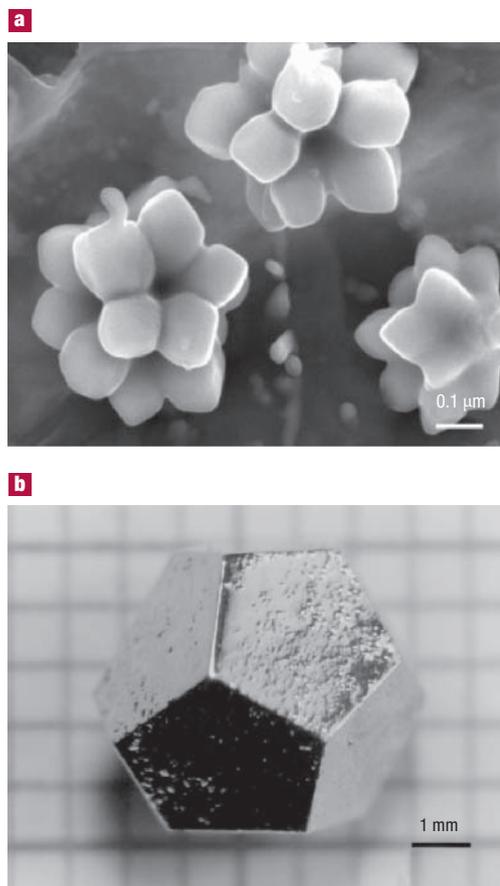
Figure 1 Morphologies of faceted single grains of icosahedral quasicrystals. a, Scanning electron microscope image of icosahedral-symmetry grains formed in a rapidly solidified Al-6at.%Mn alloy (courtesy of An-Pang Tsai, unpublished results). b, Optical micrograph of a large dodecahedral grain of $Zn_{56.8}Mg_{34.6}Ho_{8.7}$ quasicrystal successfully grown from the melt via a slow-cooling method (courtesy of Ian Fisher & Paul Canfield[63]).

that had been believed to be possible only for periodic crystals, can no longer be explained with the model structures discussed in early times. Representative early
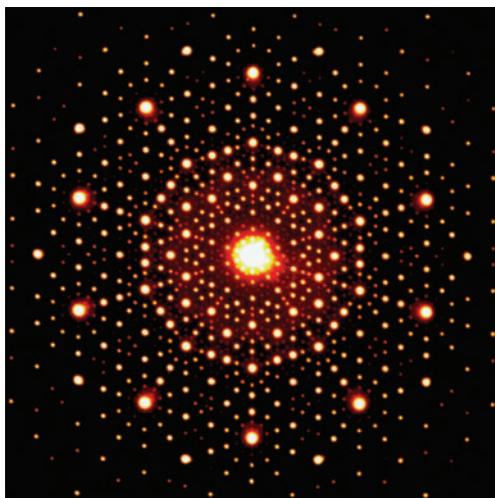
models are an icosahedral glass model[6] that assumes only a short-range icosahedral order distributed randomly to form the solid, and the so-called Pauling's model[7] that uses multiply twinned configurations of giant cubic crystals to generate a pseudo-fivefold symmetry pattern. Nowadays we interpret this interesting long-range order as true quasiperiodicity[8], which is not a simple periodic arrangement of a unit cell as a normal crystal, but instead is composed of an array of two length-scales as represented by the Fibonacci sequence (Fig. 3). This is a precisely defined sequence that is able to generate the delta-function diffraction peaks and account for the experimental observations. In time, this revolutionary discovery led to a redefinition of the term 'crystal' to mean any solid giving essentially discrete diffraction peaks, as declared by the International Union of Crystallography in 1991. Microscopic unit cells that repeat periodically are not necessary any longer for a material to be called a crystal, and within the family of crystals we now distinguish between periodic and aperiodic (incommensurate) solids based on their diffraction features. The term quasicrystal is a short form for 'quasiperiodic crystal', and never means an imperfect, pseudo-crystal as one might guess from the expression. Rather, quasiperiodicity represents just as rigorous an ordering as periodic order, even though in many systems the rules for defining the ordering remain to be discovered[9]. In any case, it is important to recognize that quasicrystals indeed represent a well-ordered condensed state of matter that has been generally accepted as a new form of solid; a third phase following the classical crystalline (periodic) and amorphous (random) solids.

"Where are the atoms?" This has been the fundamental key question since it was used as the title of an early article[10]. It is important from the perspective of basic physics, but also if the unique physical properties of quasicrystals are ever to be understood and controlled to provide new materials with useful properties, as has long been the case with crystalline and amorphous materials. We describe quasicrystal structure based on a quasiperiodic lattice (quasilattice), which is constructed by a set of two or more unit cells, and a proper atomic decoration of it.

Diffraction intensity calculations of any quasicrystal model structures are carried out in the framework of hyperspace crystallography[11,12], a mathematical recipe that treats a quasicrystal as a periodic structure embedded in a hyperspace (for example, a cubic lattice defined in six dimensions generates the icosahedral quasilattice in three dimensions; an example of generation of a one-dimensional quasiperiodic order from a two-dimensional square lattice is shown in Fig. 3). As an effective guide for local atomic decorations, though Pauling's model[7] was found to be invalid, the giant cubic crystals he used have significant implications. One commonly finds multiple-shell icosahedral atomic clusters in many of the giant crystals (Fig. 4) that occur near to compositions known to form quasicrystals[13–15], prompting the idea that these clusters are also the building blocks of quasicrystal structures. In this sense, quasicrystals can be viewed as the consequence of linking the basic clusters in a quasiperiodic way — a quasicrystalline cluster aggregate[16]. This concept is supported by hyperspace crystallography that clearly correlates such cubic crystals as a variant structure of quasicrystals[13].

But, unlike the structure determination of crystals, in the case of quasicrystals a unique structural solution cannot be easily obtained solely based on the standard X-ray diffraction experiments. This is due to the local isomorphic nature of a quasilattice[8]. To illustrate this feature of a quasicrystal, consider the one-dimensional quasiperiodic lattice in Fig. 3; several quasiperiodic arrangements of S and L can be generated when the square lattice is uniformly translated along the $E_\perp$ direction, and they are locally isomorphic to the original. Each gives rise to identical diffraction intensity distributions[17]. That is, multiple structural solutions — arrangements of clusters — intrinsically occur from the diffraction data. Atomic-resolution electron microscope images are unique in this regard, as they directly represent the local atomic structure and can therefore investigate details of the cluster packing and relevant local atomic configurations. Electron diffraction is also available to probe the average features seen in an image, in a comparable manner to X-ray diffraction. The picture that is emerging from these studies supports the picture of a quasicrystal as a cluster aggregate: a quasilattice successfully decorated by atomic clusters that have the same point symmetry of the quasicrystals.

Nevertheless, there is still significant information lacking concerning the local packing of the clusters. In real quasicrystalline material, are the clusters always placed at the ideal quasiperiodic positions? What types of characteristic disorder (defects) do they possess? These local structure issues are especially important for quasicrystals, because they have direct influence on physical properties such as conductivity, and also on their thermodynamic stability, which in turn is important for understanding why quasicrystals form. Yet these issues have not been clarified sufficiently because of experimental limitations of standard X-ray techniques and conventional high-resolution electron microscopy. Below we describe some recent insights made into these critical issues, which have been

provided through direct structural observations by advanced transmission electron microscopy.

CLUSTER PACKING AND STABILTY OF QUASICRYSTALS

Decagonal quasicrystals[18] are the planar realization of a quasiperiodic order, whose structure is described as a periodic stack of quasiperiodic layers and is composed of decagonal columnar clusters as a building unit. Because of their two-dimensional character, quasiperiodic planar arrangements of atoms can be directly addressed through high-resolution electron microscope observations viewing along the tenfold-symmetry axis. Individual decagonal clusters appear as decagons in the projected images, so that their packing, or tiling, may be directly observed[19]. (Note that for icosahedral quasicrystals, the atomic images are the projections of three-dimensional quasiperiodic structures so that individual icosahedral clusters cannot be distinguished; see ref. 20, for example). Previous observations, mostly made on Al–transition metal decagonal alloys, provided evidence that their structures are quasiperiodic arrangements of the decagonal tiles. All models assumed either tenfold or fivefold symmetric atomic configurations within the clusters; typical and well-known examples are the large decagonal clusters with a diameter of 2 nm, commonly found in Al-Ni-Co, Al-Cu-Co and Al-Pd-Mn decagonal alloys[19,21,22]. These cluster symmetries, in particular the tenfold rotation axis, originated not from confident experimental evidence, but rather from the notion that the symmetry of every component cluster should directly reflect the entire symmetry seen in the diffraction pattern, in other words, that the microscopic and macroscopic symmetry should be the same, similar to the unit cell concept for a regular crystal. Hence there still remained ambiguities in terms of detailed atomic distributions within the clusters.

Some decagonal quasicrystalline samples were found to have a cluster arrangement similar to a Penrose pattern[23], a planar tiling composed of two different tiles with matching rules. The matching rule is a strict mathematical rule that forces the tiles to join uniquely into a perfect quasiperiodic pattern; however, such a rule is purely mathematical and does not provide any physical insight on why the atoms should favour such a complicated structure. It cannot explain how quasicrystals arise as a minimum free-energy state against competing periodic crystals. As an alternative to the two-tile Penrose tiling (or its subset tiling composed of multiple shapes of tiles), Burkov[24] described the quasiperiodic pattern in a broader sense that discards the matching rule, describing the model structure of Al-Cu-Co as a random packing of decagon clusters having tenfold symmetry. The clusters are allowed to overlap with their neighbours, in the sense that they partially share atoms with neighbouring clusters. In random packing, there are no rules that force the clusters into a unique arrangement, and hence many possible configurations appear due to a large degree of freedom on how to join or overlap the neighbour decagons — many degenerate ways of packing are an unavoidable consequence of this model. This idea, in turn, suggests
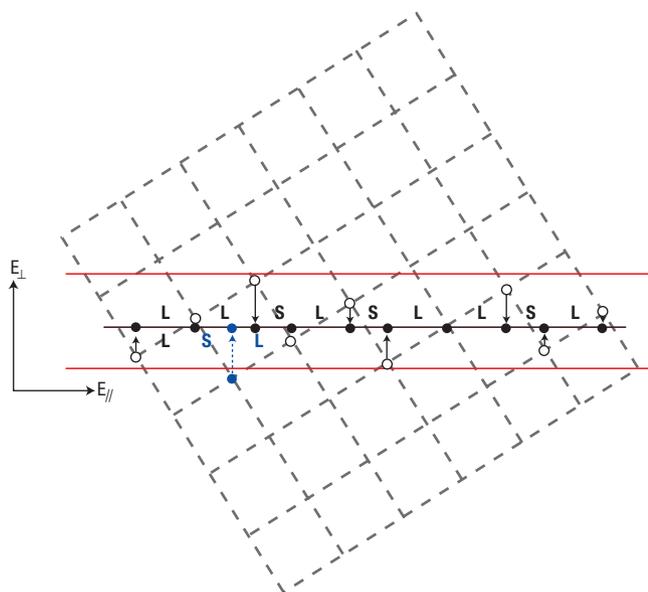
that configurational entropy might be an important factor causing quasicrystals to be more stable than crystals. The so-called random tiling model would give significant contributions of configurational entropy[25], and seems to be consistent with the fact that the stable quasicrystalline phases discovered so far occur only at high temperatures[5], and most transform into periodic structures at lower temperatures. In the random-packing picture, resultant structures should appear to have a considerable amount of chemical disorder — most atomic sites are mixed with constituent atoms. Atomic disorder is, of course, another contribution to configurational entropy[26].

More recently, however, a striking feature of cluster packing has become apparent through investigations of a decagonal $Al_{72}Ni_{20}Co_8$ (so-called Ni-rich Al-Ni-Co phase[5,27]). This material exhibits the highest quasicrystalline structural perfection available today, as confirmed from microscopic[26] to macroscopic scales[28], and therefore is an excellent candidate to investigate the intrinsic features of a quasiperiodic structure. The insights have come from the use of Z-contrast scanning transmission electron microscopy[29,30], an alternative to classical high-resolution phase-contrast transmission electron microscopy (see Box 1); the first application of the technique to the quasicrystal[31–33] provided immediate insights into the veiled structural details. The first significant breakthrough to emerge is a breaking of the tenfold symmetry within the 2 nm decagonal cluster, see Fig. 5a. The brightest spots in the Z-contrast image represent atomic columns of Ni or Co (Ni and Co are neighbouring elements in the periodic table and are not distinguishable). In the cluster centre they are clearly not arranged in a tenfold form, but appear to show only mirror symmetry. Moreover, such local broken symmetries in every decagon are found to be not in random orientations but in accord with a perfect quasiperiodic pattern[33]. The pattern can be well represented by the novel form of decagon packing proposed by Gummelt[34]

Figure 3 Generation of 1D quasiperiodic order from a 2D square lattice. The slope of the square lattice with respect to the $E_{//}$ direction is $-1/\tau$, where τ is an irrational number ($= (1+\sqrt{5})/2$) known as the golden mean. By projecting the 2D lattice points (open circles) contained within an acceptance window bound by the red lines along the $E_\perp$ direction, a 1D quasiperiodic lattice (filled circles) is obtained along the $E_{//}$ direction. This is a Fibonacci sequence of the two length-scales L and S. Translation of the lattice along $E_{//}$ corresponds to spatial translation of the quasicrystal, distortion along $E_{//}$ corresponds to a phonon. Translation along the $E_\perp$ direction causes some external lattice points to move into the acceptance window and some of the original points to move outside the window. As an example, if the blue lattice point comes into the window a new local sequence LSL (blue) is generated instead of the original LLS sequence. This is a phason flip, a special kind of diffusive motion that is specific to a quasicrystal; details are described in the text.

Box 1: Annular-dark-field scanning transmission electron microscopy (ADF-STEM).

This technique provides atomic-resolution images by effectively illuminating each atomic column one-by-one as a finely focused electron probe (< ~2 Å) scans across the specimen, generating an intensity map at the annular detector (Fig. B1). The atomic images may, to a good approximation, be interpreted assuming independent scattering from individual atomic columns, and hence the observed intensity distribution ($I(\mathbf{R})$) can be simply described by a convolution between a probe-intensity function ($P(\mathbf{R})$) and a scattering object function ($O(\mathbf{R})$) (the mathematical definition of incoherent imaging[30]);

$$I(\mathbf{R}) = O(\mathbf{R}) \otimes P(\mathbf{R}) \tag{1}$$

Here, $O(\mathbf{R})$ represents the columnar scattering cross-section that contributes to the annular detector. By detecting high-angle scattering ($s > \sim 1\text{Å}^{-1}$), the intensity at the detector is dominated by phonon scattering events; that is, thermal diffuse scattering (TDS). An Einstein model of independently vibrating atoms is usually sufficient to describe the multiphonon contribution that dominates high-angle diffuse scattering and to estimate the integrated intensity reaching the detector. Therefore, the intensity of each illuminated atomic column will be directly related to the TDS cross-section (σ_{TDS}), which is given by integrating an absorptive form factor[65] ($f'_{HA}(M,s)$) over the angular range of the detector[30]:

$$f'_{HA}(M,s) \approx \sigma_{\text{TDS}} \propto \int_{\text{detector}} f^2(s)[1-\exp(-2Ms^2)]\, d^2\mathbf{s} \tag{2}$$

where the $f(s)$ is the atomic form factor for elastic scatterings (with $s = \theta/2\lambda$, θ is a scattering angle, λ is the electron wave-length) and M is the Debye–Waller factor defined by mean-square thermal vibration amplitude of the atoms. Because σ_{TDS} is proportional to the square of $f(s)$ (equation (2)), ADF-STEM provides a significant atomic-number-dependent contrast[29] (Z-contrast). Furthermore, σ_{TDS} is a function of M (see the upper-right hand side of Fig. B1), and hence the ADF-contrast is also sensitive to the Debye–Waller factors[54] at individual atomic sites (columns).
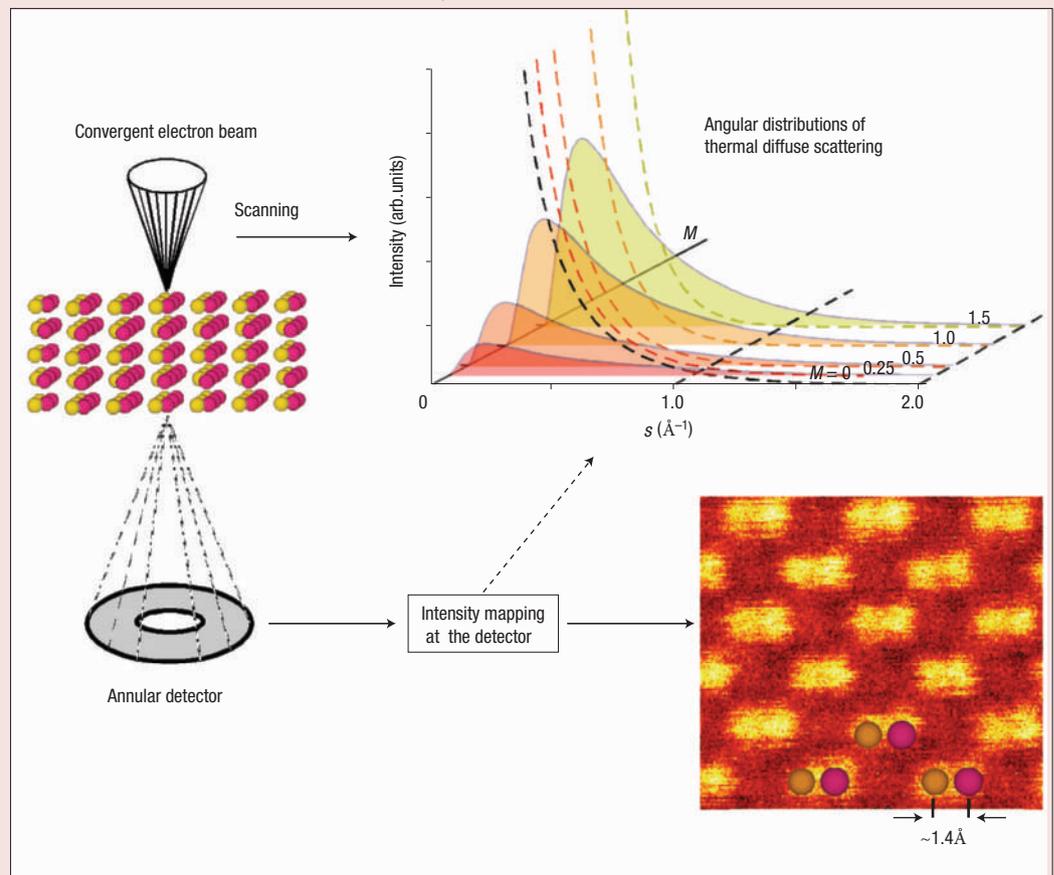

Figure B1 Schematic drawing of atomic-resolution ADF-STEM. The resolution is primarily determined by the size of the convergent electron beam. The intensity of electrons reaching the annular detector ($f'_{HA}(M,s)$, given in equation (2)) is dominated by TDS, and depends strongly on Z. The angular distribution depends on the M values; M-dependent changes of $f'_{HA}(M,s)$[65] are shown for an aluminium atom.

(Fig. 5b). In Gummelt's construction plan, decagons are not tenfold symmetric, and they overlap with their neighbours according to the well-defined rule (overlap rule) that is equivalent to the Penrose matching rule, and forces the decagons into a perfect quasiperiodic arrangement.

This remarkable mathematical proof at last has led to a physically plausible picture for the origin of quasicrystals. A subsequent but important proof by Steinhardt and Jeong[35] has shown that the overlap rule realizes the condition that the density of the decagons is maximized. Suppose the atomic configuration within a decagon, that is, the atomic cluster in the form of Gummelt's decagon[33,36], is energetically favoured. Then, quasicrystals occur as a consequence of simple energetics, following 'density maximization of energy minimized clusters'. The fact that the $Al_{72}Ni_{20}Co_8$ structure appears to be the realization of a unique packing of symmetry-breaking clusters (Gummelt's decagon) therefore suggests that the phase is dominantly stabilized by energy; if there were significant entropy contributions, a considerable amount of random structural disorder or deviations from an ideal tiling would be observed. Symmetry-breaking atomic decorations on the 2 nm decagonal cluster of the $Al_{72}Ni_{20}Co_8$ in fact provide a remarkably better fit to electron microscope images on some details, such as triangular arrangements of Al atoms[36] around the cluster centre and closely spaced (~0.13 nm) pairs of transition metal atoms[32], which did not exist in any previous tenfold symmetric models.

Strong supporting evidence on the cluster stability comes from a first-principles total energy calculation[37,38], which demonstrates that the symmetry-breaking cluster is energetically more favoured than any symmetric-based models. Shown in Fig. 5c are three representative cluster models[37] for three different symmetries; mirror symmetry, fivefold rotation symmetry and tenfold rotation symmetry (in the calculations, Ni atoms were used for all transition metal atoms). Note that the three structures in the calculations have the same unit-cell dimension and the same number of each atom species, so that their total energies can be directly compared. We find that the structure with broken symmetry, the mirror symmetry, has the lowest energy, about 12 eV per unit cell lower than the structure with tenfold symmetry, and 5 eV per unit cell lower than the structure with fivefold symmetry. This is clear evidence that the symmetry-breaking cluster is energetically more favoured than any symmetric cluster. Remember that most of the decagons identified in Fig. 5a reveal the symmetry-breaking feature; the broken symmetry provides an atomistic explanation for Gummelt's overlap rule and gives insight at a fundamental level into why these decagonal clusters would form a perfect quasiperiodic arrangement, even though the detailed atomic configurations in each cluster slightly differ depending on their local environments[36].

$Al_{72}Ni_{20}Co_8$ has turned out to be a quasiperiodic intermetallic compound with nearly perfect atomic order — it is definitely not comparable to order–disorder type alloys, which take the form of a disordered solid solution at high temperature to account for significant entropy contributions.
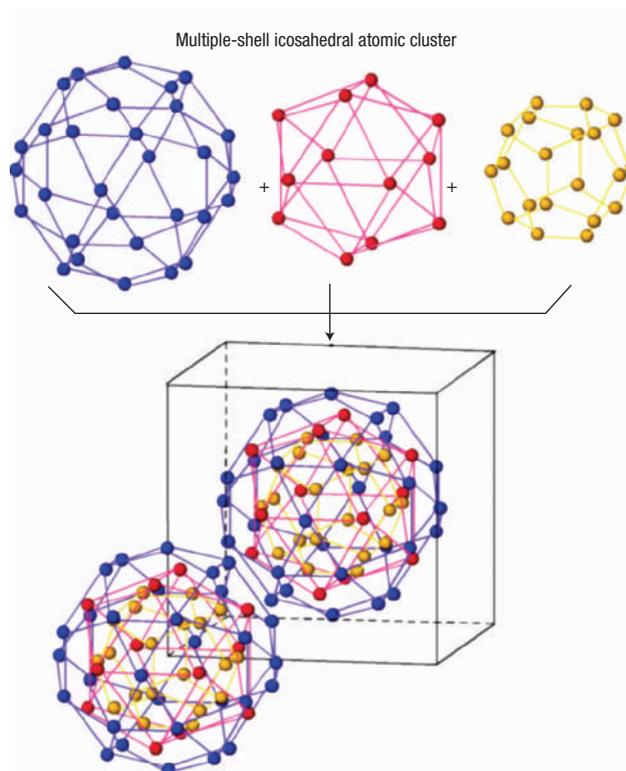

Multiple-shell icosahedral atomic cluster

Good chemical order between the Al and transition metal, directly observed in the Z-contrast images, seems to be consistent with the fact that the present highly perfect Al-Ni-Co structure occurs only for a narrow composition range, within a few atomic percent for both the Al and transition metal contents[39]. If the structure could tolerate a considerable amount of chemical disorder, essential for a random-packing model, then the single-phase region would extend to a much wider composition range at high temperatures — this is evidently not the case. In this sense, the $Al_{72}Ni_{20}Co_8$ compound is close to its ideal stoichiometry, being tuned in favour of structural energy. This may well be explained by optimized average valence electron concentration per atom (e/a)[5], which is known as Hume–Rothery's empirical rule[40] that concerns structural stability of ordered alloys in terms of Brillouin-zone/Fermi-surface interactions. When the composition deviates from the ideal stoichiometry, Al-Ni-Co alloys form several types of less-ordered quasicrystalline phases[5,41] with diffraction patterns that show a strong diffuse background and broadened Bragg peaks — direct signs of significant disorder. For such disordered quasicrystals, their average structures may be well described by random packing of clusters[20]. The apparent high symmetry of these patterns is then a result of averaging over the local random disorder. Structural variations of the basic cluster (at some conditions, fivefold symmetric decagonal clusters occur for the decagonal Al-Ni-Co alloys[42]) will then simply depend on the alloy composition and annealing temperature, in the same way as ordinary crystalline alloys behave, and can be depicted through equilibrium phase diagrams. Nevertheless, we now

Figure 4 Atomic configurations commonly found in Cd_6X intermetallic compounds. X = Ca, Sr, Y and most of the rare-earth elements. The structure is a typical example of a giant cubic crystal constructed by a body-centred-cubic type packing of large icosahedral atomic clusters. These clusters are believed to be a building block of $Cd_{5.7}X$ (X = Ca and Yb) icosahedral quasicrystal structures[64].

see that the best quasicrystalline sample appears to be a highly ordered intermetallic compound with only a minimal amount of disorder on the atomic scale, within the resolution limit of the STEM imaging ~0.1 nm. The fundamental reason for the existence of such well-ordered quasicrystals is that their structure is energetically favoured. Only rarely do practical experimental conditions allow the perfect structure to be realized, and therefore most quasicrystalline phases do not reach that degree of perfection. The situation seems to be quite analogous to that of normal crystals; that is, highly perfect, almost defect-free single crystals can only be grown for a limited range of materials under carefully controlled conditions.

LOCALIZED BEHAVIOUR IN CLUSTER COMPOUNDS

Clusters outlined by high-symmetry polyhedra are a good representation of short-range atomic order in quasicrystals, and are also found in some crystalline compounds with giant unit cells. In this section, we briefly describe how these clusters not only provide effective motifs to represent the geometrical substructure of quasicrystals or giant crystals, but they also define the length scales of characteristic localized fluctuations, which in turn have a critical effect on the conduction properties. In the case of quasicrystals, these localized fluctuations may be described in terms of phason[43–45] fluctuations specific to quasiperiodic order, as will be demonstrated below. But the concept of a localized fluctuation has a more general importance to a broad class of structurally complex systems, in which the cluster substructure essentially dominates their major physical properties[46].

Even though the best quasicrystalline materials show delta-function-like diffraction peaks, sharp enough to compare with the best crystals, we may still expect substantial diffuse scattering to originate from phason-related fluctuations or disorders[47–50]. Here, a phason[43–45] is a unique elastic degree of freedom that arises as a consequence of defining the quasicrystal through an n-dimensional hyperspace lattice ($n > 4$); see Fig. 3. Suppose that the square lattice (hypercrystal) is elastically excited to give a non-uniform translation of the lattice points. Along the $E_{//}$ direction it corresponds to phonons as in the normal crystals, whereas along the $E_{\perp}$ direction it gives rise to an extra degree of freedom, phasons, that occur only for quasiperiodic structures. Locally, phason excitations may turn out to switch S and L at some places, which, in the example illustrated in Fig. 3, flips a sequence LLS into the sequence LSL. In the real quasicrystal structure, primary phason effects are often manifested as fluctuations or occupational disorders at pairs of atomic sites that are separated by less than a typical interatomic distance[51]. These closely spaced sites are termed phason-flip sites, where, due to simple geometrical constraints, one site should be vacant when the other is occupied; the atom may be hopping[51] between them. Therefore, within this context, the lattice dynamics of quasicrystals can be described by a combination of lattice vibrations (phonons) and atomic fluctuations or jumps (phasons). When these local atomic fluctuations show long-range correlations, phason dynamics modes

may be characterized by long wavelengths of the order of ~100 nm (ref. 52) and slow relaxation times, several tens of seconds[52,53] due to the diffusive nature of a phason excitation[44]. Here we describe only local behaviour. Atomic fluctuations at such local phason-flip sites do not destroy the long-range quasiperiodic order, but instead give rise to significant diffuse scattering in the same manner as thermal vibrations[50].

Thermal diffuse scattering (TDS) is described by the mean-square thermal vibration amplitude of the atom (Debye–Waller factor), see equation (2) in Box 1. Having in mind that the high-angle annular detector mainly captures TDS[30], annular-dark-field scanning transmission electron microscopy (ADF-STEM) is able to detect any local thermal vibration anomaly through investigations of the image intensity with variations in temperature and/or detector angle range[54]. For the highly perfect decagonal $Al_{72}Ni_{20}Co_8$, significant local fluctuations are in fact observed as an anomalously large Debye–Waller factor at specific Al sites. The anomalous sites are located around the core of the 2 nm decagonal clusters and can be represented by a pentagonal quasiperiodic tiling with an edge length of 2 nm (Fig. 5d)[54] — the same length scale as that of the basic cluster. These localized fluctuations can be reasonably interpreted as phason fluctuations[54]; that is, the observed Al sites are the most likely to fluctuate due to their phason degree of freedom, predicted by the hyperspace description[55,56] of the decagonal $Al_{72}Ni_{20}Co_8$ structure. Though it is beyond the capability of STEM experiments, further investigations on correlated motion of these Al atoms may be an important key to understand the phason dynamics modes truly typical of quasiperiodic order. Preliminary X-ray diffraction studies on the same $Al_{72}Ni_{20}Co_8$ have confirmed significant attenuation of Bragg intensities at high temperature, a direct sign of an anomalously large Debye–Waller factor that goes on even at a macroscopic scale[57].

Apart from the phason-related fluctuations described above, similar localized atomic behaviour is also found in some crystalline metallic solids such as skutterudite[58] or clathrate[59] compounds, which are well known candidates as thermoelectric materials. Low thermal conductivities combined with reasonably good metallic electric conductivities are necessary demands to obtain better thermoelectric properties. In the above compounds, it is known that there indeed exist localized, anharmonic vibrational modes[58], which are attributed to the 'rattling' behaviour[59] of atoms that are weakly bound and located within the core of open-structured atomic cages (namely, the atomic polyhedra such as represented in Fig. 4). The rattling behaviour is believed to be responsible for the drastic reduction of thermal conductivity in these materials, by providing local scattering points that effectively suppress long-range phonon propagation. A similar effect occurs with the phasonic atomic fluctuations in the quasicrystalline compounds. In fact, some of the Al-transition metal quasicrystals and related giant crystals composed of the large clusters (~2 nm) show conducting properties that make them attractive as thermoelectric materials[60,61], although their performance is still not beyond those of the
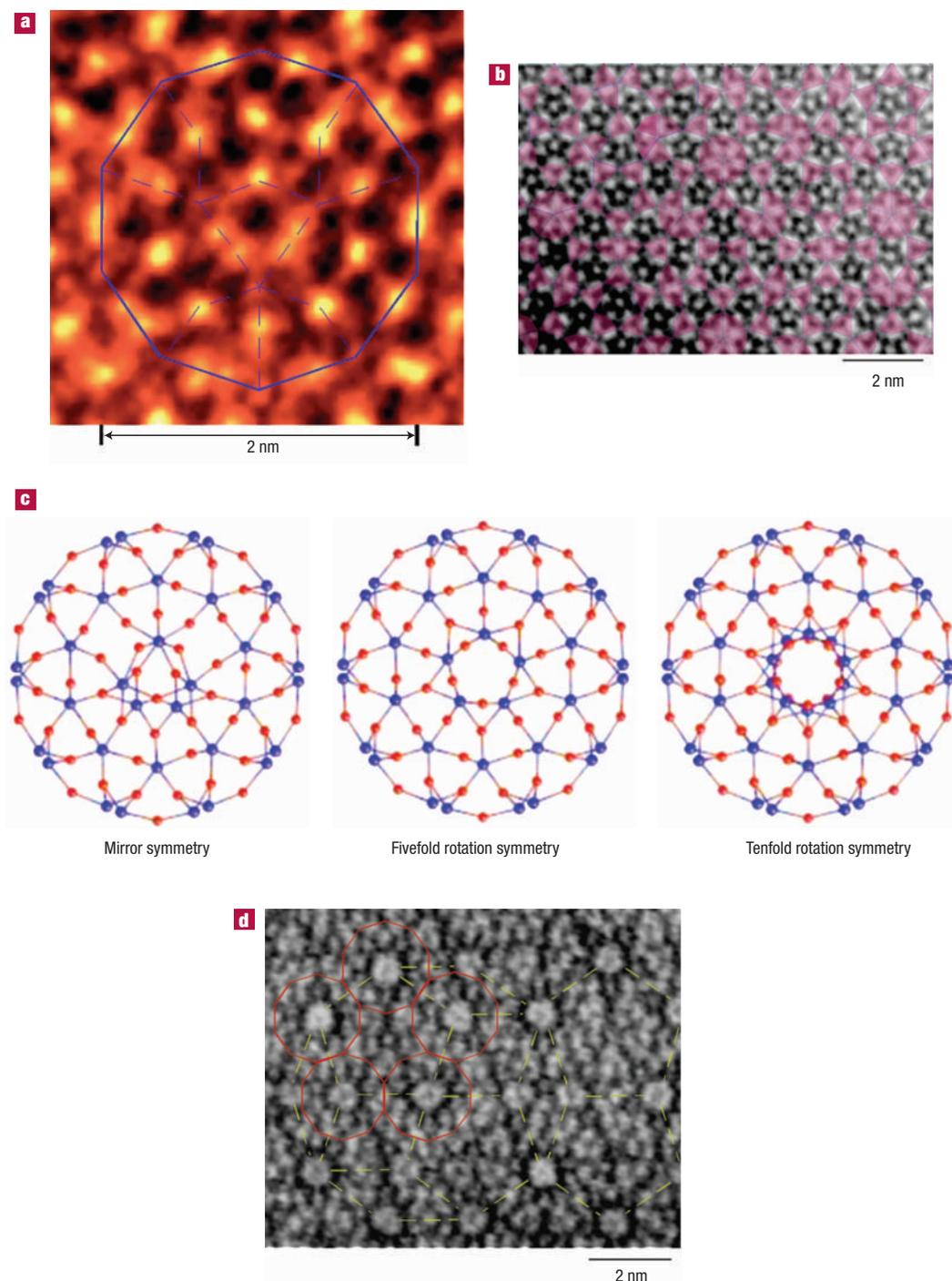
Mirror symmetry   Fivefold rotation symmetry   Tenfold rotation symmetry

Figure 5 Atomic-resolution ADF-STEM images of decagonal $Al_{72}Ni_{20}Co_8$ with cluster models. **a**, A decagonal cluster with a diameter of about 2 nm (ref. 32). Tenfold-symmetry-breaking arrangements of the bright spots are in good accordance with Gummelt's prototype decagon (blue). **b**, Superposing the decagon covering pattern over the image[33]. **c**, Structural models of the decagonal cluster for three different symmetries[37]. Red spheres indicate Al atoms, blue spheres indicate transition metal atoms. **d**, Significant ADF-contrast due to a local anomaly of the Debye–Waller factor emerges around the core of the clusters (red), during *in situ* high-temperature observation at 1,100 K (ref. 54). Occurrence of such localized fluctuations can be well represented by the pentagonal quasiperiodic tiling (yellow) with an edge length of 2 nm.

existing materials. Within the multiple-shell clusters in quasicrystalline and related crystalline compounds, the outer atomic shells are rather robust, but the atomic configurations around the core may easily show structural frustration: many possible sites with only a fraction that can be occupied causes significant fluctuation or disorder. A good example of this description can be found in the Cd-rare-earth giant cubic compounds, in which only the core atoms in the icosahedral clusters are arranged in a significantly disordered manner[62]. An important and encouraging implication of this cluster-based notion is that we

may be able to tune the balance between electrical and thermal conductivities if we can control localized fluctuations, perhaps by designing new cluster structures in either quasiperiodic or periodic forms.

In a general sense, we expect localization phenomena in solids at any disordered or defected area. For the simple close-packed metallic solids such as face-centred-cubic or hexagonal-close-packed structures, occurrence of such structural disorder is basically random, even if the defect density is artificially enhanced by some processing method. The most exciting and potentially useful aspect of

complex metallic structures[46], including quasicrystals and giant unit-cell crystals, is that localized fluctuations or disorder is intrinsically involved in the structure in many cases. These localized sites can be reasonably represented by the cluster substructure. Although there is no available example at the moment, the effective use of such a dense, three-dimensional 'ordered' array of disordered parts in the structure, may in the future lead to the development of new functional compounds. For example, such sites could be used as a template to substitute additional atoms not originally part of the crystal or quasicrystal structure, and impart new electrical, thermal or magnetic properties.

SUMMARY

The discovery of quasicrystals has provided a paradigm shift in solid-state physics because it had long been assumed, though never strictly proven, that the best and most stable long-range order should be realized in the form of a periodic solid constructed by regularly repeating unit cells. Quasicrystals are now established as a second well-ordered form of solids, and in fact the best quasicrystalline materials available today possess a highly perfect long-range order that is comparable with the best available crystalline materials, if 'order' is judged by the sharpness of their diffraction peaks. Although quasicrystals cannot be defined as packing of identical unit cells, their structures can be effectively viewed in terms of packing of clusters, and their ideal state may be described as a unique way of packing by overlapping clusters that realizes the most stable, energetically favoured atomic configurations. The clusters are also found to define the length scales of the characteristic localized fluctuations in quasicrystals, explaining the origin of the substantial diffuse scattering that exists even for the best quasicrystalline materials, and providing a critical influence on long-range thermal and electrical conduction properties. This cluster-based concept can also be invoked to describe crystalline intermetallic phases with giant unit cells, which frequently occur at compositions near to those where quasicrystals form. Like quasicrystals, these giant unit-cell crystals also show many unusual properties, and represent a natural extension for research into cluster-based compounds, whether periodic or quasiperiodic, with the potential for the discovery of new properties and new applications to materials. We may even see a whole new field emerge: cluster-engineered materials.

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Competing financial interests

The authors declare that they have no competing financial interests.