Electron microscopy of quasicrystals – where are the atoms?†

Eiji Abe*

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Quasicrystals represent aperiodically ordered form of solids with symmetries long thought forbidden in nature. Since their discovery, the fundamental key question has been “where are the atoms?” in these novel aperiodic solids, and electron microscopy has indeed provided images of real atomic arrangements in quasicrystals. In this tutorial review, we describe the microscopic view of quasicrystals using state-of-the-art scanning transmission electron microscopy, providing intriguing details that had never been unveiled by the early diffraction-based structural analyses.

1. Introduction

“Discovery of quasicrystals is the victory of transmission electron microscopy.” In the Nobel lecture,1 Dr Shechtman emphasized the indispensable role of electron microscopy for his serendipitous finding of the novel-structured material.2 In fact, a series of diffraction patterns that convinced the solid of definite icosahedral symmetry was only obtainable within the electron microscope, because the first quasicrystalline phase occurred with tiny grains of a few microns in a rapidly solidified Al-Mn alloy. For the same reasons, the following discoveries of the unique symmetry solids, such as having twelve-fold3 and eight-fold4 rotation axes, were all identified by electron microscopy techniques, leading to the establishment of the birth of new materials.

At present, quasicrystals are available in a variety of metallic alloys as thermodynamically stable phases,5–8 and some of the quasicrystalline alloys can be indeed grown into large single grains of millimetre-centimetre in size under nearly equilibrium conditions9 (e.g., temperature-controlled slow cooling, as used for a normal crystal growth). Given such high-quality specimens, X-ray diffraction investigations also confirmed the striking features of quasicrystals.10 The best-quality quasicrystalline specimens of today exhibit a remarkable diffraction pattern; see Fig. 1 for a representative example. Firstly, a large number of peaks appear, which are aperiodically arranged and precisely located at the positions consistent with fivefold/tenfold symmetry. Secondly, the diffraction peaks are remarkably sharp,10 the sharpness of which almost reaches the instrumentation limit and is comparable to that from nearly-perfect crystals like silicon. These diffraction features, in particular the sharp diffraction peaks represented by delta-functions, which had been believed to be possible only for periodic crystals, can no longer be explained according to a classical framework of incommensurate crystals.

Nevertheless, in an early period, quasicrystal structure was discussed in relation to a rather disordered/imperfect state of solids. It was intuitively presumed that the quasicrystal is a somewhat intermediate state between crystal and amorphous, and therefore an icosahedral glass model was proposed,11 which assumes only short-range icosahedral order that are distributed randomly to form the solid. Of course, this model does not explain the occurrence of reasonably sharp Bragg peaks. One of the most prominent early models that denies a novel structural order was raised by Pauling,12 who strongly claimed that the apparent icosahedral symmetry is just a mimicry of normal crystals; multiply-twinned configurations of giant cubic crystals are able to generate a pseudo-fivefold symmetry pattern. This model was fairly valid to explain the features of the first Al-Mn icosahedral phase, since the relevant diffraction peaks are considerably broadened and distorted,2 which are remarkable signs of imperfections of long-range order and hence seem to be consistent with the...
heavily twinned crystals. The arguments whether or not the Al-Mn represents a novel type of order were intensely discussed at that time; though, one electron microscopy picture concluded this early issue. See Fig. 2 that demonstrates "A picture is worth a thousand words". In the high-resolution TEM image, the bright spots, although which do not represent atoms owing to a resolution limit at that time, are not arranged periodically at any places but strictly aligned along the tenfold directions (bond-orientation order), verifying immediately that the structure is not twinned crystals but a unique aperiodic order.

Nowadays we interpret this unique aperiodic order as true quasiperiodicity, 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, which is in fact seen in the array of the bright dots in Fig. 2. This is a precisely defined sequence that is able to generate the delta-function diffraction peaks and account for the experimental observations. In time, the discovery of quasicrystals 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 1992. 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 solids based on their diffraction features. We particularly emphasize that the term quasicrystal is a short form for ‘quasiperiodic crystal’, and never means an imperfect, pseudo-crystal as one might guess from the expression. It is important to recognize that quasicrystals indeed represent a well-ordered condensed state of matter that is now accepted as a new form of solid; a third phase following the classical crystalline (periodic) and amorphous (random) solids.

1.1 Where are the atoms?

As described in the relevant articles of the present themed issue, the diffraction intensity calculations of any quasicrystal model structures are carried out by hyperspace crystallography, a mathematical recipe that treats a quasicrystal as a periodic structure embedded in a hyperspace. However, due to the local isomorphic nature of the quasilattice, a unique structural solution may not be easily obtained solely based on standard X-ray diffraction experiments; see Fig. 3. These are locally isomorphic quasilattices constructed by an identical set of tiles, fat and skinny rhombi. Concerning the structure factor, each of these quasilattices gives rise to quite similar diffraction intensity distributions, as shown in the bottom in Fig. 3 (namely, a phase problem along the extra directions defined in the hyperspace crystallography). Therefore, multiple structural solutions intrinsically occur from the diffraction data for a quasicrystal structure analysis, similar to the case known as “homometric structures” in normal crystals.

“Where are the atoms?” – this has been the fundamental key question because of the above intrinsic reasons. Atomic-resolution electron microscope investigations are unique in this regard, as

![Fig. 1](image1.png)

**Fig. 1** Precession electron diffraction pattern taken along the tenfold symmetry axis of the Al$_{72}$Ni$_{20}$Co$_{8}$ decagonal quasicrystal, one of the best quasiperiodic ordered materials available today.

![Fig. 2](image2.png)

**Fig. 2** High-resolution TEM image of the first icosahedral phase in rapidly solidified Al$_{55.5}$Mn$_{44.5}$ alloy, taken along the fivefold symmetry axis (adapted from ref. 14 with permission).

![Fig. 3](image3.png)

**Fig. 3** Examples of two-dimensional quasiperiodic lattices constructed by an identical set of tiles, fat- and skinny-rhombic tiles in the Penrose tiling. These quasilattices belong to a class of local isomorphism, generating the almost identical structure factors shown in the bottom (reproduced from ref. 19 with permission).
they directly provide the (local) atomic arrangements even for aperiodic solids, and hence are able to distinguish one of the patterns in Fig. 3. In early structural studies of quasicrystals, high-resolution phase-contrast TEM imaging provided evidence that their structures are indeed represented by a combination of clusters and the corresponding quasiliattices. Yet there were still significant information lacking concerning the local atomic configurations of quasicrystals, particularly on how the different elements are arranged in the quasiperiodic structure (i.e., chemical order configurations). This is a critical aspect, since the most stable quasicrystalline phases of high-structural quality occur as multicomponent (mostly ternary) intermetallic compounds with a good chemical-order. In this regard, scanning transmission electron microscopy (STEM) has provided significant strides in determining the chemical order structure of quasicrystals, based on its atomic-number dependent contrast (Z-contrast). We believe this lays some novel insights that have been unveiled through advanced STEM observations, which lead to immediate inspiration on the issue of why quasicrystals form.

2. Imaging basis of atomic-resolution electron microscopy

Fig. 4 shows schematic drawings of atomic-resolution phase-contrast and Z-contrast imaging. In phase contrast imaging, a parallel beam illuminates the specimen, and the atomic image is formed by interference between direct and diffracted waves; this is exemplified by one diffracted wave in Fig. 4. Given the successful $-\pi/2$ phase shift (ideally) to diffracted waves for a wide scattering range at the objective lens (known as the Scherzer condition), the resultant image contrast reveals the electrostatic potential of the specimen. Therefore, the projected atomic positions are expected to be imaged as a dark region; though, it is noted in particular that the contrast appearances vary significantly depending on the defocus values, which control the phase difference between the direct and diffracted waves. On the other hand, STEM combined with an annular-detector provides atomic-resolution images by effectively illuminating each atomic column one-by-one as a finely focused electron probe ($<\sim 2$ Å) scans across the specimen, generating an intensity map at the annular detector (Fig. 4, right). The atomic images may, to a good approximation, be interpreted assuming independent scattering from individual atomic columns, and hence the observed intensity distribution $I(R)$ can be simply described by a convolution between a probe-intensity function $P(R)$ and a scattering object function $O(R)$:

$$I(R) = O(R) \otimes P(R)$$

This feature is referred to as incoherent imaging, in the sense that it always reveals atomic positions as bright dots without any contrast reversal, as represented by eqn (1). This is in sharp contrast to the phase-contrast TEM imaging based on wave interferences (i.e., coherent imaging), by which, again, the atomic positions appear to be either dark or bright depending on the conditions. With a simple imaging basis, STEM provides the intuitive atomic images that can be directly related to the atomic structure.

It is noted here that the incoherent imaging can only be realized when detecting high-angle scattering ($>\sim 1$ Å$^{-1}$) with the annular detector. At high-angle scattering, the Bragg intensities are significantly attenuated, and instead the background diffuse scattering becomes dominant; see the scattering ranges larger than $\sim 1$ Å$^{-1}$ in Fig. 5(b). The origin of this diffuse scattering is mostly due to a thermal vibration of atoms (i.e., phonon scattering events), and hence it is denoted as thermal diffuse scattering (TDS). TDS intensities at given detector ranges can be estimated based on inelastic (or quasi-elastic) scattering described by an absorptive potential added as an imaginary component, which phenomenologically leads to loss of electrons and instead gives rise to the TDS as a counter-part. Angular distribution of the TDS is well represented by the absorptive atomic form factor $f'$.

$$f'(s, M) \propto \int f(s') f(s - s') [1 - \exp(-2M(s'^2 - s' \cdot s))] \, ds'$$

where $f$ is the atomic form factor for elastic scattering. The absorptive form factor is given as a function of $s = \sin(\theta)/\lambda$, $\theta$ is a scattering angle, $\lambda$ is the electron wavelength, and $M$, which is the Debye–Waller (DW) factor defined by the mean-square thermal vibration amplitude, $\langle u^2 \rangle$, of the atoms. The high-angle TDS is dominated by multi-phonon scattering, which makes an Einstein model of independently vibrating atoms valid enough for the estimation of the scattering intensity.

![Fig. 4](image-url) Imaging principles of atomic-resolution phase-contrast TEM and Z-contrast STEM.

![Fig. 5](image-url) Electron diffraction patterns of the decagonal quasicrystal Al$_4$Ni$_2$Co$_8$, taken by (a) parallel beam and (b) convergent beam illuminations. In (b), the intensity distributions at low angle scattering ranges are adjusted to show up the Bragg reflection disks.
reaching to the detector.\(^{22}\) Accordingly, eqn (2) may be further simplified for high-angle scattering, and the TDS cross section \(\sigma_{TDS}\) can be derived as a high-angle approximation of \(TDS\).

\[f_{HA}(s, M) \approx \sigma_{TDS} \propto \int_{\text{detector}} f^2(s)[1 - \exp(-2M \cdot s^2)]d^2s\]  

(3)

where the integration is carried out over the detector angle range. With this simplified cross-section description, each atom site is reasonably supposed to be an independent source for TDS generations, and therefore \(\sigma_{TDS}\) becomes relevant to \(\theta(R)\) in eqn (1) when the detector is at the high-angle scattering range (high-angle annular dark-field condition, termed as HAADF). The resultant image intensity, \(I(R)\), after illumination by the probe, \(P(R)\), is thus dependent on the \(\sigma_{TDS}\). Since the \(\sigma_{TDS}\) is proportional to the square of \(f(s)\) (eqn (3)), the STEM–HAADF image is able to reveal a highlight contrast for heavy atom positions, and thus is termed as atomic-number dependent Z-contrast.\(^{22}\)

Fig. 6 shows the representative atomic-resolution phase-contrast and Z-contrast images of the quasicrystalline compound Al\(_{72}\)Ni\(_{20}\)Co\(_{8}\).\(^{23,26}\) The former reveals the projected potential of the total structure, while the latter exhibits the significant highlight-contrast for the heavier atoms, which should be the transition metals, Ni or Co (note that the Ni and Co are hardly distinguished even if they are ordered). This is seen clearly in the comparisons with the relevant atomic model, whose details will be described later. All the atomic positions appear as dark regions in the phase-contrast where the Al and TM atoms are hardly distinguishable, while the Z-contrast selectively shows up the TM atom positions. The application of the STEM technique to the quasicrystal provided a significant breakthrough for quasicrystal research, as described below.

3. Decagonal quasicrystals

Decagonal quasicrystals are the planar realization of a quasiperiodic order,\(^{27,28}\) see Fig. 7. Decagonal structure is described as a periodic stack of quasi-periodic planes 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 observed through high-resolution electron microscopy viewing along the tenfold-symmetry axis.\(^{29}\) Individual decagonal clusters appear as decagons in the projected images, so that their planar arrangements can be directly identified. We note that, for icosahedral quasicrystals, the atomic images are the projections of three-dimensional quasiperiodic structures, and therefore the relevant three-dimensional configurations of individual atoms and/or icosahedral clusters cannot be distinguished uniquely (see ref. 30 for example).

Thermodynamically stable decagonal phases occur in a large number of alloy systems,\(^{8}\) among which the Al-transition metal (TM) ternary alloys are the largest family of decagonal-forming systems. During early studies, the decagonal phases were believed to occur in a relatively broad composition range around Al\(_{30}\)(TM1, TM2)\(_{30}\) at.%; i.e., the conditions seem to allow the phase to form with non-stoichiometry compositions largely deviated from the ideal stoichiometry. However, significant features become apparent from the detailed phase-diagram investigations,\(^{31,32}\) from which the decagonal phase region is found to be further divided into several modifications depending on the slight changes of composition/temperature; see Fig. 8. In the well-known system Al-Ni-Co, the decagonal structure turns out to reveal rich variations, as carefully identified based on electron diffraction experiments.\(^{31}\) Decagonal Al-Ni-Co phases mostly occur with an existence of disorder to some degree, as manifested by diffuse streaks and/or

Fig. 6 Atomic-resolution (a) phase-contrast TEM and (b) Z-contrast STEM images, taken along the tenfold symmetry axis of the Al\(_{72}\)Ni\(_{20}\)Co\(_{8}\) decagonal quasicrystal. Decagonal clusters of 2 nm across are shown by dashed lines in both images. Image (a) was obtained from the very thin region (~60 Å; near-edge of a cleavage grain) and under nearly Scherzer defocus (~45 nm with 400 kV STEM (JEM-4000EX)). Image (b) was taken from a slightly thicker region than that of (a), approximately ~120 Å, with 200 kV-STEM (JEM-2010F).

Fig. 7 Decagonal structure is a 2-dimensional quasicrystal, whose characteristic is well represented by a regular decagonal prism, as schematically shown with the relevant electron diffraction patterns of tenfold and twofold symmetries.
background in the relevant diffraction patterns. However, the decagonal Al72Ni20Co8 at 1073 K–1273 K ("bNi" in Fig. 8) is found to occur with exceptionally less diffuse features33,34 (see again Fig. 1), demonstrating that an extremely high-degree of quasiperiodic order can be realized when the alloy is precisely tuned in a limited range of compositions/temperatures. The decagonal Al72Ni20Co8 in fact qualified several structural-quality tests from microscopic33,35 to macroscopic scales36 confirming that this is an excellent quasicrystalline material to investigate intrinsic features of a quasiperiodic order.

### 3.1 Structure of an ideal decagonal Al72Ni20Co8

Early high-resolution phase-contrast TEM observations provided evidence that decagonal structures are quasiperiodic arrangements of decagonal clusters.29 The picture emerging from these studies is that the quasicrystal can be viewed as a cluster aggregate, for which the basic atomic clusters are supposed to have the same point symmetry of the corresponding quasi-crystalline phases.37 Namely, all early 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,37 Al-Cu-Co38 and Al-Pd-Mn39 decagonal alloys. These cluster symmetries, in particular the tenfold rotation axis, were 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 in terms of true cluster symmetry.

Some decagonal quasicrystalline samples were found to have a cluster arrangement similar to a Penrose pattern,40 a planar tiling composed of two different rhombic tiles with matching rules (Fig. 9). The matching rule is a strict mathematical rule that forces the two types of tiles to join uniquely into a perfect quasiperiodic pattern. Note that more complicated matching rules become necessary for the variant patterns shown in Fig. 3 (e.g., multiple edge rules41 for the tile joints), even though they are constructed by the same set of rhombic tiles. In this sense, the Penrose pattern is definitely a unique tiling with a minimized local rule, and accordingly the variant patterns of local isomorphism are termed generalized Penrose patterns. The matching rule implies a trick that governs the local growth of quasicrystals; though, the rule is still purely mathematical and does not provide any physical insight on why the atoms should favor such a complicated structure. Namely, 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 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.42 In the context the tenfold clusters may be allowed to overlap with their neighbors, in the sense that they partially share atoms with neighboring clusters. There are no rules given to force the clusters into a unique arrangement in random packing, and hence many possible configurations appear due to a large degree of freedom on how to join or overlap the neighboring decagons – many degenerate ways of packing are an unavoidable consequence of this model. This situation is supported by the scenario that configuration entropy might be an important factor causing quasicrystals to be more stable than competing crystals.43–45 The so-called random tiling model would give significant contributions of configuration entropy, and seems to be consistent with the fact that the stable quasicrystalline phases discovered so far occur only at high-temperatures, and some of them indeed transform into periodic structures at lower temperatures. Besides, in a random-packing picture, resultant structures may 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 configuration entropy.35

![Fig. 8](https://www.chem.soc.revs.org/content/41/21/6787/fig/08.large)

**Fig. 8** Vertical section of the complex Al-Ni-Co ternary phase diagram, along the composition Al_{72}Co_{28}-Al_{93}Ni_{31} (reproduced from ref. 31 with permission). There are rich variant structures of the decagonal (D) phases.

![Fig. 9](https://www.chem.soc.revs.org/content/41/21/6787/fig/09.large)

**Fig. 9** Penrose tiling, the first aperiodic tiling constructed by two types of rhombic tiles. The entire pattern is generated by a local joint rule referred to as the "matching rule", which requires each of the tiles to complete types and directions of the arrowheads on the tile edges, as shown in the figure. The pattern appears to be complicated, but there are only eight local environments (vertex symmetry), as indicated by the black dots.
Striking features of cluster symmetry and their arrangement have become apparent through investigations of decagonal Al$_72$Ni$_{20}$Co$_8$, the highest quasicrystalline structural perfection as described above. The first application of the STEM technique to the quasicrystal has provided immediate insights into the veiled structural details, which were difficult to figure out based on phase-contrast TEM imaging. Firstly, a significant breakthrough to emerge is a breaking of the tenfold symmetry within the 2 nm decagonal cluster; see again Fig. 6(b). The brightest spots in the Z-contrast STEM image represent atomic sites of Ni or Co. As indicated by arrows, in the cluster center they are clearly not arranged in a ten-fold form, but appear to show only mirror symmetry. Secondly, such local broken-symmetries in every decagon are found to be not in random orientations but in accord with a perfect quasiperiodic pattern (Fig. 10(a)) – the pattern can be well represented by the novel form of decagon packing proposed by Gummelt (Fig. 10(b)). In Gummelt’s construction plan, decagons are not tenfold symmetric, and they overlap with their neighbors according to a well-defined overlap rule (Fig. 10(b)) that is equivalent to the Penrose matching rule. Therefore, the overlap rule forces the decagons into a perfect quasiperiodic arrangement. This remarkable mathematical proof has led to a physically plausible picture for the origin of quasicrystals. A subsequent but important proof by Steinhardt and Jeong showed that the overlap rule realizes the condition that the density of the decagons is maximized. Suppose the atomic configuration within a decagon, i.e. the atomic cluster in the form of Gummelt’s decagon (Fig. 11), is energetically favored. 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 therefore suggests that the phase is dominantly stabilized by energy; if there were significant entropy contributions, a considerable amount of random structural disorder including site mixing by Al and Ni/Co atoms (chemical disorder), or deviations from an ideal tiling would be observed.

On these bases, it is concluded that the decagonal clusters have intrinsic broken symmetry that is a built-in aspect of the atomic decoration; the symmetry breaking feature is definitely not a consequence of random chemical and occupational (vacancy) disorder, as likely to occur for Burkov’s random packing scenario. As seen in Fig. 6, symmetry-breaking atomic decorations on the 2 nm decagonal cluster in fact provide a remarkably better fit to TEM/STEM images on some details, such as triangular arrangements of Al atoms around the cluster center and closely spaced (~1.3 Å) pairs of transition metal (TM) atoms, 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, which demonstrates that the symmetry-breaking cluster is energetically more favored than competing symmetric-based configurations. Fig. 12 shows three representative cluster models for three different symmetries; mirror symmetry, fivefold rotation symmetry, and tenfold symmetry (in the calculations, Ni atoms were used for all TM atoms). Note that the three structures in the calculations have the same unit cell dimensions and the same number of each atom species, so that their total energies can be directly compared. It is found that the structure with broken symmetry (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 clear evidence that the symmetry-breaking cluster is energetically more favored than any symmetric clusters. Remember that most of the decagons identified in Fig. 10(a) 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 could slightly differ depending on their local environments.

Decagonal Al$_72$Ni$_{20}$Co$_8$ has turned out to be a quasiperiodic intermetallic compound with nearly perfect atomic order – it is
Fig. 11 Atomic model of the decagonal Al\textsubscript{72}Ni\textsubscript{20}Co\textsubscript{8} (adapted from ref. 51 with permission). The structure has two distinct atomic layers, and solid and open circles represent different levels along the tenfold axis, \(c = 0\) and \(c = 1/2\) respectively. A perfect quasiperiodic atomic order can be constructed from the decagonal cluster properly decorated according to Gummelt’s motif. The average decagonal cluster in Fig. 6, derived by averaging over the local variations that occur in the perfect decoration, fairly well explains both the phase-contrast/Z-contrast images.

![Atomic model of the decagonal Al\textsubscript{72}Ni\textsubscript{20}Co\textsubscript{8}](image)

Fig. 12 Different atomic decorations of the decagonal cluster for three different symmetries (reproduced from ref. 52 with permission); mirror symmetry, fivefold rotation symmetry and tenfold symmetry.

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. Good chemical order between the Al and TM, directly confirmed by the Z-contrast STEM imaging, 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 TM contents\textsuperscript{51,52} (see again Fig. 8). If the structure could tolerate a considerable amount of chemical disorder, as being 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\textsubscript{72}Ni\textsubscript{20}Co\textsubscript{8} compound is close to its ideal stoichiometry, being tuned in favor of structural energy. This may well be explained by an optimized average valence electron concentration per atom (\(e/\alpha\)),\textsuperscript{54} which is known as Hume-Rothery’s empirical rule\textsuperscript{54} 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, as described earlier with Fig. 8. For such less-ordered quasicrystals, their average structures may be well described by random-packing of clusters, and the relevant high-symmetry is then a result of averaging over the local random disorder. Nevertheless, we now see that the best quasicrystalline Al-Ni-Co 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. The fundamental reason for the existence of such well-ordered quasicrystals is that their structure is energetically favored. 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; i.e., highly-perfect, almost defect-free single crystals can only be grown for a limited range of materials under carefully controlled conditions.

3.2 Atomistic fluctuations in decagonal Al\textsubscript{72}Ni\textsubscript{20}Co\textsubscript{8}

For quasicrystals, we expect an extra elastic degree of freedom termed a phason,\textsuperscript{55,56} and therefore the lattice dynamics of quasicrystals can be described by a combination of lattice vibrations (phonons) and atomic fluctuations (phasons). Because of these unique dynamics, even the best quasicrystalline specimen such as decagonal Al\textsubscript{72}Ni\textsubscript{20}Co\textsubscript{8} may reveal substantial diffuse scattering that originates from phason-related fluctuations.\textsuperscript{57–59} Understanding phason-related atomic behaviors is critical for the thermodynamic stability of quasicrystals, whatever their origin; the context could be a random-tiling-like realization\textsuperscript{45} where phason fluctuations are essential to provide entropic stabilization, or an unlocked state\textsuperscript{60} of an intrinsically energy-minimized perfect quasicrystal. In either case, phason fluctuations are expected to be significant above some critical temperature. So far, numerous experimental measurements on phason-related disorders/dynamics have been attempted by various experimental techniques; however, there has been no direct evidence on where such localized atomic fluctuations take place in the real-space quasicrystal structure. This is because the local disorder/fluctuation effects are all averaged in the X-ray and other diffraction patterns, and therefore it is difficult to specify the local source for diffuse scattering. We use STEM to tackle this issue.\textsuperscript{61}

Phason-related atomistic fluctuations, if any, may cause a local anomaly of the Debye-Waller (DW) factor at the corresponding atomic sites. Note that this phasonic perturbation does not destroy the long-range quasiperiodic order, but causes a reduction in the Bragg intensity and generates some additional diffuse scattering, as in the same manner as the TDS generation.\textsuperscript{57–59} The phason has no counterpart in periodic crystals, and hence the DW factor of a quasicrystal may have both phonon and phason contributions, written as:

\[
M = M_{\text{phonon}} + M_{\text{phason}}
\]

The DW factor anomaly at the specific atomic sites was successfully detected, through in situ high-temperature and angle-resolved STEM observations of the decagonal Al\textsubscript{72}Ni\textsubscript{20}Co\textsubscript{8}.\textsuperscript{61} Meanwhile, the results provided the first direct, real-space imaging of a local thermal vibration anomaly in a solid.

In the STEM image of the highly-perfect decagonal Al\textsubscript{72}Ni\textsubscript{20}Co\textsubscript{8} taken at room temperature (300 K; Fig. 13(a)), the Z-contrast highlights the TM (Ni or Co) positions relative to the Al, due to the \(f_2^2(s)\) dependence of the contrast (eqn (3)). But when the sample is heated and held at a temperature of approximately...
1100 K within the microscope, we find a remarkable change in the relative contrast; see Fig. 13(b) compared to Fig. 13(a). A significant enhancement in the image intensity appears at some specified places, which can be well represented by the pentagonal Penrose tiling with an edge-length of 2 nm (note that the pentagonal Penrose tiling is uniquely related to Gummelt’s overlap tiling (Fig. 10(b)) by connecting the specified decagons separated by 2 nm). Considering that the present highly-perfect quasicrystalline phase is obtained as a quenched-in high-temperature configuration (water-quenched after annealing at 1100 K), the image of Fig. 13(b) is showing the ‘true face’ of the decagonal Al72Ni20Co8, in the sense that it is indeed at its equilibrium situation. Such contrast anomaly is also observed even at room-temperature, when the STEM image is formed by relatively low-angle scattering electrons (LAADF),26 as shown in Fig. 14.

These angular-dependent as well as temperature-dependent anomalous STEM contrast effects can naturally be attributed to local anomalies of the DW factor, as expected from the relevant $M$ term in eqn (3). In the images of Fig. 13 and 14, it is found that the DW-factor contrast occurs at cores of the decagonal clusters; representative angular-dependent and temperature-dependent features are summarized in Fig. 15(a)–(d). Viewing carefully the interior contrast of the clusters, significant increase of intensities occurs at the positions indicated by arrowheads, which correspond to the Al sites by referring to the structural model (Fig. 15(e)). The intensity profiles confirm that these Al sites, denoted as Alx, in fact reveal a stronger intensity at 1100 K than that at 300 K. It is also noticed that, at the room-temperature condition, the intensity at the Alx sites ($I_{Alx}$) is originally stronger than that of the other Al sites (Fig. 15(b)). Besides, as confirmed by Fig. 15(a)–(c), the $I_{Alx}$ shows significant scattering angle dependence, while the intensities of the other Al and TM atoms do not ($I_{TM}/I_{Al}$ is almost constant). On these bases, the local DW factor anomaly is predominantly attributed to the Alx sites; if the DW factor effect is equivalent for all the Al sites, neither the temperature-dependence nor angle-dependence of the $I_{Alx}$ is observed.64

On the basis of the above discussions, the significant increase in $I_{Al}$ can be interpreted in terms of atomic vibration amplitudes, $\langle \vec{u}^2 \rangle$, for the observations both at 300 K and 1100 K. It was shown that both temperature- and angular-dependences of $I_{Al}$ are fairly well explained by $\sigma_{TDS}$ for different $\langle \vec{r}^2 \rangle$ values calculated based on eqn (3),61 demonstrating the first direct observation of a local vibration anomaly in a solid. Although the $\langle \vec{u}^2 \rangle$ values estimated by the STEM intensity are semi-quantitative, it is noteworthy that significantly large $\langle \vec{u}^2 \rangle$ at high temperature is consistent with the X-ray diffuse scattering measurement of the same sample of Al72Ni20Co8,62 in which the overall $\langle \vec{r}^2 \rangle$ is suggested to be on the order of $\sim 1.0 \times 10^{-3}$ nm$^2$ (at 1100 K) when compared with a uniform harmonic vibration (the local anomalies of $\langle \vec{r}^2 \rangle$ presently observed may imply significant anharmonicity at the Alx site). Further supporting evidence comes from molecular-dynamics simulations of the structure at 1000 K,63 which predicted the occurrence of DW factor anomalies for the Al atoms at the core of the 2 nm decagonal cluster.

The present observation of the local DW factor anomaly implies some intriguing physics of quasicrystals. It is quite interesting to note that the Alx atoms, located at the center of the decagonal clusters that are on the 2 nm-scale pentagonal quasiperiodic lattice, are shown to be generated from the edge of the atomic surfaces within the hyperspace structural description.64 Therefore, the present local DW factor anomaly can be attributed to significant fluctuations of the atomic surfaces in specific edge regions, which, in turn, indicate an occurrence of phasonic fluctuations realized at the relevant Alx sites in the real quasicrystal.61 This phenomenon is reasonably interpreted as a perturbation of quasiperiodic order that can be described through $M_{phason}$ in eqn (4).
The clusters observed (a)–(c) at 300 K with different angular ranges of the detector and (d) at 1100 K, together with the corresponding line-profiles across X–Y. Images (a) and (c) were obtained by the 300 kV STEM with detector angle ranges of about 30–70 mrad (0.75 < s < 1.75) and 50–90 mrad (1.25 < s < 2.25), respectively. Images of (b) and (d) are enlargements of a part of Fig. 13(a) and (b), respectively. Viewing carefully the images (a)–(d), one notices that the contrast changes significantly at the core of the cluster, particularly at the positions indicated by arrowheads, which correspond to the AlZ sites denoted in the line-profiles. (e) Averaged model of the cluster (same as that shown in Fig. 6), but the five bright dots around the mirror cluster (Fig. 6), but the five bright dots around the centre clearly form the pentagon to represent the relevant symmetry. Accordingly, distributions of Al and TM atoms within the cluster are fairly well deduced (Fig. 18), given the prior knowledge that the compositions between the layers can be different due to the lack of screw or glide symmetry.

We have demonstrated that the quasicrystal may intrinsically possess a phason degree of freedom, based on successful STEM observations of the real structure of Al72Ni20Co8. Direct, real-space imaging provides a unique approach to the phason issue, with an entirely opposite way to diffraction analysis; see Fig. 16. The idea of extra dimensions and the accompanying properties is a compelling matter in physics, and the phason in quasicrystals provides one of the relevant issues.

3.3 Non-centrosymmetric decagonal Al64Cu22Co14

After the first application of the technique, the Al-TM decagonal phases including the less-ordered Al-Ni-Co have been extensively studied using Z-contrast STEM, and it has turned out that the fivefold symmetry cluster (see Fig. 12) frequently occurs as a structural unit. There have been no tenfold-symmetry clusters identified so far, and the symmetry-breaking mirror cluster is only available for very limited systems; stable-Al72Ni20Fe4 and metastable-Al72Ni20Al atomic sites, I$_{Al}$/I$_{Al}$ measured for the decagonal clusters located at the 2 nm-scale pentagonal Penrose lattice (Fig. 13(a) and (b)) (adapted from ref. 61 with permission).

The convergent beam electron diffraction (CBED) technique is able to distinguish the non-centrosymmetry owing to a dynamical diffraction effect of electrons; see Fig. 17. In the CBED patterns, intensity modulations clearly appear for the diffraction disks to identify the fivefold-rotation symmetry axis, leading to the point group as being non-centrosymmetric $P\bar{1}m2$. and consequently the space group of the decagonal Al64Cu22-Co14 is determined to be $P\bar{1}m2$. The structure of this non-centrosymmetric decagonal Al64Cu22-Co14 is well represented by the fivefold symmetry decagonal cluster of 2 nm across; see the Z-contrast STEM image in Fig. 18. The cluster apparently shows the entire bright dot arrangements similar to that in the mirror cluster (Fig. 6), but the five bright dots around the centre clearly form the pentagon to represent the relevant symmetry. Accordingly, distributions of Al and TM atoms within the cluster are fairly well deduced (Fig. 18), given the prior knowledge that the compositions between the layers can be different due to the lack of screw or glide symmetry.

The fivefold symmetry cluster is indeed confirmed to be an effective structural motif for the highly-perfect decagonal Al64Cu22-Co14 with non-centrosymmetry. (1) the clusters are arranged in accordance with the pentagonal Penrose tiling with significantly less phason disorders, (2) almost all the fivefold clusters are arranged with the same orientations, representing directly the polarization of the decagonal structure. Here we above belongs to $P10_5/mmc$, and provided the highest atomic order within the centrosymmetric family. Non-centrosymmetric Al-TM decagonal phases mostly occurred as less ordered quasicrystals, but we have successfully tuned the composition/temperature of the decagonal Al-Cu-Co alloys and found that Al64Cu22Co14 provides the first example of a highly-perfect non-centrosymmetric decagonal structure.

![Fig. 16](image-url) Experimental approaches to the quasicrystal-hypercrystal structures; diffraction versus microscopy.

![Fig. 17](image-url) Convergent beam electron diffraction patterns taken along the periodic axis of the decagonal quasicrystals; Al64Cu22Co14 (left) and Al72Ni20Co8 (right).
should note that the inversion domains are formed within the present specimen, whose scale is approximately \(100\) nm. Therefore, the high-quality structural features described above, such as (1) and (2), are only realized within the single domains, and it seems to be still difficult for the non-centrosymmetric decagonal \(\text{Al}_{64}\text{Cu}_{22}\text{Co}_{14}\) to grow into a large single grain without forming inversion domains. This is in sharp contrast to the case of the highly-perfect decagonal \(\text{Al}_{72}\text{Ni}_{20}\text{Co}_{8}\) with centrosymmetry, which can be grown into a reasonably large single grain to perform X-ray structure analysis. Further studies are essentially necessary to understand the intrinsic features of the non-centrosymmetric decagonal structure.

We should mention that fivefold symmetry clusters are also able to construct the centrosymmetric decagonal structure, in which the cluster polarizations are equivalently mixed in accordance with up and down configurations to form super-lattice order, as clearly revealed by the STEM observations. There are many structural variations in decagonal quasicrystals, for which it is always important to understand how the local cluster symmetry can be correlated to an entire symmetry seen in the diffraction pattern. In this regard, electron microscopy is a powerful comprehensive tool that provides both real-space imaging and electron diffraction to probe an average symmetry seen in the image, as demonstrated with the present example of the decagonal \(\text{Al}_{64}\text{Cu}_{22}\text{Co}_{14}\).

4. A new era of electron microscopy

STEM indeed led to remarkable progress for quasicrystal structure analysis by selectively highlighting the heavy atom positions, as described in the previous sections. The STEM imaging, however, also provided a trade-off effect for light atom positions, which become hardly detectable by the atomic-number dependent Z-contrast mode. Recently, the spherical aberration (Cs) correction of the objective lens has been successful in converging the electron beam into the sub-Å scale (see Fig. 19), providing a much sharper/brighter electron probe \((P(R)\) in eqn (1)) and hence remarkably improving the STEM resolution. Cs-corrected ultrahigh-resolution STEM is now capable of simultaneous imaging both the heavy and light atom positions even under the Z-contrast conditions.

Fig. 20 shows the Z-contrast image of the decagonal \(\text{Al}_{72}\text{Ni}_{20}\text{Co}_{8}\), obtained by Cs-corrected 300 kV STEM. The improved resolution can be immediately noticed for the brightest dots representing the Ni/Co atoms, which appear to be remarkably sharper than those in the non-Cs-corrected image; see again Fig. 6(b) for comparison. By looking carefully at the Cs-corrected image, many weak dots also appear between the brightest dots; these are primarily attributed to the Al sites as the smallest Z constituent in the decagonal \(\text{Al}_{72}\text{Ni}_{20}\text{Co}_{8}\). A preliminary analysis of the intensity distributions suggests that there occur a certain amount of point defects even in the highly-perfect decagonal \(\text{Al}_{72}\text{Ni}_{20}\text{Co}_{8}\), which includes chemical disorder (i.e., Al/TM mixed occupations) and fractionally occupied atomic sites.

Further demonstration of the powerful use of Cs-corrected STEM imaging comes from the observation of a decagonal \(\text{Al}_{90}\text{Mn}_{17}\text{Pd}_{13}\), as shown in Fig. 21. A remarkable feature is that all the atomic sites, which are occupied by atoms with large atomic-number differences (Al: \(Z = 13\), Mn: \(Z = 25\), Pd: \(Z = 46\)), are simultaneously imaged with the Z-contrast condition. A striking fact immediately becomes apparent in that the observed intensity distributions cannot be reproduced from the established model structure, which had been proposed based on a single-quasicrystal X-ray diffraction analysis and phase-contrast TEM imaging. The STEM observation again forces modification of the existing model structure, which reminds us that even an X-ray analysis could...
possibly mislead in the case of the complicated quasicrystal. Therefore, the real-space imaging is always an important complementary partner to converge on a convincing, reliable structure of quasicrystals.

We are now attempting quantitative evaluations of the atomic occupation at individual atomic sites based on intensity-fitting for both the decagonal Al$_2_3$Ni$_2_0$Co$_8$ and Al$_7_0$Mn$_1_7$Pd$_1_3$. Several interesting local details have emerged indeed, which will soon be described elsewhere.

5. Conclusions

From the discovery, electron microscopy has been playing a critical role for structural studies of quasicrystals, particularly for the two-dimensional decagonal structures. Thanks to advanced scanning transmission electron microscopy, we have provided significant progress in understanding microscopic details of quasicrystals, including some answers or hints to the key questions “Where are the atoms?” and “Why do the quasicrystals form”.

Quasicrystals are now established as a new form of solids, and further veiled insights into these unique solids promise to be uncovered by aberration-corrected ultrahigh-resolution STEM, which now provides a remarkable performance not only for imaging but also spectroscopy; elucidating local electronic states will certainly lead to deeper understanding of why quasicrystals form.

Acknowledgements


References