

Aluminum Alloys in a Hyperspace ? – An Exotic View of Quasicrystals

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Quasicrystals represent aperiodically ordered form of solids with symmetries long thought forbidden in nature. The first quasicrystal was reported in a rapidly solidified Al-Mn alloy as a thermodynamically metastable phase, but a large number of stable quasicrystalline phases are now available in a variety of Al-base alloys. Nowadays we describe quasicrystal structure based on a hyperspace crystallography, 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). Suppose that the quasicrystalline order we view at our dimensions is a ‘shadow’ of a hyperspace lattice. Then, the relevant quasicrystalline Al-alloys could have an intrinsic degree of freedom along the extra dimensions. We will describe atomistic details of the Al-transition-metal quasicrystalline alloys using scanning transmission electron microscopy (STEM), and attempt to interpret several implicative characteristics as due to an intrinsic fluctuation along the extra dimensions, which is hidden but might be substantially given for quasicrystalline materials.

Keywords: *Quasicrystals, Al-transition-metal alloys, Electron microscopy, Atomic structure*

1. Introduction

Quasicrystals are aperiodic solids that exhibit rotational symmetries incompatible with conventional periodic lattice order; for example, icosahedral symmetry in three dimensions and ten-fold symmetry in the plane. A revolutionary announcement of the first quasicrystal was made for a thermodynamically metastable phase in a rapidly solidified Al-Mn alloy [1]. At present, not only metastable but also stable quasicrystalline phases are available in a variety of metallic alloys [2], and certain stable phases can be grown into a single grain several millimeters or even centimeters in size. It would appear obvious, therefore, that quasicrystals can represent a free energy minimum state at a given temperature. Some of the highly-perfect quasicrystalline materials exhibit a striking diffraction pattern; see Fig.1. There are a large number of diffraction peaks, which are aperiodically arranged and located at the ideal positions being consistent with a tenfold rotation symmetry. Besides, a remarkable fact is that the peak sharpness appears to be comparable to that from nearly-perfect crystals such as silicon, as evidenced by the high-resolution synchrotron diffraction experiments.

The observed 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. Shortly after their discovery, quasicrystal structure was discussed in relation to a rather disordered/imperfect state of solids. Representative early models are an icosahedral glass model [3] that assumes only a short-range icosahedral order distributed randomly to form the solid, and the so-called Pauling’s model [4] that employs multiply-twinned configurations of giant cubic crystals to generate a pseudo-fivefold symmetry pattern. One intuitively notices that neither of these configurations can be responsible for generating the sharp Bragg peaks. Nowadays we interpret this unique long-range aperiodic order as true quasiperiodicity [5], 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

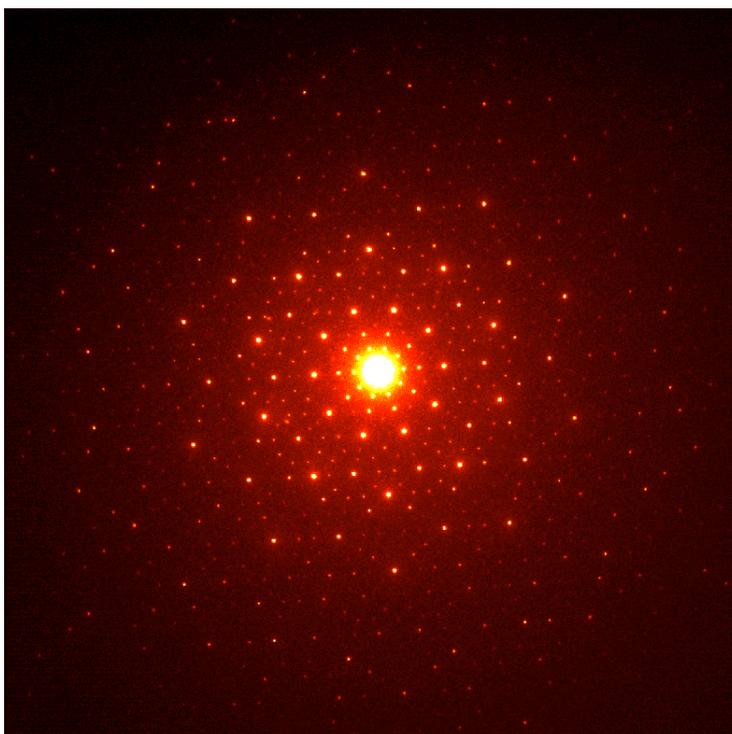


Fig. 1 Precession electron diffraction pattern of the Al₇₂Ni₂₀Co₈ decagonal quasicrystal, one of the best quasiperiodic ordered materials available today.

Fibonacci sequence. 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 1991 [6]. 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 a layperson might guess from the expression. It is important to recognize that quasicrystals indeed represent a well-ordered condensed state of matter that is now generally accepted as a new form of solid; a third phase following the classical crystalline (periodic) and amorphous (random) solids.

The striking features of quasicrystals – aperiodic order with noncrystallographic symmetry but being nevertheless compatible with sharp Bragg peaks – can be reasonably explained according to the hyperspace crystallography, which is given as a generalized form of normal crystallography by extending its framework into n -dimensions [7,8]. Suppose that the quasicrystalline order we view at our (observable) dimension is a ‘projected shadow’ of a hyperspace lattice. Then, the relevant quasicrystals should possess an intrinsic degree of freedom along the extra dimensions [9], even though they are hidden to us. On this basis, we expect an extra elastic degree of freedom for quasicrystals termed a phason. We will never be able to detect anything directly even if the hyper-lattice fluctuates along the hidden dimensions. However, such fluctuations, if any, indeed leave traces in the observable dimensions as a discontinuous change of local structures in quasicrystals. As a consequence, the lattice dynamics of quasicrystals can be described by a combination of lattice vibrations (phonons) and atomic fluctuations (phasons). Understanding phason-related atomic behaviors is critical for the thermodynamic stability of quasicrystals, and we use scanning transmission electron microscopy (STEM) to tackle this issue.

2. HAADF/Z-contrast STEM

Fig. 2 shows schematics of atomic-resolution imaging in conventional high-resolution TEM (phase-contrast) and STEM with the annular detector (Z-contrast) [10,11]. For the former, a parallel beam illuminates the specimen, and the atomic image is given as a consequence of many-beam interferences. Under the ideal conditions, the atomic positions appear as dark, which is achieved only when the sample foil is thin enough (typically less than 10nm for metallic foils). The contrast appears to be significantly different depending on the specimen thickness and/or defocus values. On the other hand, a finely-focused electron beam is used for atomic imaging in STEM. The atomic columns are illuminated one by one as the probe scans across the specimen, generating a two-dimensional intensity map of scattered electrons at the annular detector. Therefore, the atomic positions always appear to be bright. When detecting the sufficient high-angle scatterings ($> \sim 50\text{mrad}$ at 200kV accelerating voltage), the image intensity is dominated by thermal diffuse scattering (TDS), which is reasonably described by the TDS cross section (σ_{TDS}) that can be derived as a high-angle approximation of absorptive form factor f' [11],

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

where f is the atomic form factor for elastic scattering. In the absorptive description, the form factor is given as a function of s ($=\sin\theta/\lambda$, θ is a scattering angle, λ is the electron wave-length) and M , which is a Debye-Waller (DW) factor defined by the mean-square thermal vibration amplitude, $\langle u^2 \rangle$, of the atoms. In Eq. (1), integration is carried out over the detector angle range. Since the σ_{TDS} is proportional to the square of $f(s)$ (Eq. (1)), the high-angle annular dark-field (HAADF)-STEM is well-known for its atomic-number dependent contrast referred to as Z-contrast. Fig. 3 shows different appearances of the image contrast between the HRTEM and HAADF-STEM.

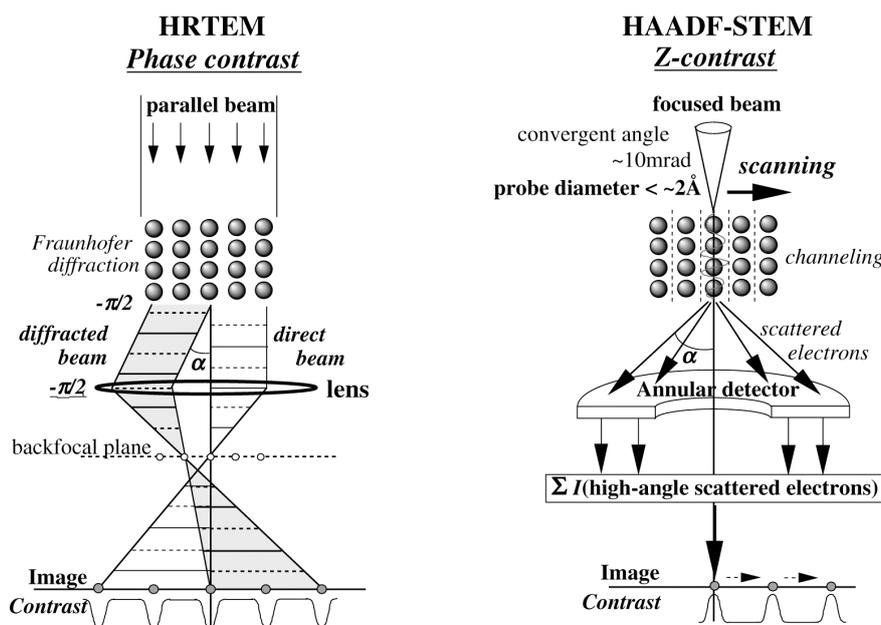


Fig. 2 Schematic drawing of atomic-resolution imaging of high-resolution transmission electron microscopy (HRTEM, left) and scanning transmission electron microscopy (STEM, right). By capturing the scattered electron at high-angles with the annular detector, STEM provides significantly atomic-number dependence contrast (Z-contrast).

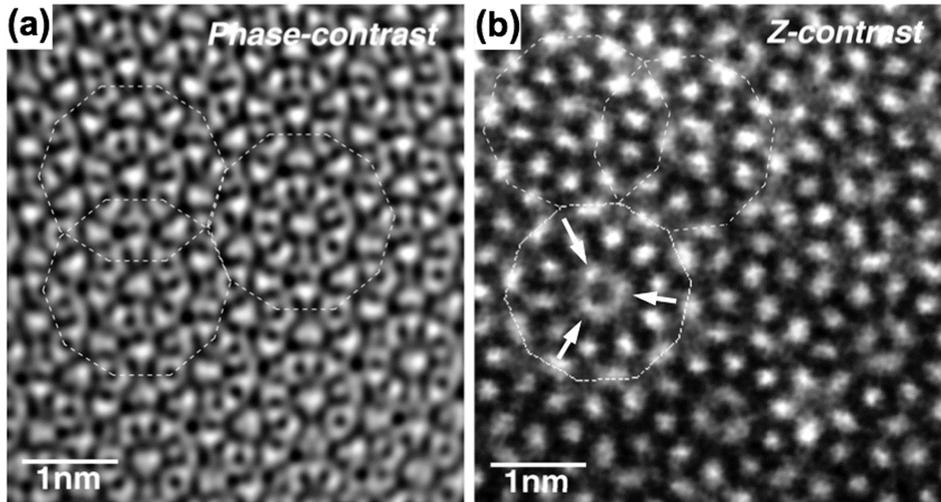


Fig. 3 Atomic-resolution (a) phase-contrast TEM and (b) Z-contrast STEM images, taken along the tenfold symmetry axis of the $\text{Al}_{72}\text{Ni}_{20}\text{Co}_8$ decagonal quasicrystal. Decagonal clusters of 2 nm across are shown by dashed lines in the both images. The image (a) was obtained from the very thin region ($\sim 60\text{\AA}$; near-edge of a cleavage grain) and under nearly Scherzer defocus ($\sim 45\text{nm}$ for the JEM-4000EX with $C_s=1.0\text{mm}$). The image (b) was taken from a slightly thicker region than that of (a), approximately $\sim 120\text{\AA}$ thick evaluated by EELS plasmon method.

3. Decagonal quasicrystals in Al-Ni-Co alloys

Decagonal quasicrystals are the planar realization of a quasiperiodic order [12], whose structure is described as a periodic stack of quasiperiodic layers. Al-Ni-Co alloys form a large number of decagonal quasicrystalline variants depending on the slight differences of compositions/temperatures, as represented by its complicated phase diagram (Fig. 4) [13]. Among these variants, decagonal $\text{Al}_{72}\text{Ni}_{20}\text{Co}_8$ (represented as “bNi” region in Fig. 4) has turned out to possess a nearly perfect atomic order, as proved by the direct observation using Z-contrast STEM (Fig. 5).

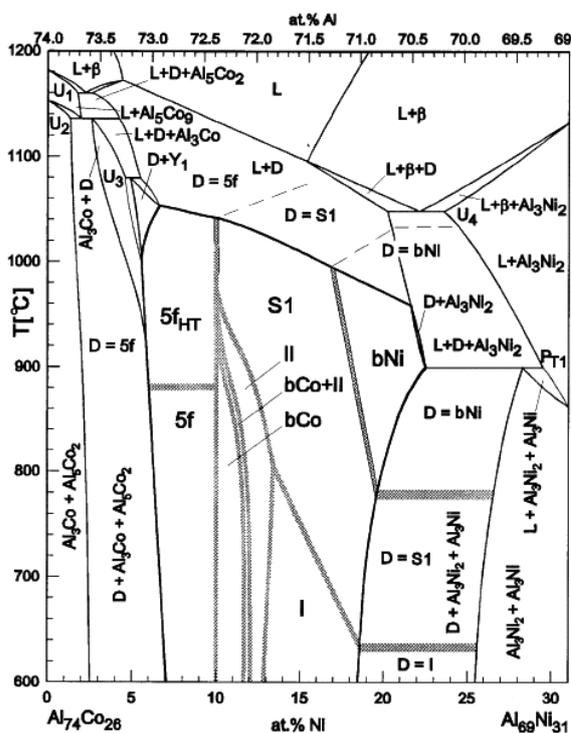


Fig. 4 Experimentally determined partial Al-Ni-Co phase diagram along the composition line $\text{Al}_{74}\text{Co}_{26} - \text{Al}_{69}\text{Ni}_{31}$ [13]. There are at least nine structural types of the decagonal quasicrystalline phases within this composition/temperature range. Note that even a few at.% difference in compositions causes a structural change.

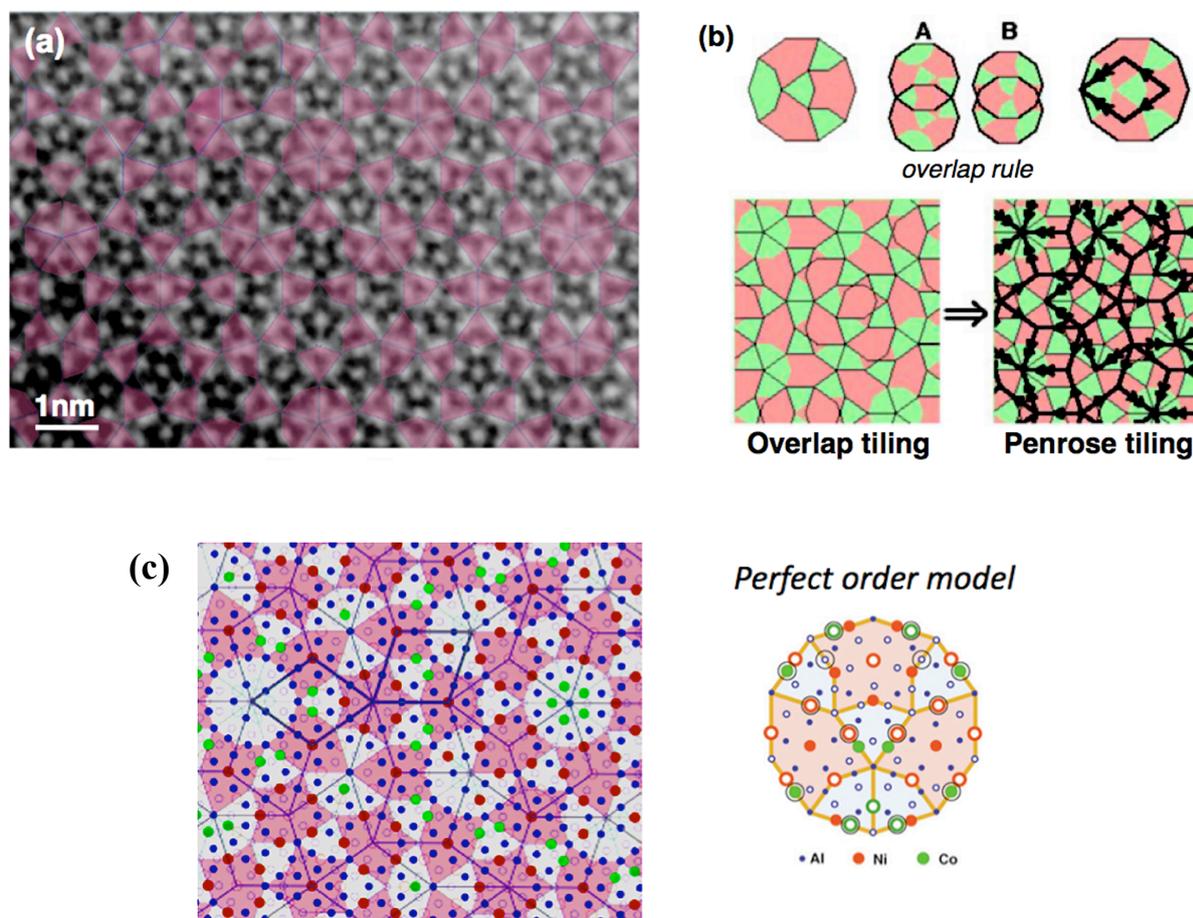


Fig. 5 (a) Long-range structure of the decagonal $\text{Al}_{72}\text{Ni}_{20}\text{Co}_8$ can be well represented by the novel decagon tiling that is equivalent to a perfect Penrose tiling [14,15]. (b) Using the decagons marked so as to break their tenfold-symmetry, a quasiperiodic tiling can be forced if the decagons are permitted to overlap only if shaded regions overlap, limiting the possible overlaps to just two ways, A-type and B-type (overlap rule). By inscribing a fat rhombus within each decagon, a decagon-overlapping tiling (left) is converted into a Penrose tiling with the matching rule (right). (c) Atomic model of the decagonal $\text{Al}_{72}\text{Ni}_{20}\text{Co}_8$ [15]; 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 (left) can be constructed from the decagonal cluster (right) properly decorated according to internal symmetry-breaking motifs.

Good chemical order between the Al and TM (transition metals) confirmed by the Z-contrast imaging suggests that the $\text{Al}_{72}\text{Ni}_{20}\text{Co}_8$ compound is close to its ideal stoichiometry, being tuned in favor of structural energy. The important fact is 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. This may well be explained by an optimized average valence electron concentration per atom (e/a) [2], which is known as Hume-Rothery's empirical rule [16] that concerns structural stability of ordered alloys in terms of Brillouin-zone/Fermi-surface interactions. 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.

4. Atomistic fluctuations in the decagonal quasicrystalline $\text{Al}_{72}\text{Ni}_{20}\text{Co}_8$

Suppose if the quasicrystalline Al-alloys intrinsically possess the phason degree of freedom, which is characteristic of the crystals in a hyperspace, we expect localized fluctuations that may be realized as a local DW factor (M in Eq. (1)) anomaly at the particular atomic sites in the quasicrystal structures. 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.

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;

$$M = M_{\text{phonon}} + M_{\text{phason}} \quad (2)$$

Below we describe successful direct observations of DW factor anomalies at the specific atomic sites in a quasicrystal [17], based on an *in-situ* high-temperature STEM observation.

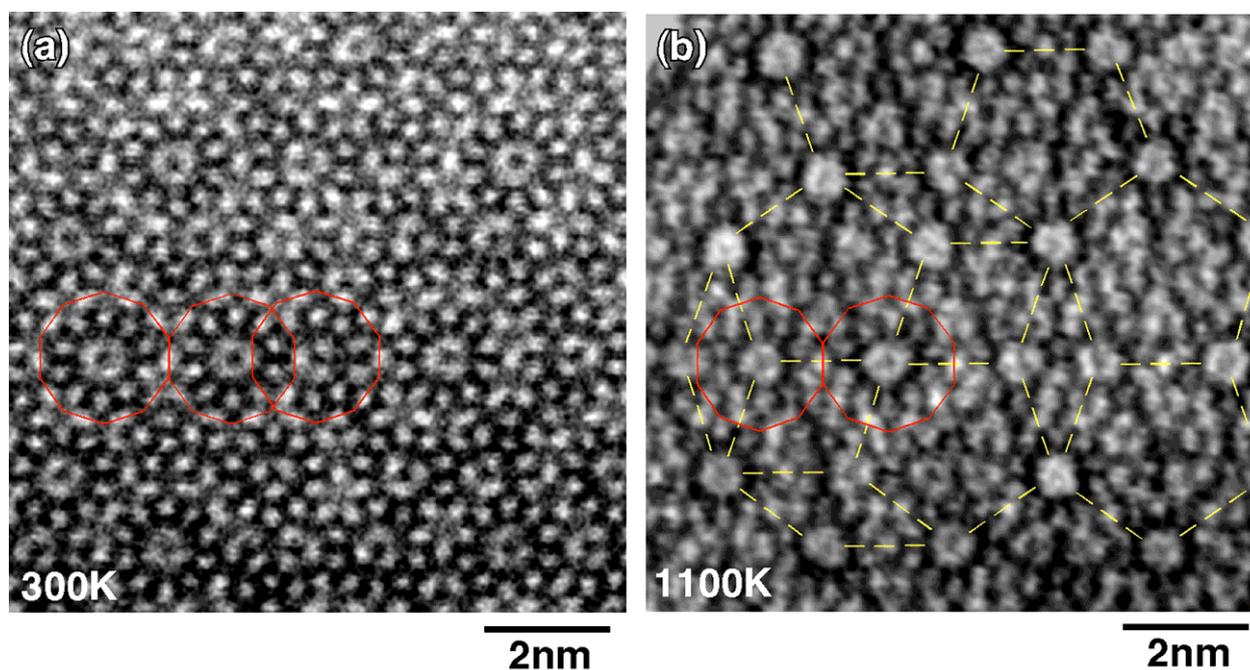


Fig. 6 HAADF-STEM images of the decagonal $\text{Al}_{72}\text{Ni}_{20}\text{Co}_8$. These were taken at (a), 300K and (b), 1100K by collecting the electrons scattered at angles approximately between 45 and 100 mrad ($0.9 \leq s \leq 2.0$) with a 200kV-STEM. Contrast differences between (a) and (b) are due to the different temperature. By connecting the center of the 2nm decagonal clusters (red) that reveal significant temperature-dependent contrast changes, a pentagonal quasiperiodic lattice (yellow) with an edge length of 2nm can be drawn in (b).

In the ADF-STEM image of the highly-perfect decagonal $\text{Al}_{72}\text{Ni}_{20}\text{Co}_8$ taken at room temperature (300K: Fig. 6(a)), Z-contrast highlights the transition metal (TM: Ni or Co) positions relative to the Al due to the $f^2(s)$ dependence of the contrast (Eq. (1)). But when the sample is heated and held at a temperature of approximately 1100K within the microscope, we find a remarkable change in the relative contrast; see Fig. 6(b) compared to Fig. 6(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 2nm. Considering that the present highly-perfect quasicrystalline phase is obtained as a quenched-in high-temperature configuration (water-quenched after annealing at

1100K), the image of Fig. 6(b) is showing the ‘true face’ of the quasicrystalline $\text{Al}_{72}\text{Ni}_{20}\text{Co}_8$, in the sense that it is indeed at its equilibrium situation. We found that the temperature-dependent anomalous STEM contrast in Fig. 6(b) can naturally be attributed to local anomalies of the DW factor at the specific Al sites, as expected by local difference of M in Eq. (1) (Debye-Waller contrast [17]). Here it is quite interesting to note that, by viewing the present $\text{Al}_{72}\text{Ni}_{20}\text{Co}_8$ structure as that in the hyperspace, the occurrence of such DW anomaly at the specific Al sites can be reasonably interpreted as a perturbation of the hyperspace crystalline potentials, being realized through M_{phason} in Eq. (2). This strongly implies that the quasicrystals intrinsically have the extra degree of freedom along the hidden dimensions. Details of this intriguing interpretation will be described in the talk.

5. Summary

The discovery of quasicrystals provided a paradigm shift in solid state physics since 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 repeating unit cells. Quasicrystals are now established as a well-ordered form of solids, being supported by discoveries of a large number of stable phases in the Al-based alloys. Nowadays we interpret the structural characteristics of quasicrystals according to hyperspace crystallography, which assumes a periodic lattice in the hyper-dimensions. The idea of extra dimensions is a compelling, universal issue in physics [18], and some Al-based quasicrystalline alloys indeed provide an important testing ground to challenge this issue [19,20].

References

- [1] D. Shechtman, I. Blech, D. Gratias, J. W. Cahn: Phys. Rev. Lett. 53 (1984) 1951.
- [2] A. P. Tsai: in *Physical Properties of Quasicrystals* (ed. Z. M. Stadnik, Springer, 1999), pp. 5-50.
- [3] P. W. Stephens, A. I. Goldman: Phys. Rev. Lett. 56 (1986) 1168, *ibid* 57 (1986) 2331.
- [4] L. Pauling: Nature 317 (1986) 512.
- [5] D. Levine, P. J. Steinhardt: Phys. Rev. Lett. 53 (1984) 2477.
- [6] International Union of Crystallography: Acta Crystallogr. A48 (1992) 928.
- [7] T. Janssen: Acta Crystallogr. A 42 (1986) 261.
- [8] A. Yamamoto: Acta Crystallogr. A 52 (1996) 509.
- [9] P. Bak: Phys. Rev. Lett. 54 (1985) 1517.
- [10] S. J. Pennycook, L. A. Boatner: Nature 336 (1988) 565.
- [11] S. J. Pennycook, D. E. Jesson: Ultramicroscopy 37 (1991) 14; Phys. Rev. Lett. 64 (1990) 938.
- [12] L. Bendersky: Phys. Rev. Lett. 55 (1985) 1461.
- [13] S. Ritsch et al: Phil. Mag Lett. 78 (1998) 67.
- [14] P. J. Steinhardt et al: Nature 399 (1999) 84.
- [15] E. Abe et al: Phys. Rev. Lett. 84 (2000) 4609.
- [16] W. Hume-Rothery: J. Inst. Met. 36 (1926) 295.
- [17] E. Abe, S. J. Pennycook, A. P. Tsai: Nature, 421 (2003) 347.
- [18] L. Randall: Physics Today 60 (2007) 80.
- [19] E. Abe, Y. Yan, S. J. Pennycook: Nature Materials 3 (2004) 759.
- [20] E. Abe: in *STEM: Imaging and Analysis* (edited by P. Nellist and S. J. Pennycook, Springer, New York, 2010, in press).