Phason Related Stacking Disorder in Decagonal Al-Co-Ni

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(Received 30 October 1995)

High-resolution transmission electron microscopy images of decagonal Al-Co-Ni quasicrystals are presented, which show the existence of phason related stacking disorder along the periodic tenfold axis. The image contrast in the interior of hexagon-shaped tiles shows an inner vertex only if no phason defect is present. This interpretation of the high-resolution micrographs is substantiated by electron microscopic image simulations based on a realistic structure model.

PACS numbers: 61.44.Br, 61.16.Bg, 61.72.Ff, 66.30.Fq

Since the discovery of materials showing crystallographically forbidden icosahedral [1], twelvefold [2], tenfold [3], and eightfold [4] symmetries of their diffraction spectrum, there had been extensive debate [5–7] about the nature of the long-range translational order of these new materials termed quasicrystals. Two general types of models have been proposed: In the quasiperiodic crystal models [8,9] (the prototype being the Penrose tilings) quasicrystals are assumed to be energetically stabilized, while for the random tiling models [10,11] entropic stabilization is favored. Both types of model structures can be related to a higher-dimensional periodic structure by embedding the physical space $E^{\parallel}$ and its complementary (perpendicular) space $E^{\perp}$ in this n-dimensional space [12,13]. However, for the random tiling models this description can give only the average structure, since in this case the 3D physical space $E^{\parallel}$ corresponds to a continuous (but generally wavy) 3D surface, while for quasiperiodic structures it corresponds to a 3D plane. The elastic excitations associated with the two subspaces $E^{\parallel}$ and $E^{\perp}$ correspond to phonons and phasons, respectively [14]. Whereas phonons in the long wavelength limit are related to uniform translations of the entire system, phasons are associated with atom jumps and are thus diffusive modes of quasicrystals. In the tiling picture of quasicrystal models phasons are correlated with local rearrangements of tiles [10,15,16]. Moreover, phason flips are regarded as the key mechanism for phase transitions between quasicrystals and approximant phases [17].

In computer random tiling simulation investigations, series of hexagon flips (flip of the tiling vertex inside a hexagon formed by three rhombic tiles, cf. Fig. 1) were introduced in a quasiperiodic tiling. Each phason flip was assigned a finite energy cost. As a result, the validity of the random tiling model for 2D decagonal quasicrystals could be shown in several studies [18–20]. Burkov pointed out that the periodicity of decagonal quasicrystals poses a severe problem for pure entropy stabilization in random tiling models [21]. A phason flip in one of the layers automatically results in a local stacking defect in the periodic layer arrangement along the tenfold axis of decagonal quasicrystals. As a consequence, depending on the strength of coupling between individual layers, decagonal quasicrystals have more or less correlated layers arranged periodically. Similar simulations of a 3D stack of decagonal quasicrystal layers have recently been presented [16,22]. Furthermore, Jeong and Steinhardt [16], in simulations with their quasiperiodic tiling model, found a phason related phase transition between a low-temperature quasiperiodic state and a random-tiling-like high-temperature state.

The simulations by Gähler and Roth [23] showed that the existence of vacancies (and half vacancies) is an important prerequisite for phason mobility in 1D periodic twelvefold quasicrystals. They also proved that the atom movement was predominantly along the periodic axis.

In spite of all these studies related to phasons in quasicrystals, no experimental evidence for local stacking defects related to phason flips has so far been established. It is the purpose of this study to present such experimental evidence. Newly obtained high-resolution transmission electron microscopy (HRTEM) images show phason related stacking defects in decagonal Al-Co-Ni. We also present corresponding image contrast calculations based on a recently proposed realistic structure model [24]. The simulations allow a microscopic interpretation of phason flips

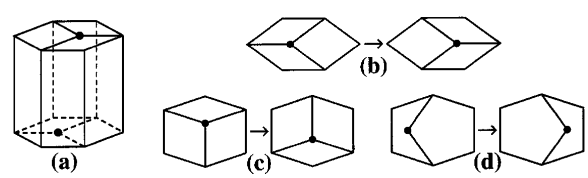

FIG. 1. Hexagon flips on tiling level: (a) Schematic drawing of a stack of skinny hexagons with a flip of the inner vertex. (b) Skinny hexagon, rhomb tiling. (c) Fat hexagon, rhomb tiling. (d) Fat hexagon, pentagon tiling. Solid circles indicate positions of inner vertices (cluster centers).

0031-9007/96/76(14)/2507(4)$10.00

and reveal the differences between a periodic arrangement of decagonal clusters in columns along the tenfold axis and arrangements with a stacking defect [cf. Fig. 1(a)].

Samples with nominal compositions of $Al_{70}Co_{15}Ni_{15}$ and $Al_{70}Co_{13}Ni_{17}$ were produced from high-purity elements by melting under Ar atmosphere in an induction furnace. After remelting the ingots in Ar atmosphere, they were cooled down to room temperature at a rate of 5 K/min. Parts of the samples were subsequently annealed at 850 °C for 3 days or at 920 °C for 2 days. The HRTEM images were obtained with a Philips CM30ST transmission electron microscope (TEM) having a C_s of 1.1 mm operated at 300 kV. TEM specimens were prepared by crushing small pieces of the samples in an agate mortar and dispersing the resulting powder on holey carbon foils supported by Cu grids. All computer simulated images were calculated with the EMS program package of Stadelmann [25].

In the 3D structure of a 1D periodic decagonal quasicrystal a single flip is represented by exchanging the tiling vertex inside a hexagon above a certain level along the periodic stack. In the simulations we used a stack of 32 layers, corresponding to a specimen thickness of 6.5 nm. Also, the fact was taken into account that for Al-Co-Ni two different types of superstructures have been found, both showing a fivefold symmetric contrast around the cluster centers [26,27]. Yet the overall tenfold diffraction symmetry of the material is preserved because of the antiparallel orientation of two adjacent cluster centers having 2 nm distance. Relevant details about these superstructures have been reported by Ritsch *et al.* [27].

Defocus series of decagonal Al-Co-Ni, taken with the electron beam parallel to the tenfold axis at a defocus of -27 ± 5 nm, exhibit a very prominent contrast feature having the shape of wheels with 2 nm diameter, which correspond to decagonal clusters. These wheels allow us to readily superimpose onto the micrographs a unique tiling with tiles of 2 nm edge length. The defocus values of the images presented in this study have been determined to a precision of ± 5 nm from HRTEM images, which showed a defocus variation along the edge of a slightly inclined grain. The images taken at -27 nm defocus display the decagonal clusters with a higher contrast than those taken at the so-called Scherzer defocus (-57 nm; in this defocus condition thin parts of the specimen, i.e., below 8 nm in thickness, reflect the projected potential of the atom arrangement). Therefore we have used images taken at -27 nm defocus to present the phason flips. Clusters consisting of four layers along the periodic axis, as suggested for either of the two decagonal superstructures [24], were used for the computer simulations. The structure model contains approximately (1–2)% vacancies (including half vacancies)—this appears to be a realistic value if compared to positron annihilation experiments [28]. These vacancies are essential for the mobility of phason flips in quasicrystals [23].

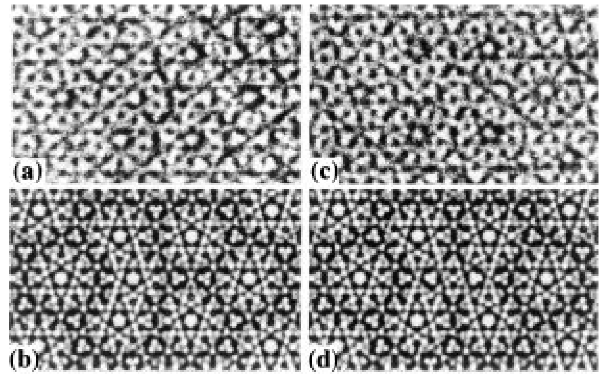

FIG. 2. Flip inside skinny hexagon, rhomb tiling, -27 nm defocus. (a),(c) HRTEM images. (b),(d) image contrast simulations. Inner vertex in left position throughout the stack [(a),(b)] and flipped from left to right position after half of the stack [(c),(d)]. The distance between two cluster centers corresponds to 2 nm.

In Figs. 2 and 3 a skinny hexagon from a rhomb tiling [cf. Fig. 1(b)] is presented for both -27 nm (Fig. 2) and Scherzer defocus conditions (Fig. 3), respectively. The vertex inside the hexagon (inner vertex) shows the typical contrast of a decagonal cluster, if the cluster is located only on the left flip position throughout the whole stack of layers [Figs. 2(a), 2(b), 3(a), and 3(b)]. This allows us to define the inner vertex for the tiling which can be superimposed onto the HRTEM image. On the contrary, the unique contrast of a decagonal cluster cannot be found if the inner vertex is flipped to the second possible position for the second half of the periodic stack [Figs. 2(c), 2(d), 3(c), and 3(d)]. Simulations with the phason flip located between the center and the top of the stack were also made. These demonstrated that a unique definition of the inner vertex position is only possible if this vertex is flipped after more than 20% of the stack. Note that it is not important whether the stacking defect is located near the top or the bottom of the stack.

Figures 4(a)–4(d) and 5(a)–5(d) present analogous sequences of HRTEM micrographs and simulated images

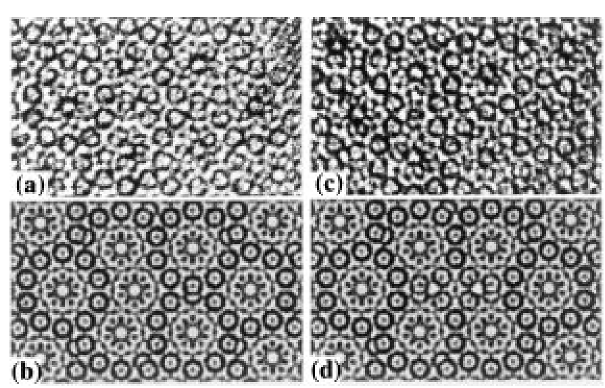

FIG. 3. Analogous to Fig. 2 for Scherzer defocus condition.

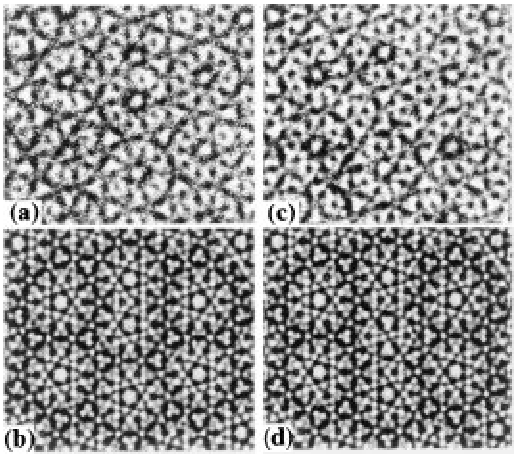

FIG. 4. Analogous to Fig. 2 for fat hexagon, rhomb tiling, −27 nm defocus.

at −27 nm defocus of a fat hexagon for a rhomb tiling [cf. Fig. 1(c)] and for a pentagon tiling [cf. Fig. 1(d)], respectively. Again it is possible to define the inner vertex position only for Figs. 4(a) and 4(b) as well as 5(a) and 5(b) which correspond to the cases without a phason flip. Comparison of Figs. 4(c) and 4(d) as well as 5(c) and 5(d) shows that these images are almost identical. However, they represent the situations with the phason flips after half of the stack in the fat hexagon for a rhomb tiling and for a pentagon tiling, respectively, which correspond to the two different decagonal superstructures [27].

The good correspondence between the simulations and the experimental images presented here allows the conclusion that stacking defects related to phason flips cause hexagon-shaped tiles, where an inner vertex position cannot be defined. In this case the hexagons do not allow a decomposition into rhombi or pentagons with 2 nm edge length. It is a general problem in the interpretation of HRTEM images that the presence of such phason related stacking defects is difficult to recognize; this is shown here on the basis of realistic image contrast simulations. Shin *et al.* [22] have pointed out the difficulty to identify phason defects in a simple projection of atom positions of a 3D stack of decagonal quasicrystal layers containing such stacking defects. Nevertheless, HRTEM is the only technique which allows us to decide to what extent phason defects are actually present.

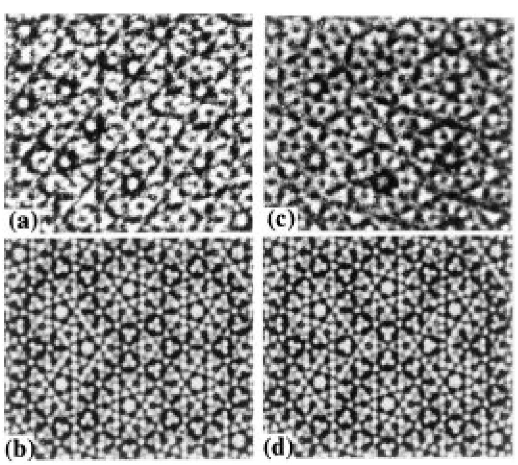

FIG. 5. Analogous to Fig. 2 for fat hexagon, pentagon tiling, −27 nm defocus.

The three possible types of overlap of the clusters are shown in Fig. 6 using a projection of two layers of the structure model. For all these overlaps the central region of the cluster up to the decagon with a diameter of 1.24 nm remains unaffected. These types of linkage are evident from Fig. 6 and can also be recognized in Fig. 8 of the x-ray structure refinement of Al-Co-Ni by Steurer *et al.* [29]. Hiraga, Sun, and Yamamoto [30], however, have proposed another possible linkage inside a 36° Penrose rhomb. Yet, with their proposal, the vertex position inside a skinny hexagon cannot be defined: Regardless of the position of the flip in the periodic stack of layers, the same contrast is obtained in all simulations [the contrast gained is similar to that in our Fig. 2(d)]. This leads to the conclusion that the model of Hiraga, Sun, and Yamamoto [30] is a model for a disordered structure deduced from an average structure full of phason related stacking defects [compare Fig. 7 of Hiraga, Sun, and Yamamoto [30]; note the large amount of skinny hexagons where the inner vertex *cannot* be defined, as is evident from the tilings in their Figs. 7(b) and 10(b)].

Tilings superimposed onto HRTEM images of decagonal quasicrystals observed in $Al_{70}Co_{15}Ni_{15}$, respectively, in $Al_{70}Co_{13}Ni_{17}$ specimens annealed at 850 °C for 3 days or at 920 °C for 2 days, contain almost no rhombi or pentagons. These tilings consist of larger tiles like elongated

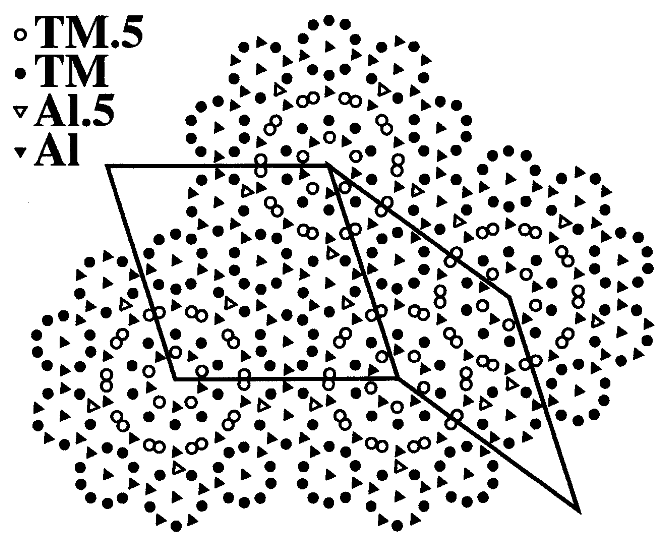

FIG. 6. Arrangement of atom clusters on tiles showing all three types of overlaps of clusters occurring for hexagon-shaped tiles.

hexagons, "kidneys" ("bananas") and S-shaped tiles—besides the fat and skinny hexagons. All of these tiles can be composed of rhombi and/or pentagons, however, the inner vertices cannot be defined on the HRTEM images. Moreover, they all exhibit contrast features in their interior similar to those presented in this work for the fat and skinny hexagons. It is therefore suggested here that the appearance in HRTEM images of larger tiles, where the inner vertices cannot be defined, is caused by the presence of phason-related stacking defects. Since this has been observed in specimens homogenized at relatively high temperatures (850 °C, respectively, 920 °C), the presence of a high density of phason defects indicates an additional entropic stabilization of decagonal Al-Co-Ni quasicrystals by phason disorder.

We have presented clear evidence for decagonal Al-Co-Ni that hexagon-shaped tiles, where no inner vertex can be defined, are associated with stacking defects in the columns of clusters aligned along the periodic tenfold axis. These stacking defects originate from phason flips of a single vertex inside the hexagons to a second possible vertex position. The results demonstrate that phasons are an important inherent feature of decagonal Al-Co-Ni quasicrystals. We assume that this also holds for other related decagonal alloy systems.

We gratefully acknowledge helpful discussions with T. Ishimasa. Our special thanks are due to R. Lück and T. Gödecke for providing the specimens and for many fruitful discussions. We are grateful for financial support by the Schweizerischer Nationalfonds.

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