High Resolution Transmission Electron Microscopy Observation of Thermally Fluctuating Phasons in Decagonal Al-Cu-Co

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(Received 13 March 2000)

In situ high-temperature, high resolution transmission electron microscopy (HRTEM) was performed on an Al-Cu-Co decagonal quasicrystal, to investigate thermal fluctuation of phasons. A tiling pattern constructed from the HRTEM image was analyzed in the framework of the strip-projection method. Transitions between two local tile arrangements were observed at high temperature for the first time, and were shown to correspond to a thermal phason fluctuation.

PACS numbers: 61.44.Br, 61.16.Bg, 61.72.Ff, 65.50.+m

Quasicrystals have incommensurate structures where the incommensurate length scales are determined by geometrical constraints associated with noncrystallographical point group symmetry such as the icosahedral symmetry [1,2]. Originating in the incommensurability, quasicrystals have a special type of elastic degrees of freedom, not found in conventional crystals, which are termed phason degrees of freedom [3]. Quasicrystals are accompanied by the phason elastic field $\boldsymbol{w}(\boldsymbol{r})$ in addition to the conventional elastic field $\boldsymbol{u}(\boldsymbol{r})$. Elastic excitations associated with $\boldsymbol{w}(\boldsymbol{r})$ are called phasons in contrast to phonons which are associated with $\boldsymbol{u}(\boldsymbol{r})$. The hydrodynamic theory for the quasicrystal predicts that, whereas the conventional strain $\nabla \boldsymbol{u}$ relaxes rapidly, the phason strain $\nabla \boldsymbol{w}$ relaxes diffusively with relaxation times that are estimated to be extremely long [4,5]. Quenched phason strains are often observed experimentally as shifts and broadenings of diffraction peaks [6–9], which correlate with the phason momentum $G_\perp$, and as jogs in atomic rows [6,10] in high resolution transmission electron microscopy (HRTEM) images.

Up to now, two distinct models have been proposed for the physical origin of the quasicrystalline structural order. One is the perfectly quasiperiodic model [1,2]. In this model, the existence of local atomic interactions which force the formation of the quasiperiodic order is assumed, and thus the quasicrystal is assumed to be energetically stabilized, analogously to conventional crystals. The other is the random tiling model [11], in which the quasicrystal is assumed to be stabilized by a configurational entropy originating in many nearly degenerate ways of packing structural units. In the perfectly quasiperiodic state, the elastic free energy F has the form $F \propto |\nabla \boldsymbol{w}|$ [11–13] and thermal phason fluctuations are believed to be strongly suppressed. The state having this form of elastic free energy is called a locked state. In contrast, the random tiling quasicrystals exhibit $F \propto (\nabla \boldsymbol{w})^2$ [11–13] and the state with this form of elastic free energy is generally called an unlocked state. In the unlocked state, phasons can be thermodynamically excited. Although the locked state was historically believed to be characteristic of any energetically stabilized quasicrystal, it was shown to be possible, by Monte Carlo simulations, that some energetically stabilized models of 3D icosahedral [14] and 3D decagonal [13] quasicrystals undergo phase transition from a locked state at low temperature to an unlocked state at high temperature.

So far, there have been several reports on experimental observations of phason disorders in decagonal quasicrystals [15–19]. The perpendicular-space profiles have been constructed from tiling structures extracted from HRTEM images of various decagonal quasicrystals to analyze the nature of the phason disorders. The existence of stacking disorder created by interlayer phason fluctuation was shown in a decagonal Al-Co-Ni by HRTEM with the help of image simulation [20]. Recently, phason disorder in a decagonal Al-Cu-Co has been investigated by ion channeling combined with particle-induced x-ray emission [21]. In all of these works, the phason disorders studied were either grown-in or quenched ones. In this Letter, we report on the observation of thermally fluctuating phasons in a decagonal Al-Cu-Co by *in situ* high-temperature HRTEM experiments. Thermal phason fluctuations were observed by neutron scattering [22–24], by Moessbauer spectroscopy [25], and by NMR [26,27]. However, this is the first *direct* observation of thermal phason fluctuations in any quasicrystalline system.

An alloy with the composition of $\mathrm{Al_{65}Cu_{20}Co_{15}}$ was prepared from the elemental constituents by arc melting under an argon atmosphere. The alloy ingot was remelted at 1433 K and slowly cooled down to 1173 K with a controlled cooling rate of 10 K/h and then furnace cooled to room temperature. Columnar grains of the decagonal quasicrystal of 3–5 mm in length and 0.2–0.5 mm in diameter were taken out by crushing the ingot. Disks with a thickness of 0.4 mm were cut out perpendicularly to the longitudinal direction of the columnar grains. They were thinned mechanically and then further thinned by ion milling. The normal of the disks is approximately parallel to the tenfold axis of the decagonal quasicrystal. For the thinned

0031-9007/00/85(8)/1674(4)$15.00

disks, *in situ* high-temperature HRTEM experiments were performed using a 200 kV JEOL JEM-2010 transmission electron microscope equipped with a double-tilting heating stage. The sample was heated to 1123 K at a heating rate of about 10 K/min and held at 1123 K for about 1 h. After image drift due to heating became sufficiently small, HRTEM observations were made at this temperature with the incident beam parallel to the tenfold axis. The images were recorded on video tape.

Figure 1(a) shows a HRTEM image observed at a certain moment, in which we recognize an arrangement of white dots. So far, several groups have analyzed tiling patterns constructed from HRTEM images of various decagonal quasicrystals [15–19]. In those studies, a ringlike contrast with the diameter of about 2.0 nm was chosen as the most recognizable structural unit to construct the tiling pattern. However, in our high-temperature experiments, the ringlike contrast was not clearly observed, irrespective of the defocus value. Instead, the pattern of white dots was obtained in relatively thick regions. A tiling pattern can be constructed by connecting the white dots by the usual five-star basis vectors $\boldsymbol{p}_i$ $(i = 0, \ldots, 4)$ with a length of about 2.0 nm, as shown in the image of Fig. 1(a). The tiling pattern consists mostly of the following elements: a regular pentagon, two kinds of rhombus (fat and skinny rhombi in a rhombic Penrose tiling), a hexagon which can be divided into a fat rhombus and two skinny rhombi, and another hexagon which can be divided into two fat rhombi and a skinny rhombus. In some portions, two or more fat rhombi are found to be linked sequentially, indicating local phason disorder.

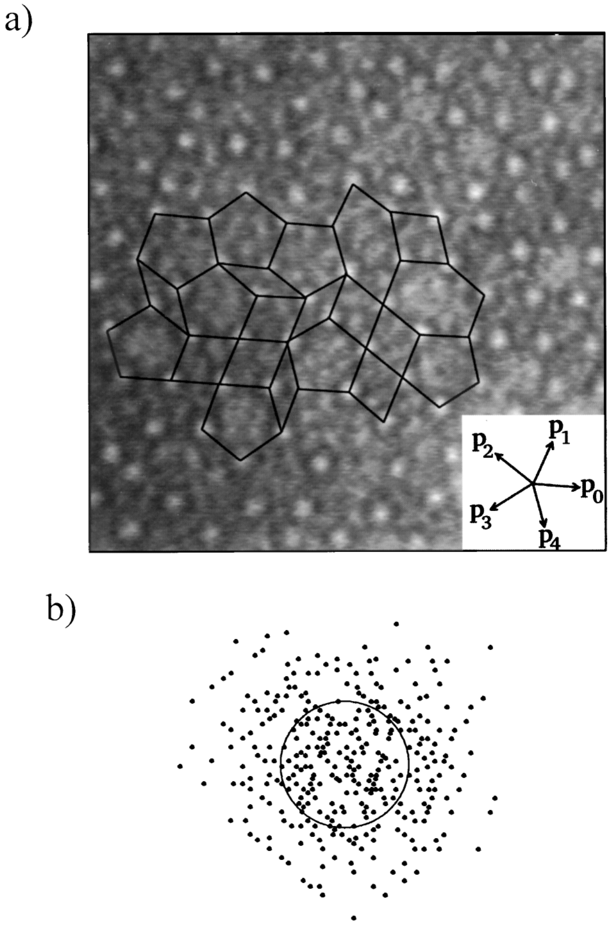

FIG. 1. (a) A portion of HRTEM image observed at 1123 K. An arrangement of white dots is seen. A tiling pattern is constructed by connecting the white dots by $\boldsymbol{p}_i$ $(i = 0, \ldots, 4)$ with the length of about 2.0 nm. (b) The perpendicular-space profile for the tile vertices, together with a circular window with the radius of $1.02|\boldsymbol{q}_i|$. The radius is deduced from the average density of the tile vertex.

In the framework of the strip-projection method [28,29] describing decagonal quasicrystalline tilings, the tile vertex $\boldsymbol{r}_\parallel$ can be lifted to the five-dimensional lattice point $(n_0, n_1, n_2, n_3, n_4)$ by the relation $\boldsymbol{r}_\parallel = \sum_{i=0}^{4} n_i \boldsymbol{p}_i$. The projection $\boldsymbol{r}_\perp$ of the lifted point onto the perpendicular space can be calculated as $\boldsymbol{r}_\perp = \sum_{i=0}^{4} n_i \boldsymbol{q}_i$, where $\boldsymbol{q}_i$ are defined by $\boldsymbol{q}_i = \boldsymbol{p}_{(2i \bmod 5)}$. In Fig. 1(b), the distribution of the points $\{\boldsymbol{r}_\perp\}$ calculated for the tile vetices $\{\boldsymbol{r}_\parallel\}$ observed at a certain moment within an area of 1.1×10^3 nm^2 is shown, together with a circular window which yields the tiling pattern with the same vertex density as that in the observed pattern. The average density of the tile vertex in the observed pattern was evaluated to be 2.86×10^{-1} nm^{-2}. The corresponding circle radius is calculated to be $1.02|\boldsymbol{q}_i|$, which is approximately the same as the center-to-vertex distance of the decagon window for the pentagonal Penrose tiling [16,19], which is equal to $|\boldsymbol{q}_i|$. We notice that the point distribution is considerably scattered and extends largely beyond the boundary of the window. This fact indicates the existence of a large amount of phason disorder. The large distribution of $\boldsymbol{r}_\perp$ points can be interpreted as a spatial phason fluctuation, in contrast to a temporal phason fluctuation described later; the window position in the perpendicular space fluctuates, depending on the position in the parallel space. Similar results have been reported for some class of decagonal quasicrystals [15,17].

Figure 2 presents an example of the change in the HRTEM image observed at 1123 K. For the images in Figs. 2(a)–2(f), elapsed times are 0, 5, 8, 110, 113, and 115 s, respectively. In these images, we notice the change in the arrangement of the white dots, which is schematically shown in Fig. 3(a). In Fig. 2(a), the dot arrangement in the left part of Fig. 3(a) is seen. In the image of Fig. 2(b) where the elapsed time is 5 s, the dot at the position *A* becomes blurred while a new dot emerges at the position *B* indicated in the pattern in the right part of Fig. 3(a). In Fig. 2(c), the dot at *A* completely disappears while the dot at *B* becomes intense. The tiling pattern seen in Fig. 2(c) is depicted in the right part of Fig. 3(a). After that, essentially no change was observed until an elapse of about 110 s when the dot at the position *B* becomes blurred and the dot at *A* becomes visible again, as shown in Fig. 2(e). Finally, in the image of Fig. 2(f) with the elapsed time of 115 s, essentially the same dot arrangement as that in Fig. 2(a) is observed. During our observation for about 20 minutes, the transition between

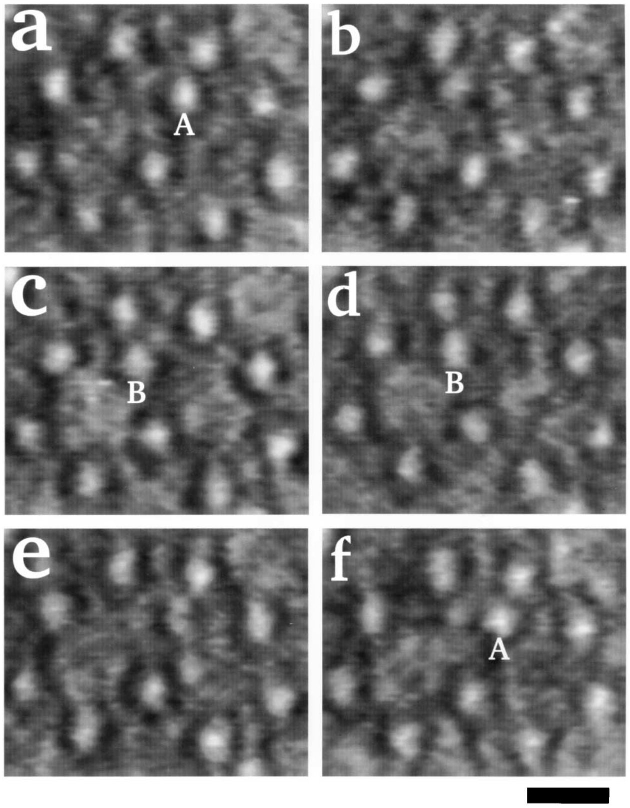

FIG. 2. An example of the change in the HRTEM image observed at 1123 K. Elapsed times for (a)–(f) are 0, 5, 8, 110, 113, and 115 s, respectively. The scale bar indicates 2.0 nm.

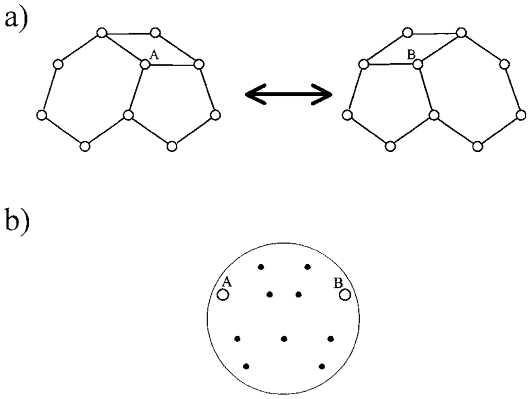

FIG. 3. (a) The transition between the two tile configurations observed in Figs. 2(a)–2(f). (b) The perpendicular-space profile for the tile vertices in (a), together with a circular window with the radius of $1.02|\boldsymbol{q}_i|$.

the two configurations in Fig. 3(a) was observed several times irregularly at intervals ranging from a few tens of seconds to about ten minutes. It should be noted that the transitions were rather sharp; the staying time at the transient configurations such as those seen in Figs. 2(b) and 2(e) was shorter than 10 s. The short staying time at transient configuration is suggestive of a relatively strong interlayer interactions along the tenfold direction.

In Fig. 3(b), the distribution of the $\boldsymbol{r}_\perp$ points calculated for the tile vertices in the patterns of Fig. 3(a) is shown, together with the circular window deduced from the average density of the tile vertices [the same window as that in Fig. 1(b)]. The $\boldsymbol{r}_\perp$ points for A and B in Fig. 3(a) are indicated by the same letters in Fig. 3(b). It is shown that the window can accommodate all of the points. In Fig. 3(a), the distance between A and B is $|\boldsymbol{p}_i|/\tau$, where τ denotes the golden mean. Correspondingly, the distance between A and B in the perpendicular space is $\tau|\boldsymbol{q}_i|$ and these two points are located near the boundary of the window, as shown in Fig. 3(b). With this configuration, the transition of points $A \leftrightarrow B$ may be interpreted as a result of temporal fluctuation of the position of the window in the horizontal direction in Fig. 3(b). When the window moves to the left, it gets rid of the point B while keeping the point A inside, and vice versa when the window moves to the right. The temporal fluctuation of the window is attributed to a thermal phason fluctuation. The observation of the thermal phason fluctuation implies that the phase is in an unlocked state.

The structural change of the same type as that shown in Fig. 3(a) was observed at several other places. Besides this type, more complicated structural changes involving five or more dots have also been observed. The perpendicular-space analysis has shown that some of them cannot be simply interpreted as phason fluctuations, in contrast to the structural change presented in Fig. 3(a). Detailed analysis of such complicated structural changes will be reported elsewhere.

In summary, *in situ* high-temperature HRTEM experiments were performed for an Al-Cu-Co decagonal quasicrystal to investigate thermal fluctuation of phasons. We have constructed a tiling pattern from the arrangement of white dots observed in the HRTEM image. Transitions between two local tile arrangements were observed at 1123 K irregularly at intervals ranging from a few tens of seconds to about ten minutes. The transition has been analyzed in the framework of the strip-projection method and shown to correspond to a thermal phason fluctuation.

We thank Y. Kamimura and S. Ohta of IIS, University of Tokyo for his cooperation in preparing the manuscript. This work has been supported by Core Research for Evolutional Science and Technology, Japan Science and Technology Corporation.

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