Direct observation of the local atomic structure in two types of Au-Ge-Yb 1/1 approximants

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Abstract. The local atomic structure in two types of Tsai-type 1/1 quasicrystal approximants in the Au-Ge-Yb system were observed using scanning transmission electron microscopy (STEM). The high-angle annular dark-field (HAADF) imaging method in STEM was employed to detect the difference in local atomic structure at the cluster centers for both compounds. Two types of cluster centers were observed in the different compounds: a tetrahedron with various orientations and a single Yb atom. Furthermore, atomic-resolution energy-dispersive X-ray spectroscopy showed direct evidence for the presence of a single Yb atom at the cluster center for the later compound.

1. Introduction
Quasicrystals and their approximants are considered as materials built from atomic clusters, and are classified based on their cluster structure. One such cluster type is the Tsai-type cluster that has a nested structure with five atomic shells [1]. In most Tsai-type clusters, the innermost shell is a disordered tetrahedron, in some cases a single M position (M= Ca, Yb) can replace the disordered tetrahedron for example in Au-Ge-M 1/1 approximants. The two types of approximants are distinguished by the local structure of their innermost shells, and are called Phase I (tetrahedron) and Phase II (rattling M atom) [2]. Figure 1 shows schematics of the atomic structures for Phase I and II viewed along the [001] axis; both phases belong to the space group Im$ar{3}$ with lattice parameters of 14.769(2) Å for Phase I and 14.633(2) Å for Phase II [2].

![Figure 1](image_url)

Figure 1. Crystal structure of (a) Phase I and (b) Phase II along the [001] axis [2]. Yellow, purple, and blue balls represent Au, Ge, and Yb atoms, respectively.
It has been reported that structural variations of the Tsai-type approximants affect their magnetic and electrical properties [3, 4]. Direct observation of local atomic structures along with X-ray structure analysis is an effective method for the analysis of local structures with subtle variations in structure or chemical composition. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) has recently made it possible to observe the local atomic structure of complex metallic alloys, such as approximants, at atomic level resolutions [5]. The aim of this study is to demonstrate the direct observation of local atomic structure in the two types of Au-Ge-Yb approximants using STEM, and show that this technique is effective for the detection of the subtle structural differences in Tsai-type clusters.

2. Experimental methods
The starting materials were pure elements: Au (99.99 wt%), Ge (99.999 wt%) and Yb (99.9 wt%). Alloys with various compositions were arc-melted in argon atmosphere. The arc-melted ingots were sealed in evacuated quartz tubes and annealed at 500°C for 100 hours, then quenched in cold water. Lattice parameters were obtained from powder X-ray diffraction (PXRD) patterns traced using Cu Kα radiation. Samples for STEM observation were prepared by crushing the alloys in an agate mortar followed by dispersing on a copper micro grid mesh. Atomic resolution HAADF-STEM observations and energy-dispersive X-ray spectroscopy (EDS) mapping were carried out with 200 kV STEM (JEM-ARM200F, JEOL). For STEM observations, we used a probe size of ~1 Å, a probe convergence semi-angle of 24 mrad, and the collection semi-angles for HAADF imaging were in the range 90–370 mrad. HAADF image simulations were performed using xHREM (HREM Research) based on multislice simulation theory. The simulated images were convoluted with a Gaussian function with a 1/e full width of 1 Å, assuming a thickness of 440 Å.

3. Results and discussion
From the PXRD patterns in figure 2, the two alloys Au_{63.75}Ge_{21.25}Yb_{15} and Au_{63.5}Ge_{20.5}Yb_{16} aged at 500°C for 100 h are identified to be Phase I and II, respectively. The lattice parameters of the body-centered cubic (bcc) lattices were calculated to be 14.77 Å for Phase I and 14.66 Å for Phase II. The experimentally observed PXRD patterns and the lattice parameter values are consistent with previously reported values obtained from single crystal data: 14.769(2) Å for Phase I and 14.633(2) Å for Phase II [2].

![Figure 2. PXRD patterns of Au_{63.75}Ge_{21.25}Yb_{15} and Au_{63.5}Ge_{20.5}Yb_{16} aged at 500°C for 100 h. Red and Blue patterns were obtained from simulations using single crystal data [2].](image-url)
Figure 3 shows the HAADF-STEM images for Phase I and II taken along the [001] axis. In a HAADF image, a bright spot can be interpreted as an atomic column and the HAADF intensity is proportional to the square of the average atomic number in the column [6]. As can be seen in figure 3(a) and 3(b), both the HAADF images show similar contrast, except at the cluster center; the contrast at the cluster center in Phase II is brighter than that in Phase I. The intensity profiles taken across the cluster center highlight the apparent difference in the intensity between the two structures, as shown in figure 3(c) and 3(d). The average atomic number of each atomic column along the incident electron probe direction is the principal contributor to the HAADF intensity. Thus, the presence of a single Yb atom at the cluster center in Phase II should be responsible for the difference in intensity at the cluster center between the two phases. Note that there is no obvious evidence for the presence of a tetrahedron in Phase I. This is because of the several possible orientations of the tetrahedron at room temperature, which is consistent with previously reported observations on other 1/1 approximants [7, 8]. Calculated images using models for Phase I and Phase II closely reproduced the experimental images, lending further support to our experimental results.

![Figure 3](image)

**Figure 3.** (a) and (b) HAADF images of Au$_{63.75}$Ge$_{21.25}$Yb$_{15}$ (Phase I, left) and Au$_{63.5}$Ge$_{20.5}$Yb$_{16}$ (Phase II, right) taken along the [001] axis. Black square insets in (a) and (b) show calculated HAADF images based on the models [2]. (c) and (d) show the intensity profiles taken across the cluster center denoted by the line AB, where the profiles (c) and (d) were averaged over 44 and 45 unit cells, respectively.

We further performed atomic-resolution EDS mapping on Au$_{63.5}$Ge$_{20.5}$Yb$_{16}$ (Phase II), as shown in figure 4; characteristic X-rays (Au-M, Ge-L, and Yb-L) were used in the mapping. For atomic-resolution EDS, the X-ray intensity depends on the position and the number density of each element in atomic columns, and the contrast in (a)-(c) thus represents the spatial distribution of the constituent elements. The solid square in figure 4 corresponds to the unit cell of Phase II with a lattice parameter of 14.66 Å. The bright contrast position of each map agrees with the atomic position of the structure model [2]. For the Yb-L maps in (c) and (f), a significant contrast is observed both at the cluster center.
and at icosahedral vertices, providing direct evidence for the presence of a Yb atom located at the cluster center. Note that the occupation of the Wyckoff 8c position, as well as that of the cluster center, depends on alloy systems and compositions [2-4]. Our results demonstrate that the presence of atoms at the 8c position can also be detected using STEM-EDS; for the Ge-L map in (b) and (e), Ge atoms located at the 8c position are clearly visualized.

4. Conclusion
Two types of Au-Ge-Yb 1/1 approximants of quasicrystals, Phase I and Phase II, were formed in Au63.75Ge21.25Yb15 and Au63.5Ge20.5Yb16 alloys aged at 500°C for 100 h. HAADF-STEM observations revealed that a single Yb atom was present at the cluster center in Phase II, but not in Phase I. The presence of this single Yb atom was confirmed from atomic resolution EDS mapping. These results suggest that STEM is effective for the detection of subtle variations in the local structure in approximants, such as the presence of a tetrahedron or a single atom at the cluster center.

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