Formation and magnetic properties of Ga–Pd–Tb 2/1 approximant

Y G So¹, K Takagi¹ and T J Sato²

¹Department of Materials Science, Graduate School of Engineering Science, Akita University, Tegata Gakuen-machi, Akita, 010-8502, Japan
²Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Katahira, Aoba-ku, Miyagi 980-8577, Japan

so@gipc.akita-u.ac.jp

Abstract. The formation and magnetic properties of Tsai-type approximants in the Ga–Pd–Tb system were investigated. The 2/1 approximant with a lattice parameter of 2.313 nm formed in the Ga₅₀.₂Pd₃₅.₃Tb₁₄.₅ alloy annealed at 973 K for 100 h. The 2/1 approximant transformed into the corresponding 1/1 approximant through annealing at 1073 K in the alloy. For the 2/1 approximant, magnetic susceptibility measurements showed a sharp cusp at $T_N \approx 5.8$ K, and both the field-cooled and zero-field-cooled susceptibilities coincided, indicating an antiferromagnetic transition at $T_N$. This is the first instance of long-range magnetic order in 2/1 approximants. On the other hand, spin-glass-like behavior was observed in the susceptibility for the 1/1 approximant, which may be attributed to the relatively large frustration of the icosahedral clusters in the 1/1 approximant.

1. Introduction

Magnetism in Tsai-type icosahedral quasicrystals has so far been known to show spin-glass-like behavior, e.g., Cd–Mg–R (R: rare earth metal) [1] and Cd–R [2] systems. However various magnetic properties have recently been observed in their 1/1 approximants: spin-glass behavior in Ag–In–R [3], ferromagnetism in Au–SM–R (SM= Si, Ge, or Sn) [4], antiferromagnetism in Cd₄Tb [5] and spin-glass to ferromagnetism or antiferromagnetism in Au–Al–R (R = Gd or Tb) systems, depending on the alloy compositions [6]. Despite the variety of magnetic quasicrystals and approximants available, there is little information on the magnetism of higher-order approximants, such as 2/1 approximants. As the atomic structure of 2/1 approximants is closer to that of quasicrystals compared with 1/1 approximants, studies on magnetic 2/1 approximants that exhibit long-range magnetic order provide important insights for understanding magnetism in quasicrystals.

Recently, we discovered a series of Ga–Pd–R 1/1 approximants (where R= Y, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu) [7]; thus, the formation of a 2/1 approximant is expected in the alloy systems with compositions close to the 1/1 approximants. In this study, we focused on searching for a magnetic 2/1 approximant in the Ga–Pd–Tb system and revealed the Tsai-type 2/1 approximant that showed antiferromagnetic behavior in its magnetic susceptibility; this is the first example of long-range magnetic order in 2/1 approximants.
2. Experimental Procedures
Alloy ingots with nominal compositions of Ga\textsubscript{57.5-x}Pd\textsubscript{28+x}Tb\textsubscript{14.5} (x = 0 to 10) were prepared from high-purity Ga (99.9999 wt.%), Pd (99.95 wt.%) and Tb (99.9 wt.%) via arc melting in an argon atmosphere. The ingots were subsequently sealed in an evacuated silica tube and annealed at various temperatures for 100 h, followed by water quenching. Powder x-ray diffraction (XRD) measurements were performed using Cu-K\textalpha{} radiation and a graphite monochromator (Rigaku, RINT2200). High-angle annular dark-field (HAADF) imaging was performed using a 200 kV scanning transmission electron microscope (STEM, JEOL, JEM-ARM200F) equipped with a spherical aberration corrector. The convergence semi-angle of the electron probe was 24 mrad, and the collection semi-angle of the HAADF detector was in the range of 90–370 mrad. Magnetic susceptibility and magnetization were measured by a superconducting quantum interference device (SQUID) magnetometer (Quantum Design, MPMS-XL) in the temperature range from 2 K to 300 K and in external dc fields up to 50 kOe.

3. Results and discussion
In our investigation, both 1/1 and 2/1 approximants were found to form a single phase in the Ga\textsubscript{57.5-x}Pd\textsubscript{28+x}Tb\textsubscript{14.5} alloy systems depending on the composition and annealing temperature: x = 3 to 7.5 annealed at 1073 K for the 1/1 approximant and x = 7–7.5 annealed at 973 K for the 2/1 approximant. For the alloys with x = 7–7.5, phase transformations between the 1/1 and 2/1 approximants were observed during annealing. Figure 1(a) shows the XRD patterns for x = 7.3, namely the Ga\textsubscript{50.2}Pd\textsubscript{35.3}Tb\textsubscript{14.5} alloy. The 2/1 approximant formed in the alloy when annealed at 973 K for 100 h, whereas the 1/1 approximant formed through annealing at 1073 K for 100 h. Furthermore, the 1/1 approximant transformed into the 2/1 approximant through re-annealing at 973 K. The reversible phase transformation from the 1/1 to 2/1 approximant indicated that the 2/1 approximant was thermodynamically stable at low temperatures. The lattice parameters for the 1/1 and 2/1 approximants were estimated to be a\textsubscript{1/1} = 1.427 nm and a\textsubscript{2/1} = 2.313 nm, respectively, satisfying the condition a\textsubscript{2/1}/a\textsubscript{1/1} \sim \tau (\tau: golden mean). Figure 1(b) shows atomic-resolution HAADF images for the 1/1 and 2/1 approximants viewed along the [001] direction; both phases consist of Tsai-type clusters, where the Tb atoms are arranged at the vertices of an icosahedron in the Tsai-type clusters.

![Figure 1](image.png)

Figure 1. (a) XRD patterns for the Ga\textsubscript{50.2}Pd\textsubscript{35.3}Tb\textsubscript{14.5} alloys annealed at various temperatures. (b) HAADF images for the 1/1 and 2/1 approximants. (c) Schematics of icosahedral Tb clusters in the 1/1 and 2/1 approximants.
Figure 2 shows the temperature dependences of magnetic susceptibility for the 2/1 and 1/1 approximants in a dc field of 100 Oe. The magnetic susceptibility above 50 K for both 2/1 and 1/1 approximants obeys the Curie–Weiss law, from which the effective magnetic moment, $\mu_{\text{eff}}$, and paramagnetic Curie temperature, $\Theta_p$, were estimated and are listed in Table 1. For both approximants, the obtained $\mu_{\text{eff}}$ values are comparable to the theoretical value of a Tb$^{3+}$ free ion, i.e., 9.72 $\mu_B$, indicating well-localized Tb$^{3+}$ magnetic moments at the vertices of the icosahedral clusters. The negative $\Theta_p$ values indicate that antiferromagnetic interactions are dominant between the magnetic moments in the approximants. The absolute value of $\Theta_p$ for the 1/1 approximants is twice that for the 2/1 approximants.

In contrast to the similarity in their magnetism above 50 K, the two approximants showed different magnetic behaviors in terms of their low-temperature susceptibility, as can be seen in the insets of figure 2. For the 2/1 approximant, both the field-cooled (FC) and zero-field-cooled (ZFC) susceptibilities show an anomaly associated with the magnetic transition with a sharp cusp at $T_N \sim 5.8$ K, and the FC and ZFC curves show no apparent difference, indicating the occurrence of antiferromagnetic ordering below $T_N$. On the other hand, for the 1/1 approximant, spin-glass-like freezing characterized by bifurcation of the FC and ZFC curves was observed below the freezing temperature, $T_f \sim 3$ K; this may be attributed to the relatively large frustration in the 1/1 approximant. The ratio of $|\Theta_p|/|T_f|$ = 7.2 is comparable to that for other spin-glass-like 1/1 approximants [3, 6].

![Figure 2](image-url) Temperature dependence of magnetic susceptibility for the 2/1 (a) and 1/1 approximants (b). Insets show magnetic susceptibility in the low-temperature region.

| Phase          | $\mu_{\text{eff}}$ ($\mu_B$) | $\Theta_p$ (K) | $T^*$ (K) |
|----------------|-------------------------------|----------------|-----------|
| 2/1 approximant| 9.62                          | -9.55          | 5.81      |
| 1/1 approximant| 9.98                          | -21.8          | 3.02      |

Figure 3 shows magnetization as a function of the applied magnetic field for the 2/1 approximant. An anomaly associated with the metamagnetic transition at 7.5 kOe was observed in the magnetization curve obtained at 2 K, which also supports antiferromagnetism in the 2/1 approximant. Magnetization increases on increasing the applied field and reaches $\sim 4 \mu_B$ per Tb$^{3+}$ ion, approximately one-third the $\mu_{\text{eff}}$ at 50 kOe. This is due to the magnetic anisotropy of the Tb$^{3+}$ ion, and a similar behavior was observed in the antiferromagnetic 1/1 approximant Au$_{72}$Al$_{14}$Tb$_{14}$ [6].

In general, as the order of the approximant increases, the unit-cell size of the approximant increases and the structure becomes close to a quasicrystal. Thus, the magnetic structure of 2/1 approximants is
expected to be more complicated than that of 1/1 approximants, although the detailed magnetic structure of the 2/1 approximant was not clarified in this study. Further experiments such as neutron diffraction measurements are in progress. Our present results will lead to further discovery of magnetic 2/1 approximants, which is an important step toward understanding magnetism in quasicrystals. The search for a series of magnetic 2/1 approximants is also underway.

**Figure 3.** Magnetic field dependence of magnetization for the 2/1 approximant.

4. Conclusions
We found a Tsai-type 2/1 approximant in the Ga$_{57.5-x}$Pd$_{28+x}$Tb$_{14.5}$ ($x$ = 7–7.5) alloy system annealed at 973 K. The 2/1 approximant transformed into the 1/1 approximant through annealing at 1073 K. For the 2/1 approximant, a sharp cusp was observed at 5.8 K in both FC and ZFC susceptibilities, indicating antiferromagnetic ordering below 5.8 K. Furthermore, metamagnetic transition was observed in the magnetization measurements. On the other hand, magnetic susceptibility measurements for the 1/1 approximant showed that bifurcation of the FC and ZFC curves occurred below $T_f$ ~ 3 K, suggesting spin-glass-like freezing.

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