$Sc_{12}Zn_{88}$ or $Sc_{15}Zn_{85}$: structure and stability of the icosahedral phase and its 1/1 approximant from atomistic simulations

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Atomistic simulations using semi-empirical oscillating pair potentials (EOPP) [1] fitted to ab-initio data, and direct ab-initio calculations at the density-functional theory level of accuracy reveal insights into the phase diagram of the binary Sc-Zn system near the composition of the quasicrystal phase $Sc_{12}Zn_{88}$ [2]. At zero temperature the Tsai cluster splits into three variants: with Zn_4 (tetrahedron), Zn_3 (triangle) or Sc atom encapsulated within Zn_{20} dodecahedron shell. At elevated temperatures, the Zn_3+Zn_{20} variant often flips into Zn_4+Zn_{19} configuration, and the Zn-filled variants are favored by entropy. Canonical cell tiling (CCT) geometry [3] describes appropriately low-temperature icosahedral packings of the Tsai clusters, with monoclinic 1/1 approximant and (hypothetical) 2/1 approximant stable, and (hypothetical) 3/2-2/1-2/1 approximant containing all kinds of canonical cells unstable by just 1.6 meV/atom. We then compared finite temperature stability for two compositions of interest - $Sc_{12}Zn_{88}$ and $Sc_{15}Zn_{85}$ and for approximants up to 3/2 size. At ~85% of Zn, the 3/2 approximant is unstable by +5.0 meV/atom against the 1/1. At 88% Zn, the 3/2 approximant remains unstable by +5 meV/atom, but the 1/1 becomes even less stable at +6.5 meV/atom. At the same time, the vibrational entropy favors $Sc_{12}Zn_{88}$ composition by almost 10 meV/atom near 800K, due to the large vibrational entropic contribution from Zn atom substituting at the larger Sc atom site. Consequently, at elevated temperatures and higher Zn content, the 1/1 approximant looses its stability against large 3/2 approximant, and the Zn-richer composition is stabilized by vibrational entropy against the standard 85% Zn composition.

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