Structural phase transitions of Cd-based icosahedral quasicrystals and their crystalline approximants

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Icosahedral quasicrystals and their approximants are complex structure solids, which consist of icosahedral symmetric clusters. In particular, an occurrence of a unique structural phase transition related with the structure of the cluster, was discovered at ~100 K for a series of Cd₆M (M = Ca, Yb, Y) approximants [1,2], which are cubic approximants to binary Cd-based quasicrystals. The Cd based quasicrystals and their approximants are made of Tsai-type icosahedral cluster [3, 4] (Fig. 1). The Tsai-type icosahedral cluster is composed of four successive shells, which are, from the centre, a Cd₄ tetrahedron, a Cd₂₀ dodecahedron, an M₁₂ icosahedron and a Cd₃₀ icosidodecahedron. For most Cd₆M, the Cd₄ tetrahedron at the centre is positionally disordered, and the structure is an a×a×a lattice with space group Im 3 at room temperature. For Cd₆Ca, the superstructure of the low temperature phase is found to be a √2a×a×√2a C-centred monoclinic lattice by electron diffraction experiments. Then, the phase transition has been interpreted as involving orientational ordering of the Cd₄ tetrahedron which is disordered at room temperature. Similar phase transitions have also been observed in the Cd₆Eu, Cd₆Ce and Zn₆Sc approximant [5, 6], all of which consist of the same Tsai-type icosahedral cluster crystallizing with the same bcc lattice above Tc. Thus, we expected that an order-disorder transition occurs commonly over all the Cd-based quasicrystals and approximants composed of the Tsai-type icosahedral clusters. In the present work, we have investigated whether the phase transition occurs in Cd₆M approximants and Cd₅.7Yb quasicrystals by TEM study.

In the cases of Cd₆M (M = Pr, Nd, Sm, Gd and Tb), we have observed superlattice reflections at 20 K in the selected area electron diffraction patterns; the patterns for Cd₆Dy are shown in Fig. 2. The superlattice reflections are explained by a √2a×a×√2a C-centred monoclinic lattice with space group C2/c or Cc as the case of Cd₆Ca. It suggests that the C-monoclinic superlattice structures are commonly formed for Cd₆M (M = Ca, Y, Pr, Nd, Sm, Gd and Tb). In contrast, for Cd₆Ho, Cd₆Er, Cd₆Tm and Cd₆Lu, which have small atomic radii of M elements, no superlattice reflection has been observed down to 20 K. The results indicated that the Cd₄ tetrahedron at the centre of the icosahedral cluster remains disordered down to 20 K [7]. The origin of the different behavior can be attributed to the difference in the atomic radii of M elements, which indicates that the space inside the M₁₂ icosahedron plays a dominant role in the ordered phase formation.

References
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FIG. 1. Schematic illustration of a Tsai-type icosahedral cluster.

FIG. 2. SAED patterns of Cd$_6$Dy along (a)[100]$_L$, (b) [010]$_L$, (c) [001]$_L$ and (d)[110]$_L$ at 20 K.