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 Cd_6M (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 Cd_4 tetrahedron, a Cd_{20} dodecahedron, an M_{12} icosahedron and a Cd_{30} icosidodecahedron. For most Cd_6M, the Cd_4 tetrahedron at the centre is positionally disordered, and the structure is an $a \times a \times a$ lattice with space group $Im\bar{3}$ at room temperature. For Cd_6Ca, the superstructure of the low temperature phase is found to be a $\sqrt{2}a \times a \times \sqrt{2}a$ *C*-centred monoclinic lattice by electron diffraction experiments. Then, the phase transition has been interpreted as involving orientational ordering of the Cd_4 tetrahedron which is disordered at room temperature. Similar phase transitions have also been observed in the Cd_6Eu, Cd_6Ce and Zn_6Sc approximant [5, 6], all of which consist of the same Tsai-type icosahedral cluster crystallizing with the same *bcc* lattice above T_c. 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 Cd_6M approximants and $Cd_{5.7}Yb$ quasicrystals by TEM study.

In the cases of Cd_6M (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 Cd_6Dy are shown in Fig. 2. The superlattice reflections are explained by a $\sqrt{2}a \times a \times \sqrt{2}a$ *C*-centred monoclinic lattice with space group *C*2/*c* or *Cc* as the case of Cd_6Ca. It suggests that the *C*-monoclinic superlattice structures are commonly formed for Cd_6M (*M* = Ca, Y, Pr, Nd, Sm, Gd and Tb). In contrast, for Cd_6Ho, Cd_6Er, Cd_6Tm and Cd_6Lu, which have small atomic radii of *M* elements, no superlattice reflection has been observed down to 20 K. The results indicated that the Cd_4 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 M_{12} icosahedron plays a dominant role in the ordered phase formation.

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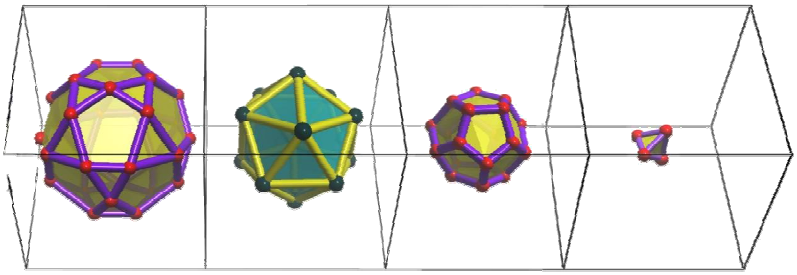

FIG. 1. Schematic illustration of a Tsai-type icosahedral cluster.

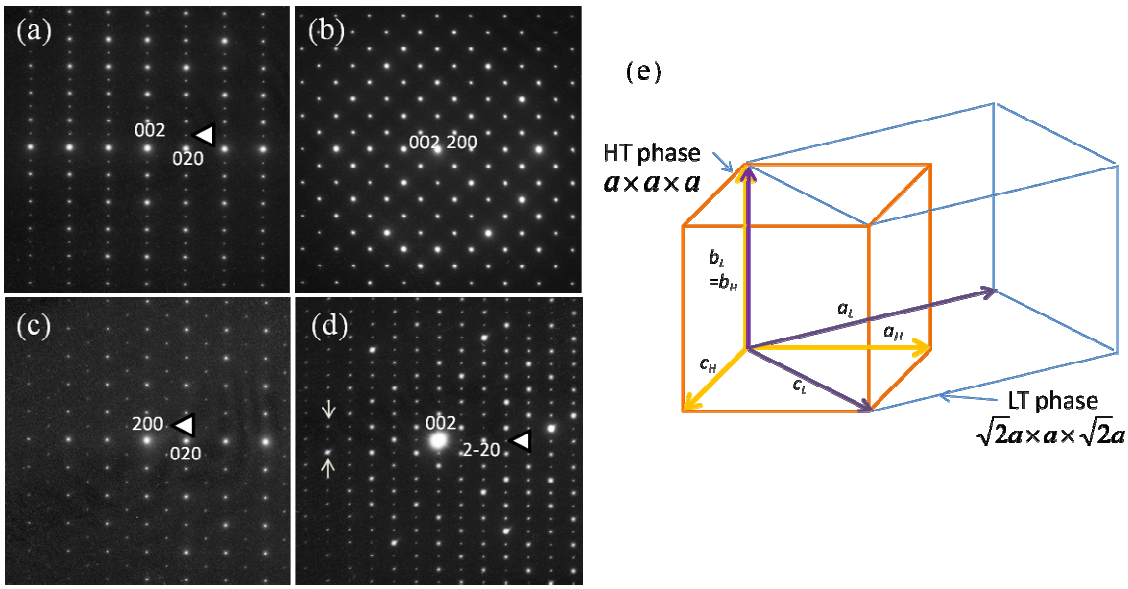

FIG. 2. SAED patterns of Cd_6Dy along (a)$[100]_L$, (b) $[010]_L$, (c) $[001]_L$ and (d)$[110]_L$ at 20 K.