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In situ transmission electron microscopy observation of an orientational order-disorder transition in Cd_6Eu and Cd_6Ce crystalline approximants

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In situ transmission electron microscopy observations of Cd_6Eu and Cd_6Ce crystals show that the crystals undergo a structural phase transition from a face-centered cubic or a primitive cubic lattice to a body-centered cubic lattice at high temperatures, respectively. The phase transitions are found to be of an order-disorder type with respect to the orientation of the tetrahedron at the center of the icosahedral cluster.

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I. INTRODUCTION

Cd_6M (M=Ca, rare earths) crystalline approximants are *bcc* cubic crystals (space group $Im\bar{3}$) composed of Tsai-type icosahedral clusters, which are regarded as the building blocks of stable binary quasicrystals $Cd_{5.7}Yb$ and $Cd_{5.7}Ca$, discovered in 2000 by Tsai *et al.*[1,2] A Tsai-type cluster is composed of four successive shells as schematically illustrated in Fig. 1: the first is a dodecahedron composed of 20 Cd atoms; the second is an icosahedron of 12 M atoms; the third is an icosidodecahedron of 30 Cd atoms; and the outermost shell is a defect rhombic triacontahedron of 60 Cd atoms. An interesting structural feature common to Cd_6M approximants is the existence of positional disorder at the center of the cluster at room temperature. It has generally been accepted that four Cd atoms reside at the center of the cluster, which presumably form an orientationally disordered tetrahedron.[3–5] With respect to disordering nature of the tetrahedron, Gómez *et al.*[6,7] observed through single-crystal x-ray diffraction experiments that positional disorder varies with the element M and can be modeled by two sets of disorders: type-1 disorder is associated with a 90° rotation of the tetrahedron around a twofold axis and type-2 disorder is associated with a triple split of the vertex positions of the tetrahedron.

In 2001, superlattice reflections were observed in the electron-diffraction patterns of Cd_6Yb and Cd_6Ca approximants below 110 K and 100 K, respectively.[8,9] Subsequent studies revealed that the Cd_6Ca approximant undergoes a phase transition to a $\sqrt{2}a\times a\times\sqrt{2}a$ C-centered monoclinic lattice with space group $C2/c$ below 100 K.[10] The phase transition has been interpreted as involving orientational ordering of the Cd tetrahedron, which is disordered at room temperature. Similar phase transitions have been observed in other Cd_6M approximants[11,12] as well as in the Zn_6Sc approximant,[13] all of which possess a *bcc* lattice ($Im\bar{3}$) at room temperature. For the latter, Ishimasa *et al.*[14] observed electron-diffraction patterns similar to those of the Cd_6Ca approximant at a low temperature. They proposed a structural model of the low-temperature phase based on the interpretation that the superlattice is formed by orientationally ordered Zn_4 tetrahedra at the center of the Tsai-type cluster. A fundamental issue that has emerged from the studies of these phase transitions is whether the superlattice is a consequence of the orientationally ordered tetrahedron. The above conjecture regarding the orientational order-disorder phase transition depends on the interpretation of the extinction rules derived from electron-diffraction experiments such as C center and c glide.

However, some problems exist concerning the interpretation of superlattice reflections. First, a superlattice can be formed not only by ordering of the structural entities but also by slight displacement of atomic positions, as often observed in ferroelectric transitions in which a purely orientational order-disorder phase transition is a rather rare case. Second, the existence of four atoms at the cluster center on their own does not have a sound experimental basis but needs justification because it is difficult to determine the precise number of atoms situated in the cluster center by x-ray diffraction. In order to obtain unambiguous evidence of an orientational order-disorder phase transition of a tetrahedron, we focus in this paper on the high-temperature behavior of the tetrahedra of Cd_6Eu (Ref. 15) and Cd_6Ce (Ref. 16) approximants for a following reason. According to single-crystal x-ray structural analyses, they are the only two systems known to possess an orientationally ordered tetrahedron at the center of a Tsai-type cluster at room temperature, which is in striking contrast to other Cd_6M (M=Ca, Y, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu) approximants.[6,7] Therefore, these systems enable us to directly probe whether an orientational order-disoder transition occurs, if it exists, by high-temperature transmission electron microscopy (TEM) observations.

The Cd_6Eu crystal is composed of two types of icosahedral clusters, one containing an orientationally ordered tetrahedron and the other containing a disordered tetrahedron, resulting in a $2a\times 2a\times 2a$ F-type superlattice with space group $Fd\bar{3}$ and periodicity $a=31.8718$ Å.[15] The Cd_6Ce crystal has a primitive cubic lattice with space group $Pn\bar{3}$ and periodicity $a=15.8082$ Å,[16] similar to other Cd_6M systems.

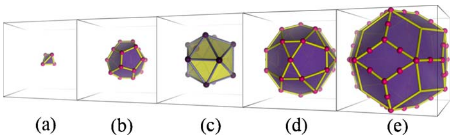

FIG. 1. (Color online) Tsai-type icosahedral cluster composed of, from center, (a) a Cd_4 tetrahedron, (b) a Cd_{20} dodecahedron, (c) an M_{12} icosahedron, (d) a Cd_{30} icosidodecahedron, and (e) a Cd_{60} defect triacontahedron.

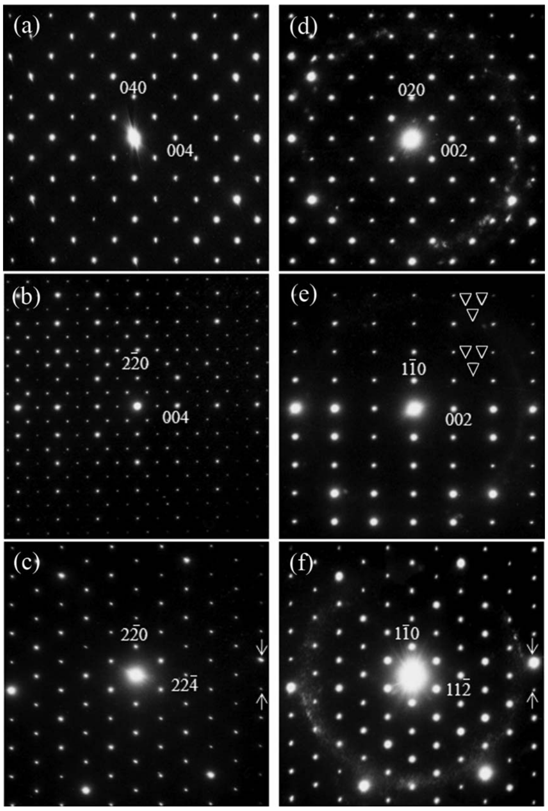

FIG. 2. Selected area electron-diffraction patterns of Cd$_6$Eu along (a) [100], (b) [110], and (c) [111] at room temperature, and along (d) [100], (e) [110], and (f) [111] at $\sim$570 K. All reflections at room temperature satisfy the reflection condition of the reported space group $Fd\bar{3}$ (Ref. 15). Open triangles indicate the positions of reflections that disappear above Tc. The reflections at $\sim$570 K are indexed as a cubic unit cell of half-lattice parameters ($a\times a\times a$ lattice) and satisfy the reflection condition of a *bcc* lattice ($hkl;h+k+l=2n$).

The orientation of the tetrahedron at the body center is related to that at the vertex by a mirror symmetry.

II. EXPERIMENTAL

Alloys of nominal compositions, Cd$_6$Eu and Cd$_6$Ce, were prepared by melting Cd and Eu/Ce metals at 1000 K for 72 h in an alumina crucible sealed in a quartz tube, followed by water quenching and annealing at 770 K for 100 h to obtain a homogeneous single phase. TEM observations were performed from room temperature to 770 K using a JEM-2010F TEM (JEOL) operating at 200 kV with a heating double-tilt specimen holder (EM-31050; JEOL). Variations in the selected area electron-diffraction pattern were investigated *in situ* during heating and cooling cycles. Schematic illustrations of structures were visualized using the programs VESTA 2.0.1.[17]

III. RESULTS

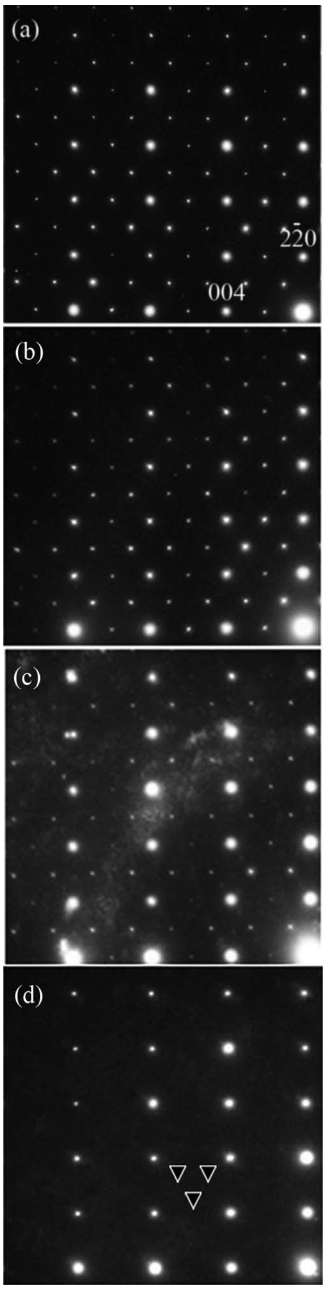

FIG. 3. Selected area electron-diffraction patterns of Cd$_6$Eu along [110] at (a) 300 K, (b) 470 K, (c) 500 K, and (d) 510 K. Open triangles indicate the positions of reflections that disappear above T_c.

Figures 2(a)–2(c) show electron-diffraction patterns of Cd$_6$Eu at room temperature along the [100], [110], and [111] zone axes, respectively. All reflections satisfy the condition h,k,l=*all even or all odd*, clearly indicating an F-type lattice. In addition, reflections such as 024, 020, and 002, which are allowed reflections in an F-type lattice, are absent in the patterns along (a) [100]. This observation is consistent with the existence of d glide ($hk0$:$h+k=4n$, $0kl$:$k+l=4n$, and $h0l$:$h+l=4n$). These reflection conditions indicate that the space group is either $Fd\bar{3}$ or $Fd\bar{3}m$. In addition, there exists no mirror symmetry perpendicular to $[1\bar{1}0]$ axis in the intensity distribution as indicated by arrows in Fig. 2(c), from which we conclude that the Laue group and space group of

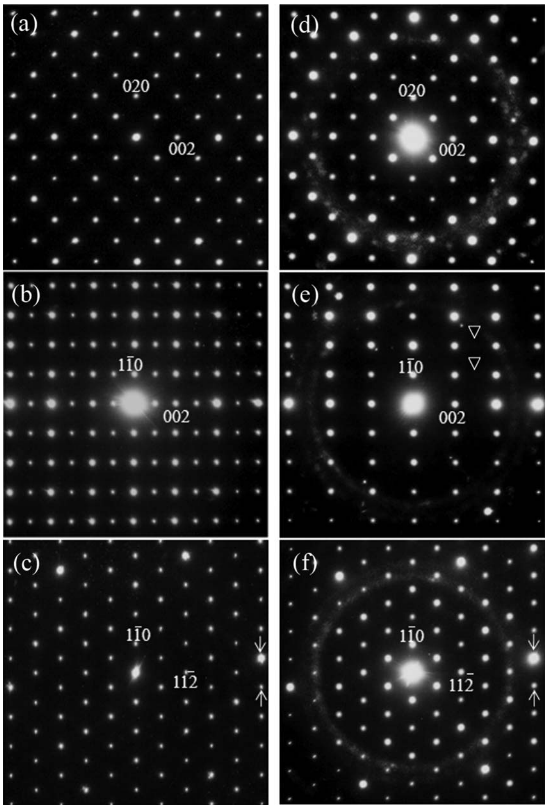

FIG. 4. Selected area electron-diffraction patterns of Cd_6Ce along (a) [100], (b) [110], and (c) [111] at room temperature, and along (d) [100], (e) [110], and (f) [111] at ~470 K. At room temperature, the reflections satisfy the reflection condition of the reported space group $Pn\bar{3}$ (Ref. 16). Open triangles indicate the positions of reflections that disappear above T_c. At ~470 K, the reflections satisfy the condition of a *bcc* lattice $(hkl;h+k+l=2n)$.

the room-temperature phase are $m\bar{3}$ and $Fd\bar{3}$, respectively. Therefore, the room-temperature phase of Cd_6Eu is consistent with the reported space group $(Fd\bar{3})$ obtained by x-ray structural analysis.[15]

Figures 2(d)–2(f) show electron-diffraction patterns of Cd_6Eu at ~570 K along the [100], [110], and [111] zone axes, respectively. Figure 3 shows electron-diffraction patterns along [110] with heating from 300 to 510 K. Some reflections [denoted by open triangles in Figs. 2(e) and 3(d)] disappear at ~570 K. The reflections continue to disappear and reappear with repeated heating and cooling across ~500 K, indicating that a structural phase transition occurs reversibly at ~500 K. Because the reflections of the high-temperature phase satisfy the condition $h,k,l=$*all even*, the high-temperature phase is explained by a cubic unit cell of half-lattice parameters, i.e., an $a\times a\times a$ lattice. The high-temperature phase reflection satisfies the condition $hkl:h+k+l=2n$, indicating that the phase has a *bcc* lattice. Thus, our *in situ* observations show that the room-temperature $2a\times 2a\times 2a$ *fcc* lattice undergoes a phase transition to an $a\times a\times a$ *bcc* lattice at ~500 K.[18]

Similarly, Fig. 4 shows electron-diffraction patterns of Cd_6Ce along the (a), (d) [100]; (b), (e) [110]; and (c), (f) [111] zone axes at room temperature and ~470 K, respectively. In Figs. 4(a)–4(c), there is no extinction for general *hkl* reflections, indicating a primitive lattice at room temperature. For special reflections, the absence of reflections such as 001 and 010 [Fig. 4(a)] is noticed, which is attributed to the existence of *n* glide $(0kl:k+l=2n,\ h0l:h+l=2n$, and $hk0:h+k=2n)$. These reflection conditions indicate that the space group is either $Pn\bar{3}$ or $Pn\bar{3}m$. In addition, as seen in Fig. 4(c), there is no mirror symmetry perpendicular to $[1\bar{1}0]$ axis in the intensity distribution as indicated by arrow. From these observations, we conclude that the Laue group and space group of the room-temperature phase are $m\bar{3}$ and $Pn\bar{3}$, respectively, which is consistent with the reported space group $(Pn\bar{3})$.[16] Figure 5 shows electron-diffraction patterns

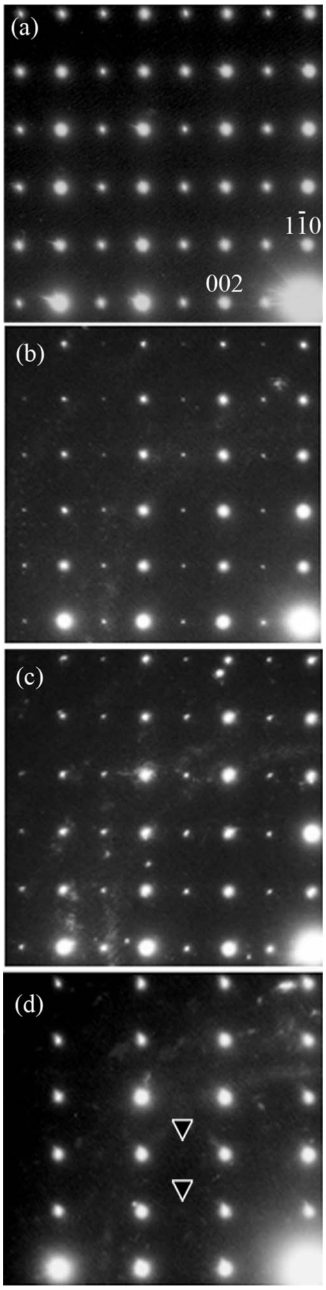

FIG. 5. Selected area electron-diffraction patterns of Cd_6Ce along [110] at (a) 300 K, (b) 430 K, (c) 460 K, and (d) 470 K.

along [110] with heating from 300 to 470 K As in the case of Cd_6Eu, some reflections (denoted by open triangles) appear at low temperatures and disappear at high temperatures. In Fig. 5, the reflections continue to disappear and appear with repeated heating and cooling across ~460 K, indicating that a structural phase transition occurs reversibly at ~460 K. The high-temperature phase reflection satisfies the condition $hkl{:}h+k+l=even$, indicating that the phase has a *bcc* lattice.[18] Thus, our *in situ* observations show that the room-temperature primitive cubic phase undergoes a phase transition to a *bcc* phase at ~460 K.

IV. DISCUSSION

Figures 6(a) and 6(b) show schematic high- and low-temperature models of Cd_6Eu and Cd_6Ce, respectively. The light (yellow online) icosahedral clusters contain an orientationally ordered tetrahedron and the dark (blue online) icosahedral ones contain an orientationally disordered tetrahedron. For Cd_6Eu, both disordered and ordered clusters coexist at room temperature, forming a $2a \times 2a \times 2a$ F-type lattice. The occurrence of a *bcc* structure above T_c means that all the clusters become crystallographically equivalent above T_c. Since there are two types of clusters in Cd_6Eu, i.e., ordered and disordered ones, it directly leads to a fact that both clusters become either disordered or ordered above T_c. (We note that the two clusters cannot become crystallographically equivalent by any structural distortion.) In both cases, the occurrence of the *bcc* lattice above T_c means that an orientational order-disorder transition occurs at the center of the cluster. Being based on these experimental evidences, we are led to a conclusion that the ordered clusters become disordered above T_c since the high-temperature phase must have higher entropy than the low-temperature phase in order for a structural phase transition to occur. In contrast, for Cd_6Ce, the room-temperature phase has a primitive lattice because the tetrahedra at the vertex and at the body-centered positions of the cubic lattice are oriented differently. The occurrence of a *bcc* lattice at high temperatures means that the clusters at the vertex and at the body-centered positions become identical above T_c. This situation is also explained by orientational disordering of the tetrahedron inside both icosahedral clusters.

V. CONCLUSION

In conclusion, we have experimentally verified by *in situ* TEM that a structural phase transition occurs in Cd_6Eu and Cd_6Ce approximants which are composed of icosahedral clusters. We have also shown that the phase transition is not due to a structural distortion but is of an order-disorder type, i.e., the high-temperature phase is entropically stabilized with respect to the orientation of the tetrahedra.

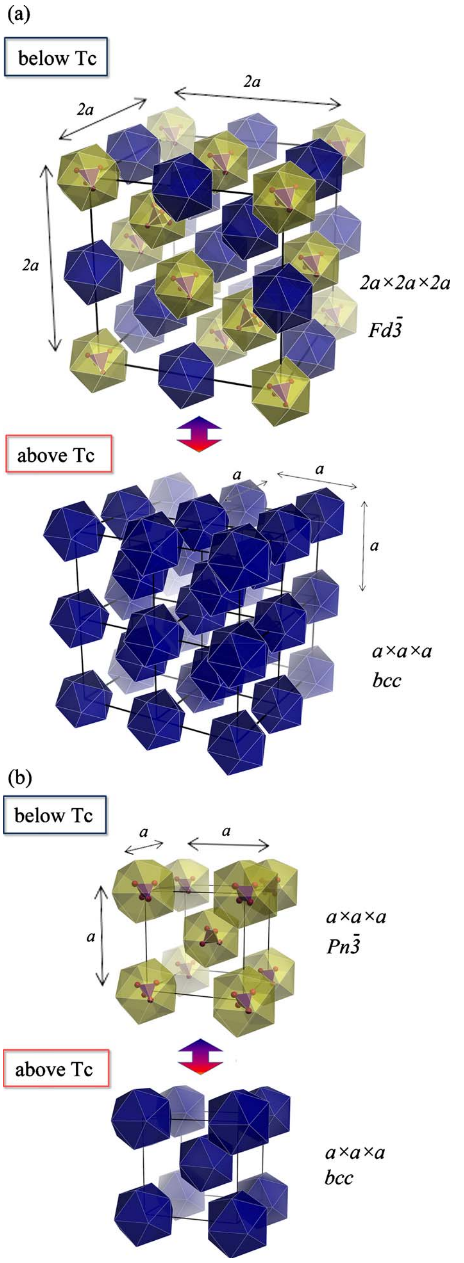

FIG. 6. (Color online) Schematic illustrations of the high- and low-temperature structures of (a) Cd_6Eu and (b) Cd_6Ce. Dark (blue online) icosahedral clusters contain an orientationally disordered Cd tetrahedron and light (yellow online) icosahedral clusters contain an orientationally ordered Cd tetrahedron.

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[18] The intensity distribution of the patterns along the [100] axis [Figs. 2(d) and 4(d)] is not of fourfold symmetry but of twofold symmetry. Also, there is no mirror perpendicular to $[1\bar{1}0]$ axis in the patterns along [111] axis [Figs. 2(f) and 4(f)]. These observations lead to the Laue group 23 or $m\bar{3}$ and space group $I23$ or $Im\bar{3}$, respectively, for the high-temperature phases.