Structural stability of an icosahedral Cd-Yb quasicrystal and its crystalline approximant under high pressure

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Abstract. Synchrotron x-ray powder diffraction studies on an icosahedral Cd-Yb quasicrystal (iCd-Yb), its crystalline approximant of Cd6Yb (cCd-Yb) and the related Cd5Eu4 (cCd-Eu) material were performed under pressures of up to about 40 GPa at room temperature. The icosahedral lattice of the atomic cluster in iCd-Yb and the bcc lattices in cCd-Yb and cCd-Eu were found to be stable under pressure. Although the Tsai-type atomic cluster can possibly be distorted in various ways, low-symmetry distortion modes do not seem to develop even at high pressure. It is considered that the cluster structure of centrosymmetric dense atomic packing prevented low-symmetry distortions and consequently provided the cluster lattice stability. The bulk moduli were also determined to be $B_0$(iCd-Yb) = 49.2(3) GPa, $B_0$(cCd-Yb) = 46.1(7) GPa and $B_0$(cCd-Eu) = 49.6(3) GPa, which were much lower than the typical reported values for other quasicrystalline alloys.

1. Introduction

An icosahedral quasicrystal of Cd5.7Yb (iCd-Yb) and its crystalline approximant of Cd6Yb (cCd-Yb) consist of the same Tsai-type atomic cluster with icosahedral quasi-periodic stacking and periodic bcc packing, respectively [Fig. 1] [1, 2]. While the Cd4 tetrahedron in the most inner part of the cluster is orientationally disordered at ambient condition [2], our previous single crystal x-ray diffraction study in a $P$-$T$ span of up to 5.2 GPa and down to 10K revealed that the Cd4 tetrahedra in cCd-Yb exhibit various types of pressure- and temperature-sensitive orientational ordering [3]. No phase transition was observed for iCd-Yb, however, the Cd4 tetrahedra are thought to have short-range orientational order which varies with pressure and temperature [4].

Depending on the ordering structure, the orientational ordering induces a distortion of the icosahedral symmetric outer shells theoretically and experimentally [5, 6]. Nevertheless, the bcc lattice of the cluster in cCd-Yb is virtually maintained. The fact indicates that the outer shells undergo a high-symmetry distortion, resulting in an isotropic contraction of the cluster lattice.

There is, however, a possibility that a lower-symmetry distortion develops in the higher pressure region, such as a uniaxial distortion of the outer shells that can deform the cluster lattice. Actually, the cCd-Yb cubic lattice was most deformed at the highest pressure in a previous study, although the
deformation ratio is still small at about 0.5%. Consequently, further compression is expected to induce a transformation to a new phase with obvious lattice deformation. Such expectation of a structural transition also arises for \( i\text{Cd-Yb} \) with icosahedral cluster lattice, even though in general quasicrystals show remarkable structural stability to compression [7]. Thus, we have examined the structural stability of the cluster lattice in both \( i\text{Cd-Yb} \) and \( c\text{Cd-Yb} \) up to approximately 40 GPa by x-ray powder diffraction measurements. A related material \( \text{Cd}_{25}\text{Eu}_4 \) \( (c\text{Cd-Eu}) \) [8] was also investigated to determine the general trends.

**Figure 1.** Successive shells of the Tsai-type atomic cluster in the \( \text{Cd}_{5.7}\text{Yb} \) icosahedral quasicrystal, its crystalline approximant of \( \text{Cd}_6\text{Yb} \) and \( \text{Cd}_{25}\text{Eu}_4 \): (a) \( \text{Cd}_4 \) tetrahedron, (b) \( \text{Cd}_{20} \) dodecahedron, (c) \( \text{Yb}_{12} \) icosahedron \( (\text{Eu}_{12} \) for \( \text{Cd}_{25}\text{Eu}_4) \), and (d) \( \text{Cd}_{30} \) icosidodecahedron.

**2. Experimental**

Synchrotron powder x-ray diffraction experiments on \( i\text{Cd-Yb} \), \( c\text{Cd-Yb} \) and \( c\text{Cd-Eu} \) were carried out to pressures of up to about 40 GPa at room temperature at SPring-8 (BL10XU), using a helium gas pressure medium in order to satisfy the hydrostatic condition [9]. Sample alloys were prepared from the nominal composition of the pure metals. Each alloy piece was formed into a foil about 10 \( \mu \text{m} \) thick and sealed in a diamond anvil cell (DAC) with the pressure medium. Sample pressure was determined by the ruby fluorescence method [10]. Powder diffraction patterns were taken on an imaging plate by using monochromatized 25 keV \( (0.0496 \text{ nm}) \) x-ray beam.

**3. Results and discussion**

Powder diffraction patterns of \( i\text{Cd-Yb} \), \( c\text{Cd-Yb} \) and \( c\text{Cd-Eu} \) at several pressures are shown in figure 2. Because of the good hydrostaticity and use of synchrotron radiation, the diffraction lines are much sharper than in the related study on an icosahedral \( \text{Cd-Ca} \) quasicrystal by Jiang J Z, et al [11]. No significant changes were observed, except for peak shifts due to the lattice contraction. Due to preferred orientation, superficial changes of the intensity ratio of several reflections appeared with increasing pressure. Superlattice reflections corresponding to the ordering of the \( \text{Cd}_4 \) tetrahedra were out of the detection limit. Figure 3 shows normalized \( d \)-values \( d/d_0 \) (where \( d_0 \) is \( d \)-value at ambient pressure) as a function of pressure. In addition to showing monotonic decrease, compression curves of several \( d/d_0 \)’s in \( i\text{Cd-Yb} \) are quite close to each other. The difference is less than 0.2 %, even at the highest pressure, which means no obvious deformation of the icosahedral lattice of the cluster was induced. As for \( c\text{Cd-Yb} \) and \( c\text{Cd-Eu} \), deformation of the \( \text{bcc} \) lattice of the cluster was not observed. With respect to \( c\text{Cd-Yb} \), the transition pressure to the orientational ordering phase at room temperature is estimated around 10 GPa from the phase diagram of our previous result [3]. The pressure range in this study have been much extended, however, the expected obvious lattice deformation did not occur.

Although a distortion of the outer shells of cluster that mediates the orientational correlation of the \( \text{Cd}_4 \) tetrahedra is thought to be enlarged by compression, we conclude that cluster lattices of these materials are stable even at pressures up to 40 GPa.

Bulk moduli of each material were derived by fitting a Birch-Murnaghan equation of state to the volume compression curves, \( B_0(i\text{Cd-Yb}) = 49.2(3) \text{ GPa}, B_0'(i\text{Cd-Yb}) = 5.4(1), B_0(c\text{Cd-Yb}) = 46.1(7) \text{ GPa}, B_0'(c\text{Cd-Yb}) = 5.2(1), B_0(c\text{Cd-Eu}) = 49.6(3), B_0'(c\text{Cd-Eu}) = 5.1(1) \) [Fig. 4]. These values are much lower than the previously reported typical ones beyond 100 GPa for quasicrystalline alloys [7], which is consistent with the report of the low Debye temperatures for the Cd-based quasicrystals and approximants [12].

The cluster lattice stability observed in each material indicates that the low-symmetry distortion of the cluster shells does not develop even at high pressures. Although the low-symmetry distortion of
Figure 2. Typical x-ray diffraction patterns of (a) Cd_{5.7}Yb icosahedral quasicrystal, (b) Cd_{6}Yb crystalline approximant and (c) Cd_{25}Eu_{4} as a function of pressure. Asterisks and closed circles denote the reflections from impurities and the rhenium gasket, respectively.

Figure 3. Normalized $d$-values for several isolated reflections of (a) Cd_{5.7}Yb icosahedral quasicrystal, (b) Cd_{6}Yb crystalline approximant and (c) Cd_{25}Eu_{4} as a function of pressure.

The cluster without lattice deformation is possible in a special case, it is not realistic that the atomic configuration keeps satisfying such condition for the wide pressure range. The distortion form should still be mainly tetrahedral, just as for lower pressures. It is considered that the absence of the low-

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symmetry modes can be attributed to the cluster structure of dense, centrosymmetric atomic packing. On the one hand, applying a low-symmetry distortion as a uniaxial or shear mode to the cluster, should induce symmetrically inequivalent, mismatched atomic motion, resulting in unrealistic cluster structure with considerable local energy differences. On the other hand, a high-symmetry distortion can be composed of equivalent atomic motions and can realize an energetically homogeneous, high-density structure. This is in contrast to the case of the closed packed layered structures. For example, a monatomic hcp structure can be transformed to an fcc one by a shear mode between layers, where each local atomic motion is equivalent. It should be noted that these considerations are not made from a continuum approximation, where the higher order modes in a spherical body have the higher energy.

These arguments also indicate that the above structural feature of the cluster is responsible for the stability of the cluster lattice, as observed for iCd-Yb, cCd-Yb and cCd-Eu. Generalizing, we can state that every known icosahedral quasicrystal consists of a cluster of centrosymmetric, densely packed atoms and consequently shows high structural stability under pressure.

In summary, the atomic cluster lattices in iCd-Yb, cCd-Yb and cCd-Eu were found to be stable under pressure of up to ~40 GPa. Even at high pressures, low-symmetry distortion modes did not develop. It is considered that the cluster structure of dense centrosymmetric atomic packing prevented low-symmetry distortions and consequently provided cluster lattice stability. The bulk moduli were also determined and were much lower than the previously reported values typical for quasicrystals.

Figure 4. Fit of a Birch-Murnaghan equation of state to the normalized volumes of Cd_{5.7}Yb icosahedral quasicrystal, Cd_{6}Yb crystalline approximant and Cd_{25}Eu₄.

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