Cd-Yb Alloy Rich in Order-disorder Transitions
– Clue to Understanding of Nature of Quasicrystalline Icosahedral Lattice –

Unlike ordinary metal crystals with translational periodic lattices, quasicrystals have icosahedral lattice components that pile up to form successively larger icosahedral units and eventually fill three-dimensional space without translational periodicity. The structural nature of quasicrystals has attracted considerable interest, particularly interest in the phase transition phenomena on the icosahedral quasi-periodic lattice. In contrast to the numerous reports on the structural phase transitions of metal crystals, very few studies have been reported on quasicrystals. The structural nature of quasicrystals is still unknown.

A Cd-Yb alloy is an advantageous system for studying order-disorder phase transition phenomena. $Cd_{5.7}Yb$ forms an icosahedral quasicrystal that consists of the icosahedral atomic clusters of four successive shells with an icosahedral quasiperiodic arrangement (Fig. 1(a)) [1]. The Cd_4 tetrahedral atomic unit in the innermost part of the cluster is orientationally disordered at ambient pressure and temperature [2]. Order-disorder transitions are hence expected to occur as a result of the pressure and/or temperature tuning of the orientational state of the Cd_4 tetrahedra.

When the atomic composition changes slightly to Cd_6Yb, Cd-Yb alloy forms a crystalline approximant of the quasicrystal [1]. The approximant consists of the same atomic clusters as the quasicrystal but they pack in a body-centered cubic (bcc) configuration showing translational symmetry (Fig. 1(b)) [2]. The major relationships between the neighboring clusters in the quasicrystal appear again in the approximant. Because of these structural similarities, studying the approximant will provide a clue to help us understand the quasicrystal, which has more complex structure.

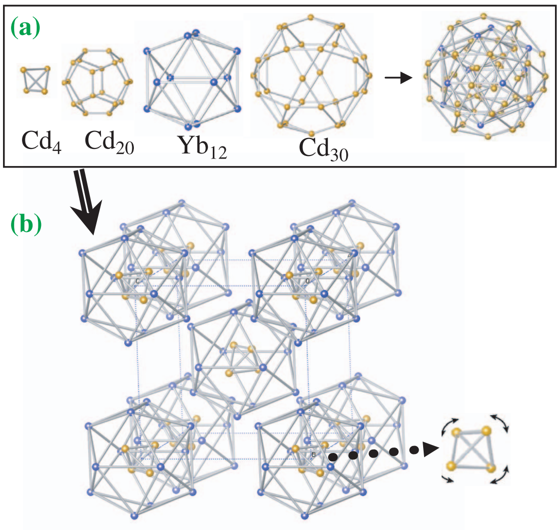

Fig. 1. Successive shells of the atomic cluster in Cd-Yb quasicrystal and its crystalline approximant **(a)**. The structure of the approximant (Cd_6Yb) is described as a bcc packing of the cluster **(b)**. The innermost shell of the Cd_4 tetrahedron is orientationally disordered at ambient pressure and temperature.

We investigated the structure of the Cd-Yb approximant under high pressure and low temperature, and revealed the rich behavior in order-disorder phase transitions [3]. The Cd_4 tetrahedra exhibit various types of orientational order that sensitively depend on pressure and temperature.

Single-crystal synchrotron X-ray diffraction experiments at pressures up to 5.2 GPa and temperatures down to 10 K were performed at beamline **BL22XU** [4]. Figure 2 shows oscillation photos acquired in isobar processes at ambient pressure, 2.7 GPa and 5.2 GPa. At room temperature, the crystal maintained a bcc structure with the orientational disorder of the Cd_4 tetrahedra continuing up to 5.2 GPa (Fig. 2(a)). However, a different behavior was observed for the bcc phase upon cooling at each pressure. At ambient pressure, superlattice spots due to the orientational order appear at 110 K (phase I) (Fig. 2(b)) as previously reported [5]. At 2.7 GPa, the bcc phase sequentially transforms into ordered phases II and III at 245 K and 135 K, respectively, as indicated by the superlattice series and the following additional weak ones (Figs. 2(c) and 2(d)). At 5.2 GPa, the bcc phase showed another sequential transition to phase IV at 225 K and to phase V at 145 K (Figs. 2(e) and 2(f)). The ordered structures of these phases differ from each other as shown by the superlattice patterns.

Figure 3(a) shows an outline of the phase diagram. Four ordered phases were newly found along with the known phase I. Besides the well-defined phases, slight modifications (III', IV') seem to appear. The main ordering structure of phases II and III are characterized by the <111> propagation direction of ordering, which is shown in Fig. 3(b), and that of phases I, IV, and V of the [110] propagation is shown in Fig. 3(c). The propagation direction mainly depends on pressure. It alternates from [110] to <111> at about 1.0 GPa and again to [110] in the range of 3.5-4.3 GPa. The two-step transitions of bcc-II-III and bcc-IV-V can be interpreted as the sequential ordering of the Cd_4 tetrahedron. Primary ordering is followed by fine ordering without alteration of the main ordering structure. The high degree of symmetry of the local structure of this material is considered to allow the Cd_4 tetrahedra to take various orientational states.

Information of an correlations between the neighboring Cd_4 tetrahedra was obtained from the analysis of the temperature variation of the superlattice intensity. Two types of interaction, namely, short- and long-range interactions exist, which are presumably attributed to the atomic packing effect and the electron-lattice interaction through itinerant electrons, respectively. In addition to the highly symmetric structure of this material, the coexistence of the two different types of interaction is considered to be responsible for the complicated phase behavior.

Since the Cd-Yb quasicrystal has a higher degree symmetry than the crystalline approximant and two different interactions exist in the quasicrystal as well, the present results lead to the expectation that there is richer behavior in the quasicrystal. In addition, we expect that further structural study of the Cd-Yb quasicrystal compared with the approximant at the corresponding *P*-*T* region will help us clarify the essential nature of the icosahedral quasiperiodic lattice.

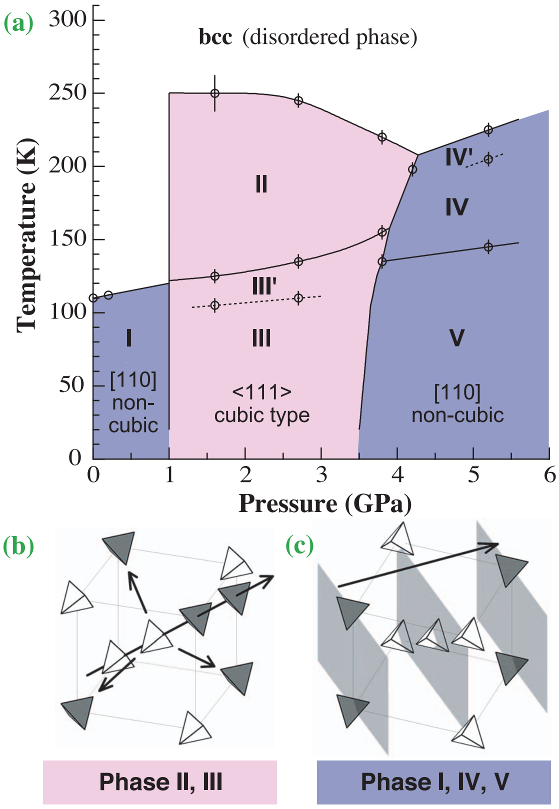

Fig. 3. Phase diagram outline of the Cd-Yb crystalline approximant **(a)**. Illustration of main ordering structure of the Cd_4 tedrahedra in phases II and III **(b)**, and in phases I, IV, and V **(c)**. The two orientations are represented by white and gray tetrahedra. Arrows represent the propagation direction of ordering along the <111> directions in **(b)** and the [110] direction in **(c)**.

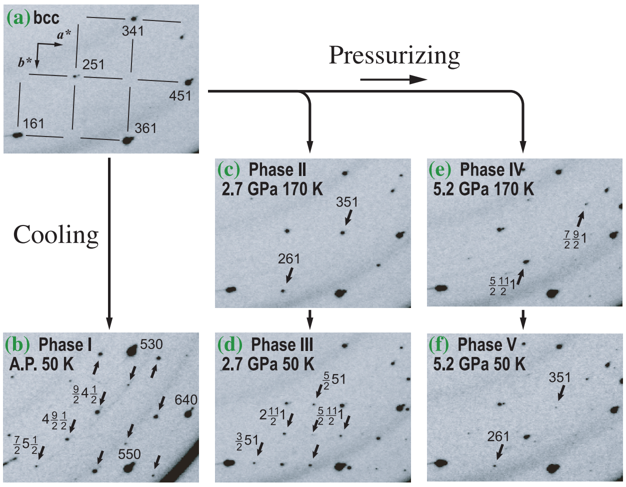

Fig. 2. X-ray oscillation photos of a Cd-Yb crystalline approximant at high pressure and low temperature. Arrows indicate representative superlattice spots that appear owing to the orientational ordering of the Cd_4 tetrahedra by cooling in the isobar process.

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References

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