Pressure-Induced Phase Transitions in the Cd-Yb Periodic Approximant to a Quasicrystal

Tetsu Watanuki,[1,*] Akihiko Machida,[1] Tomohiro Ikeda,[1] Katsutoshi Aoki,[1] Hiroshi Kaneko,[1] Takahisa Shobu,[1]
Taku J. Sato,[2] and An Pang Tsai[3,4]
[1]*Synchrotron Radiation Research Center, Japan Atomic Energy Agency, Mikazuki, Hyogo 679-5148, Japan*
[2]*Institute for Solid State Physics, University of Tokyo, Kashiwa, Chiba 277-8581, Japan*
[3]*Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai 980-8577, Japan*
[4]*SORST, Japan Science and Technology Agency, Kawaguchi, Saitama, 332-0012, Japan*
(Received 16 August 2005; published 16 March 2006)

The phase study of a Cd-Yb 1/1 approximant crystal over a wide pressure and temperature range is crucial for the comparison study between periodic and quasiperiodic crystals. The Cd_4 tetrahedra, the most inner part of the atomic clusters, exhibited various structural ordering in the orientation sensitive to pressure and temperature. Five ordered phases appeared in a P-T span up to 5.2 GPa and down to 10 K. The propagation direction of ordering alternated from $[110]$ to $\langle 111\rangle$ at about 1.0 GPa and again to $[110]$ at 3.5–4.3 GPa. The primarily ordered phases that appeared by cooling to 210–250 K between 1.0–5.2 GPa further transformed to finely ordered ones at 120–155 K. Besides the original short-range type interaction, a long-range type interaction was likely developed under pressure to lead to the primary ordering of Cd_4 tetrahedra. Coexistence of these interactions is responsible for the complicated phase behavior.

DOI: 10.1103/PhysRevLett.96.105702 PACS numbers: 64.60.−i, 07.35.+k, 61.10.Nz, 61.44.Br

Binary alloys of Cd-M ($M =$ Yb, Ca), which form both approximant crystals and quasicrystals [1,2], are ideal systems for the comparison study of the phase transition phenomena in periodic and quasiperiodic systems. Cd_6M having a bcc structure [3] is a 1/1 approximant to the icosahedral quasicrystal ($Cd_{5.7}M$). Both structures are described as a packing of the same atomic cluster with the different arrangement [4,5]. Such structural correspondence is very rare and has not been found for other alloys such as Al-Pd-Mn [6]. The atomic cluster contains four successive shells [Fig. 1] [4,5]. The feature is that the first inner shell of a Cd_4 tetrahedron has a lower symmetry than the outer shells of typical icosahedral symmetry and, consequently, gains the degree of freedom in the orientation. At room temperature, the Cd atoms of the first shell in the 1/1 approximant are broadly distributed around the eight vertices of cube due to the orientational disorder [4,7], and the first shell in the quasicrystal effectively takes the icosahedral symmetry [5]. The orientational order-disorder phase transition in both materials highlights the nature of periodic and quasiperiodic systems.

Tamura *et al.* have revealed that the 1/1 approximant undergoes an order-disorder type second order structural phase transition at low temperature (110 K for Cd_6Yb) by electron diffraction, electrical resistivity, and specific heat experiments [8,9]. Similar transitions have also been observed in the related materials, Cd_6Y [10], $Cd_{25}Eu_4$ [11], and $Cd_{37}Ce_6$ [12]. These results indicate that the orientational disorder is not static, but dynamical [8,9]. However, the mechanism of the correlation between the Cd tetrahedra is not comprehensible straightforwardly, since each Cd tetrahedron is surrounded by three outer shells and is separated from neighboring Cd tetrahedra [Fig. 1]. A similar correlation is expected for the Cd tetrahedra in the quasicrystal. No phase transition, however, has been observed [13,14].

High pressure experiments are promising for investigating the phase transition phenomena dominated by such an unknown correlation. In this Letter, various types of orientational order sensitive to pressure and temperature are exhibited for the Cd-Yb 1/1 approximant by high pressure and low temperature single crystal synchrotron x-ray diffraction study. It is also shown that coexistence of two different type interactions under pressure lead to the complicated ordering behavior.

A sample alloy with a nominal composition of Cd_6Yb was prepared from pure elements of Cd (99.99 wt %) and Yb (99.9 wt %). The mixed powder was melted in an Al_2O_3 crucible sealed with a quartz tube in an argon atmosphere and subsequently annealed at 673 K for 100 h. A single crystal sample was selected among the cracked pieces and sealed in a diamond anvil cell (DAC) with a pressure medium of methanol ethanol 4:1 mixture. Diffraction study

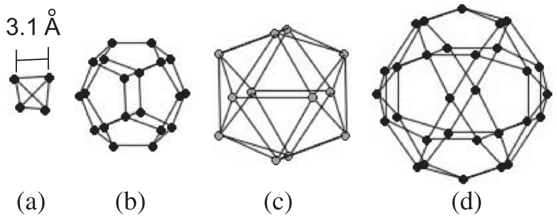

FIG. 1. Successive shells of the atomic cluster in Cd-Yb 1/1 approximant and quasicrystal: (a) Cd_4 tetrahedron, (b) Cd_{20} dodecahedron, (c) Yb_{12} icosahedron, and (d) Cd_{30} icosidodecahedron. The first shell Cd tetrahedron in the approximant bcc crystal ($a = 15.64$ Å, space group: $Im\bar{3}$ [3]) is separated by 13.54 Å from the neighboring tetrahedra and orientationally disordered at ambient temperature and pressure.

was performed at pressures up to 5.2 GPa and temperatures between 10–300 K in BL22XU at SPring-8 [15]. The DAC was mounted on a He closed cycle cryostat and oscillation photos were taken on an imaging plate by using a monochromatized x ray of 25 keV (0.4960 Å). In order to avoid a nonhydrostatic compression with a solidified alcohol mixture at low temperatures, the sample was pressurized at 300 K and cooled while maintaining a constant pressure within the deviation of 0.2 GPa. Oscillation photos were taken during temperature changes between 10–300 K at ambient pressure, 80–300 K at 0.2 GPa, 50–300 K at 1.6 GPa and 2.7 GPa, 80–300 K at 3.8 GPa, 50–300 K at 4.2 GPa and 5.2 GPa. The monitored reciprocal spaces were the $hk0$ and $hk1$ zones, the hhl and $(h+1)hl$ zones, and the three-dimensional space that contains these planes.

Figure 2 shows the oscillation photos of the $hk1$ zone taken at various pressures and temperatures. At room temperature, the crystal still took the bcc structure at a maximum pressure of 5.2 GPa [Fig. 2(a)]. On cooling the bcc phase at ambient pressure, superlattice spots due to structural order appeared at 110 K [phase I, Fig. 2(b) showing the $hk0$ and $hk\frac{1}{2}$ zones] as previously reported [8,9]. Slightly increasing the pressure to 0.2 GPa obtained a similar result at 112 K. On further compression at 300 K and successive cooling at 1.6 GPa, the bcc phase transformed to ordered phases II and III at 250 and 125 K, respectively. Their superlattice patterns [Figs. 2(c) and 2(d)] indicate that the new ordered phases are different from phase I and are closely related to each other. The II-III transition is described by the appearance of an additional weak superlattice series in the phase II pattern. Hence, phase III is interpreted as the highly ordered phase of phase II, and the main structural order of phase III is the same as phase II. At 5.2 GPa the bcc phase showed another sequential transition to ordered phases at 225 K (bcc-IV) and 145 K (IV-V) on cooling. The bcc-IV-V transition is also described by the successive appearance of a main superlattice series and an additional weak one [Figs. 2(e) and 2(f)]. Phase V is the highly ordered phase of phase IV, and the main structural order is the same as phase IV. These sequential transitions took place reversibly on heating within a monitoring step about 10 K.

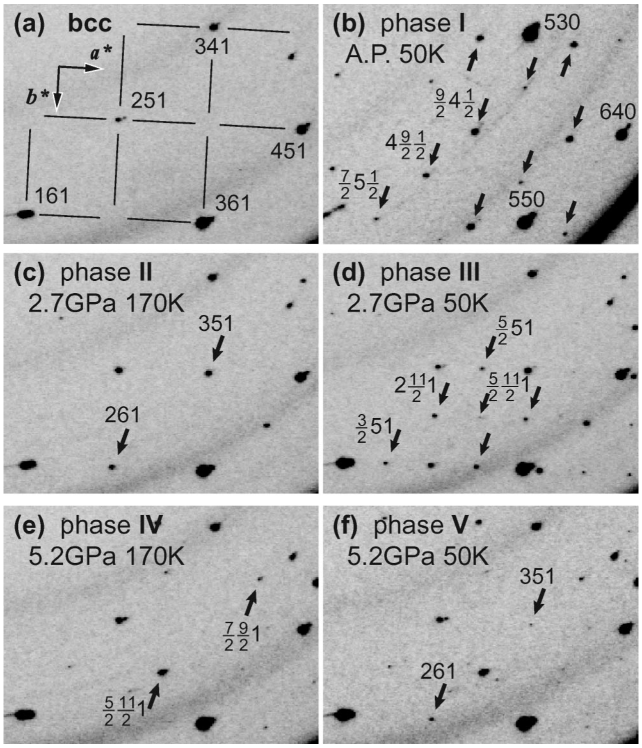

FIG. 2. X-ray oscillation photographs of Cd-Yb 1/1 approximant crystal measured for the bcc phase (a), phase I at ambient pressure and 50 K (b), phase II at 2.7 GPa and 170 K (c), phase III at 2.7 GPa and 50 K (d), phase IV at 5.2 GPa and 170 K (e), and phase V at 5.2 GPa and 50 K (f). Each photograph shows the reciprocal space around the $hk1$ zone for (a) and (c)–(f), and the $hk0$ and $hk\frac{1}{2}$ zones for (b). Arrows indicate representative superlattice spots that appear by cooling in the isobar process.

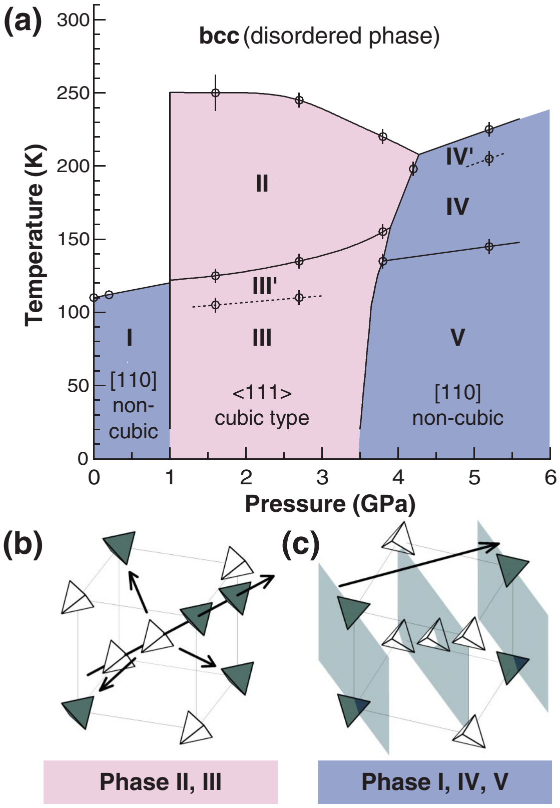

FIG. 3 (color). (a) Phase diagram outline of the Cd-Yb 1/1 approximant crystal. Besides the well-defined phases, slight modifications (III′, IV′) seem to appear. (b) Schematic drawing of the main ordering structure of the first shell Cd tetrahedra in phases II and III. Arrows represent the propagation direction of ordering along the ⟨111⟩ directions. The two orientations are represented by white and gray tetrahedra. (c) A plausible candidate [17] for the main ordering structure in phases I, IV, and V. Gray planes represent the same phase zone of structural modulation propagating along the [110] direction.

Figure 3(a) shows the outline of the phase diagram. Four ordered phases were found along with the known phase I. The ordered phases are classified into three groups from their main structural order; phase I, phases II and III, and phases IV and V. Two-step transitions occur under pressure above 1 GPa in the same group, which can be interpreted as the sequential ordering of the Cd tetrahedron. The Cd tetrahedron is primarily ordered, for instance, at the bcc-II transition where each tetrahedron vertex is roughly oriented to one of [±1 ±1 ±1] directions [Fig. 3(b)], but still has a precession motion around the oriented axis. Then the Cd tetrahedron is finely ordered at the II-III transition with freezing of the motion.

The main structural order of each group is characterized by its propagation direction of ordering that is coupled with the distortion of the cubic lattice. For phases II and III, the superlattice spots except the weak series are assigned by the index of hkl with $h + k + l =$ odd [Figs. 2(c) and 2(d)] or $\frac{h}{2}\frac{k}{2}\frac{l}{2}$ (not shown) based on the bcc lattice, indicating that the main structural order propagates in the direction of [111] [16]. Phase II maintains the cubic lattice, which means that the main ordering of this group propagates along all the equivalent directions of [±1 ±1 ±1] [Fig. 3(b)]. In phase III, the lattice distortion was detected as the slight split of the diffraction spots in the high-q region. However, it is very small within 0.1% induced by highly ordering. Hence, phase III can be categorized as the cubic group. For phase I and phases IV and V, the spots are indexed as $\frac{h}{2}\frac{k}{2}l$ or its equivalents, indicating the [110] propagation in the both groups. The propagation develops along a selected direction [Fig. 3(c)] [17], which causes the domain splitting (not shown) accompanied by the lattice distortion about 0.3% for phase I and 0.5% for phases IV and V. The propagation direction mainly depends on pressure [Fig. 3(a)]. It alternates from [110] to ⟨111⟩ at about 1.0 GPa and again to [110] at 3.5–4.3 GPa. Since the lattice contraction is only 3% at 5.2 GPa, it is concluded that the ordering type of the Cd tetrahedron is sensitive to the lattice contraction and these ordered states almost energetically degenerate each other.

The superlattice pattern of phase II provides the experimental evidence for the orientational order of the Cd tetrahedron. The index assignment and the additional rule of no spots in the $hk0$ zone and its equivalents uniquely lead to a $2a \times 2a \times 2a$ cubic lattice with a space group $Fd\bar{3}$. The space group requires the orientational order of a certain structural unit with tetrahedral symmetry and the Cd tetrahedron is the most likely candidate for it. Ordering of the outer shells can be ruled out. Spontaneous distortion from the icosahedral to tetrahedral shape is unrealistic, although it might show some distortion coupled with the orientational ordering of the Cd tetrahedron as theoretically predicted [18] and observed in the related materials [11,12]. The orientation of the Cd tetrahedron, determined from the space group, is either A (each of the four vertices roughly orient toward [111], $[1\bar{1}\bar{1}]$, $[\bar{1}1\bar{1}]$, and $[\bar{1}\bar{1}1]$ directions) or B (inversion of A), which is arranged in an AABBAABB... type quadruple array along the ⟨111⟩ directions [Fig. 3(b)].

Another classification of these transitions is introduced by focusing on the growth process of the superlattice spots. Figure 4 plots the superlattice intensity as a function of temperature. With respect to bcc-I, II-III, and IV-V transitions at temperatures of 110–155 K, each superlattice intensity rapidly rises in a narrow temperature span within 10 K below the transition temperature. In contrast, the superlattice spots that appear at bcc-II and bcc-IV transitions at temperatures of 210–250 K gradually increase over a wide temperature span. Thus, two types are found: the rapid growth type with the transition temperature of 110–155 K and the gradual growth type with the transition temperature of 210–250 K [19].

The appearance of the high transition temperature phases of II and IV is a remarkable phase behavior of this material. The transition temperature of 210–250 K approximately doubles from 110 K for phase I at ambient pressure, implying the presence of different type interaction in high pressure region above 1 GPa. This consideration is supported by the difference of the growth type of the superlattices that should reflect the nature of interactions between the Cd tetrahedra. Since the transition temperature is roughly proportional to the strength of the interaction, the interaction inducing lower temperature transitions (LT interaction) at 110–155 K gradually increase in strength by

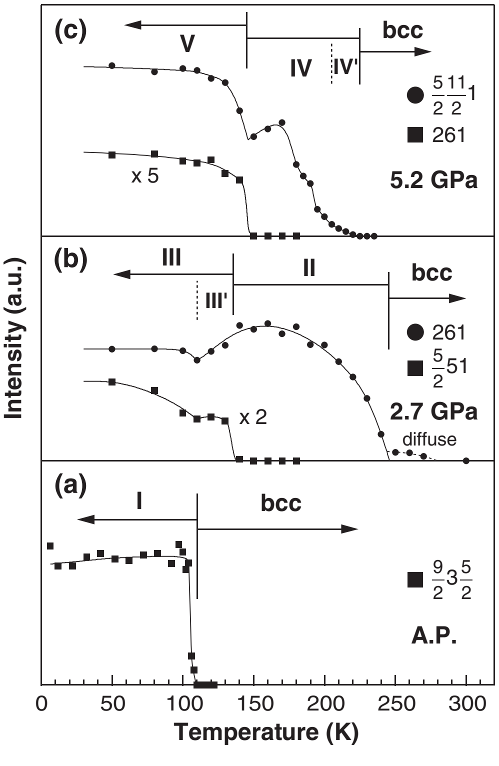

FIG. 4. Temperature dependence of the integrated intensity of superlattice spots on heating for phase I at ambient pressure (a), phases II and III at 2.7 GPa (b), and phases IV and V at 5.2 GPa (c).

compression. In contrast, the interaction inducing higher temperature transitions (HT interaction) shows singular behavior by lattice contraction. At ambient pressure it has no strength, however, develops abruptly above 1 GPa. Coexistence of the different type interactions, especially the singularity of the HT interaction, causes the complicated ordering behavior.

The bcc-I transition is known as a second order one [8,9] and also the bcc-II, IV transitions are considered to be second order ones because of the continuous growth of the superlattices. Adopting a second order transition theory, the HT interaction is considered to be a long-range type one compared with the LT interaction. The gradual growth of the superlattices with temperature suggests that the ordered state contains structural fluctuations over a wide temperature span. Long-range interactions are insensitive to structural fluctuations and hence allow the structural fluctuations for a wide temperature span [20]. By contrast, the LT interaction can be attributed to a short-range type one from the narrow temperature spans observed for the LT phase transitions. The long-range type interaction in phase II is also inferred from the quadruple arrangement of the Cd tetrahedra [Fig. 3(b)] that cannot be generated solely by the interaction between the nearest neighbors. A certain interaction that reaches the second nearest or further sites [21] should be required.

The short-range type interaction can be ascribed to the atomic packing effect. This consideration is supported by the analysis of the ordered structure in the related materials [11]. The vertices of the tetrahedron push out the outer shell atoms and consequently induce the strain of outer shells coupled with the orientation of the neighboring tetrahedra. However, this contact type effect cannot cause the long-range type interaction. Although the atomic cluster touches the second nearest neighbors [21], the contact area is much smaller than that with the nearest neighbors and the effect should be weak, which is contradictory to the high transition temperature of phase II and IV. The contribution of another effect in phase II is also indicated from the volume expansion during bcc-II transition. The fact is demonstrated by the negative slope of the phase boundary and cannot be explained by the packing effect. The long-range type interaction might arise from the electronic structure effect around Fermi edge. The electrons near Fermi edge can originate the long-range interaction because they will be delocalized further than the nearest neighbor sites. It is also considered that the unusual structure around Fermi edge due to the pseudogap formation [22] should be much affected by lattice contraction and consequently can cause the singular behavior as seen in the HT interaction.

In summary, the first shell Cd tetrahedra in a Cd-Yb $1/1$ approximant crystal exhibit various types of orientational order sensitive to pressure and temperature. Five ordered phases appeared in a P-T span up to 5.2 GPa and down to 10 K. The propagation direction of ordering alternates by pressure from $[110]$ to $\langle 111\rangle$ and again to $[110]$. In the latter two cases under pressure, two-step ordering occurs by temperature variation. In addition to the original short-range type interaction, a long-range type interaction is likely developed under pressure. Coexistence of them is responsible for the complicated phase behavior. A similar effect is expected for the quasicrystal under pressure.

We thank Dr. H. Takakura, Dr. K. Nozawa, Dr. K. Ohwada, Dr. N. Hamaya, and Dr. O. Shimomura for their fruitful discussions. This work was partially supported by a Grant-in-aid for Scientific Research (14740218, 17740238) from the Japan Society for Promotion of Science.

---

*Electronic address: wata@spring8.or.jp

[1] A. P. Tsai *et al.*, Nature (London) **408**, 537 (2000).
[2] J. Q. Guo, E. Abe, and A. P. Tsai, Phys. Rev. B **62**, R14 605 (2000).
[3] A. Palenzona, J. Less-Common Met. **25**, 367 (1971).
[4] H. Takakura, J. Q. Guo, and A. P. Tsai, Philos. Mag. Lett. **81**, 411 (2001).
[5] H. Takakura, A. Yamamoto, M. de Boissieu, and A. P. Tsai, Ferroelectrics **305**, 209 (2004).
[6] The atomic cluster of the Al-Pd-Mn quasicrystal is considered to have a different structure from the approximant crystals, because the cluster structures of the approximants vary with the degree of the approximation.
[7] C. P. Gómez and S. Lidin, Phys. Rev. B **68**, 024203 (2003).
[8] R. Tamura *et al.*, Jpn. J. Appl. Phys. **41**, L524 (2002).
[9] R. Tamura *et al.*, J. Non-Cryst. Solids **334–335**, 173 (2004).
[10] R. Tamura *et al.*, Phys. Rev. B **68**, 174105 (2003).
[11] C. P. Gómez and S. Lidin, Chem. Eur. J. **10**, 3279 (2004).
[12] M. Armbrüster and S. Lidin, J. Alloys Compd. **307**, 141 (2000).
[13] R. Tamura *et al.*, Jpn. J. Appl. Phys. **40**, L912 (2001).
[14] R. Tamura *et al.*, Mater. Sci. Eng. A **375–377**, 1002 (2004).
[15] T. Watanuki *et al.* (unpublished).
[16] Superlattice spots reflect the structural modulation, and the wave vector of the modulation corresponds to the propagation direction of the ordering.
[17] The indexing rule of superlattice spots in phases I, IV, and V indicate that these phases have orthorhombic or lower symmetry. The model structure for the highest symmetry (space group of $Ccce$) among the ones allowed are schematically shown in Fig. 3(c), which is considered to represent the character of their main structural order.
[18] K. Nozawa and Y. Ishii, Mater. Res. Soc. Symp. Proc. **805**, 47 (2004).
[19] Analysis based on the reduced temperature provides the same classification.
[20] W. Gebhardt and U. Krey, *Phasenübergänge und kritische Phänomene* (Vieweg, Wiesbaden, 1980), Chap. 3.
[21] With respect to the body center site in the bcc lattice, the corner site is the nearest neighbor one and the body center site of the next cell is the second nearest one.
[22] R. Tamura *et al.*, Phys. Rev. Lett. **92**, 146402 (2004).