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Intermediate-valence quasicrystal of a Cd-Yb alloy under pressure

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A quasiperiodic intermediate-valence system was prepared by applying pressure to an icosahedral Cd-Yb quasicrystal. In this system, each quasiperiodic lattice point has a charge degree of freedom. Yb L_{III} x-ray absorption spectroscopy experiments demonstrate that the Yb valence increases continuously upon compression from a divalent state at ambient pressure and reaches 2.33 at 31.7 GPa. A comparison study to the crystalline approximant suggests that the quasiperiodically arranged Yb ions have a homogeneous intermediate valence that takes a valence fluctuation state under pressure.

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Quasiperiodic systems possessing charge, spin, or other degrees of freedom at each quasiperiodic lattice point are expected to exhibit novel physical properties because their arrangements have inflation symmetry with self-similarity instead of ordinal translational symmetry. Quasiperiodically arranged spin systems have been realized in quasicrystalline alloys with magnetic elements.[1] For example, an icosahedral Zn-Mg-Ho quasicrystal has displayed unique phenomena, including a spin glass state with the development of quasi-five-dimensional spin correlations[2] and a temperature-independent magnetic excitation related to anomalous spin fluctuations.[3] Additionally, quasicrystals consisting of atomic clusters with orientational degrees of freedom have been synthesized; a decagonal Al-Co-Ni quasicrystal exhibits a quasiperiodic superstructure in the orientationally ordered phase.[4]

A quasiperiodic system with a charge degree of freedom as an intermediate-valence (IV) quasicrystalline compound has received attention because IV rare-earth crystalline compounds show diverse behaviors such as valence fluctuations, charge ordering, heavy-fermion behavior, and complex magnetic ordering. Furthermore, a quasicrystalline IV system should display additional novel phenomena but IV quasicrystals have yet to be realized. Although rare-earth-based quasicrystals have been systematically synthesized,[1] the rare-earth ions did not assume the IV state, but an integer valence.[5–7]

We sought to synthesize a quasiperiodic IV system by applying pressure to Yb-based quasicrystalline compounds. Typically in Yb-based crystalline compounds, divalent Yb shifts toward trivalent Yb under pressure because trivalent Yb has a smaller ionic radius.[8,9] This behavior should be applicable to quasicrystalline compounds. This study focuses on the icosahedral quasicrystal of $\mathrm{Cd}_{5.7}\mathrm{Yb}$(*i*Cd-Yb).[10] Unlike other ternary quasicrystals, Yb ions in this binary stoichiometric compound form a quasiperiodic atomic arrangement without disorder. In addition, the atomic position has been determined by x-ray diffraction structural analysis.[11] Both of these features are advantageous for investigating an unknown Yb valence state under pressure.

In this paper, we demonstrate a quasiperiodic IV system using x-ray absorption near edge structure (XANES) experiments on *i*Cd-Yb under pressure. Additionally, the valence fluctuation state of Yb in *i*Cd-Yb is suggested in the pressure range of this study.

A sample alloy with a nominal composition of $\mathrm{Cd}_{5.7}\mathrm{Yb}$ was prepared from pure elements of Cd (99.99 wt %) and Yb (99.9 wt %). The mixed powder was melted in an $\mathrm{Al}_2\mathrm{O}_3$ crucible sealed with a quartz tube in an argon atmosphere and subsequently annealed at 673 K for 100 h. A cracked piece measuring $70\times70\ \mu\mathrm{m}^2\times20\ \mu\mathrm{m}$ thick was sealed in a diamond anvil cell (DAC) with a pressure medium of Fluorinert FC70/77 1:1 mixture and a ruby-chip pressure marker. Yb L_{III}-edge XANES experiments were performed under pressure up to 31.7 GPa at room temperature in BL22XU at SPring-8. This method allows the Yb valence to be directly determined even under pressure.[8,9] The transmission XANES spectra were acquired by scanning the incident x-ray energy between 8.77–9.11 keV using two ionization chambers filled with N_2 gas to monitor the incident and transmitted x-ray intensities. The $30\times30\ \mu\mathrm{m}^2$ incident beam was exposed to the sample with a homogenous thickness utilizing the precise alignment system of the diffractometer for DAC in BL22XU.[12]

Figure 1 shows the normalized XANES spectra of *i*Cd-Yb at select pressures. At ambient pressure, a single absorption peak at 8.938 keV was observed, indicating the Yb ion is in the divalent form. This observation is similar to other reports using magnetization measurements[6] and Mössbauer studies.[7] However, as the pressure increased, the divalent peak decreased, and the trivalent component appeared at 8.945 keV. These findings indicate that the Yb valence shifts toward the trivalent one upon compression and an IV state is realized in a quasiperiodic system.

It should be noted that two types of valence states, which correspond to the two-component spectra, are possible: (1) the quantum superposition of divalent ($4f^{14}$) and trivalent ($4f^{13}$) at each site[8] and (2) a charge-disproportionated case such as a mixture of divalent and trivalent ions. The intensity ratio of the two components indicates (1) the quantum mixing ratio or (2) in a simple case, the population ratio of the ions. Regardless of the case, the intensity ratio can be used to determine the mean valence ($\bar{\nu}$) as $\bar{\nu}=2+I_{\mathrm{tri.}}/(I_{\mathrm{div.}}+I_{\mathrm{tri.}})$.

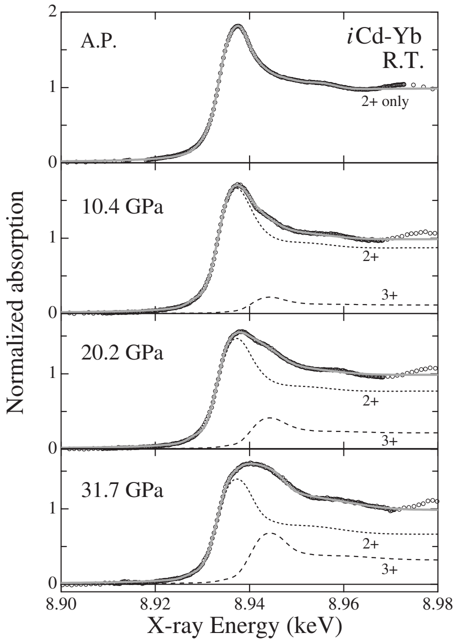

FIG. 1. Normalized Yb L_{III} XANES spectra of icosahedral Cd-Yb quasicrystal (*i*Cd-Yb) at select pressures (open circles). Background absorption is removed via Victoreen's formula adjusted to the lower energy data between 8.77–8.90 keV (not shown). Then normalization is applied so that the higher energy data up to 9.11 keV asymptotically approaches a unit. Each spectrum is fitted by the sum (gray line) of the divalent (dotted line) and trivalent (dashed line) components.

Below we discuss the character of the valence state under pressure.

The mean valence at each pressure was determined using a procedure similar to other reports.[9] Here, the divalent component $S_{\text{div.}}(E)$ was expressed as a combination of an asymmetric Gaussian and an arctangent function. The function parameters were tuned to reproduce the spectrum profile at ambient pressure. For the trivalent component, the same function with an energy shift was applied; $S_{\text{tri.}}(E)=S_{\text{div.}}(E-\Delta)$, $\Delta=7.1$ eV. Each spectrum was fitted by the sum of these two components, $(1-x)S_{\text{div.}}(E)+xS_{\text{tri.}}(E)$, and the mean valence value was obtained as $\bar{\nu}=x+2$. Figure 1 shows the fits.

Figure 2 shows the pressure dependence of the mean valence. The valence shifted upon applying pressure and increased nearly linearly until a value of 2.33 was realized at 31.7 GPa, which is the highest pressure employed in this study. This indicates that one-third of the divalent component is replaced by the trivalent component. These changes were reversible in the decompression process.

Next we considered the character of the observed IV state with an emphasis on whether every Yb site has a homogeneous mean valence or charge disproportionation, i.e., do site differences exist? The former case corresponds to a valence fluctuation state of the Yb sites whereas the latter is a quasiperiodic charge order or a charge glass. Here, we investigated mainly the following two points (1) the influence of differences in the Yb site environments, which may cause various Yb valences and (2) the electron correlation effects of Yb $4f$ system, which can induce a spontaneous charge disproportionation by stabilizing the localized $4f$ holes even when there is not a difference between the Yb-site environments.

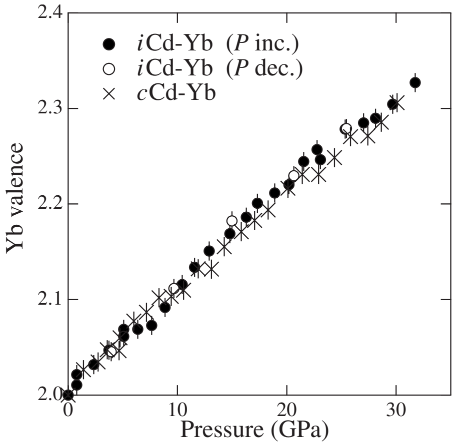

FIG. 2. Pressure dependence of Yb valence in an icosahedral Cd-Yb quasicrystal (*i*Cd-Yb) with compression (closed circles) and decompression (open circles) processes. Results of the crystalline approximant Cd_6Yb(*c*Cd-Yb) are also shown (crosses).

First, we examined the influence of differences in the Yb-site environments because *i*Cd-Yb contains structurally inequivalent Yb sites. Two types of Yb sites exist with different local structures[11] and all sites are crystallographically inequivalent due to quasiperiodicity. Because the valence is sensitive to the local structure, we initially investigated whether the valence differs between these two types of sites. One site is located in the Tsai-type atomic cluster (site *A*) where 12 positions exist in the cluster to form an icosahedron. The other site is in the gaps of the cluster packing (site *B*). Two positions exist in the gap filling unit of a 6Cd acute rhombohedron.[11] The population ratio of sites A:B in *i*Cd-Yb is 69:31.[13]

To evaluate the valences at sites *A* and *B* under pressure, it is helpful to compare *i*Cd-Yb to its 1/1 crystalline approximant of Cd_6Yb(*c*Cd-Yb) because *c*Cd-Yb forms a pure site-*A* system.[11] Although *c*Cd-Yb consists of the same atomic cluster as *i*Cd-Yb, it has a different arrangement. The structure of *c*Cd-Yb has bcc packing of the cluster where all the Yb sites are crystallographically equivalent with the same local structure as site *A* in *i*Cd-Yb. Additionally, we measured the Yb valence of *c*Cd-Yb in the same process, except the pressure medium was a methanol-ethanol mixture. Figure 3 shows the XANES spectra of *c*Cd-Yb under pressure. Each profile was similar to that of *i*Cd-Yb at the adjacent pressure. The pressure dependence of the mean valence was identical to the *i*Cd-Yb case (Fig. 2), indicating the population weighted average of the mean valence at site *A* ($\bar{\nu}_{\text{A}}^{\text{QC}}$) and *B* ($\bar{\nu}_{\text{B}}^{\text{QC}}$) in *i*Cd-Yb is equal to the mean valence of site *A* in *c*Cd-Yb($\bar{\nu}_{\text{A}}^{\text{App.}}$) at each pressure. Hence

$$0.69\bar{\nu}_{\text{A}}^{\text{QC}}(P)+0.31\bar{\nu}_{\text{B}}^{\text{QC}}(P)\simeq\bar{\nu}_{\text{A}}^{\text{App.}}(P). \tag{1}$$

The formula gives $\bar{\nu}_{\text{A}}^{\text{QC}}(P)\simeq\bar{\nu}_{\text{B}}^{\text{QC}}(P)$ on the appropriate assumption of $\bar{\nu}_{\text{A}}^{\text{QC}}(P)\simeq\bar{\nu}_{\text{A}}^{\text{App.}}(P)$. This means that the influence

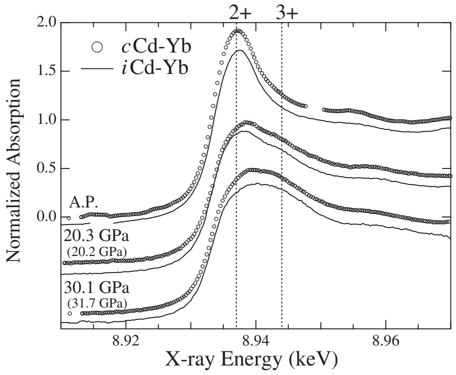

FIG. 3. Typical XANES spectra of the crystalline approximant Cd_6Yb (*c*Cd-Yb, open circles). Spectra of the icosehedral Cd-Yb quasicrystal (*i*Cd-Yb, line) at the adjacent pressure (parenthesized value) are shown as references.

of the local structural difference between sites *A* and *B* is negligible relative to the observed valence change upon compression. Consequently, the structural inequivalency due to quasiperiodicity should not be a factor.

Hence, *i*Cd-Yb is considered a quasiperiodically arranged system of Yb sites with practically identical environments. At ambient pressure, consistent data has been reported using a photoemission spectroscopy (PES) experiment.[14] The Yb $4f$ PES spectrum of *i*Cd-Yb has almost the same profile as *c*Cd-Yb, implying that the Yb $4f$ states at sites *A* and *B* are quite similar. At a given pressure, same local pressure should be applied at the two types of sites because *i*Cd-Yb has a densely packed, homogeneous structure with metallic bonding.[11] Eventually, both sites should become indistinguishable if pressure remains.

Next, electron correlation effects of Yb $4f$ system were investigated. The observed Yb valence increase corresponds to the creation of $4f$ holes due to the relationship of $\nu = n_h + 2$ (n_h: $4f$ hole number per Yb site). With respect to IV Yb-based compounds, the electronic state can be characterized by n_h because the effect of the hole-hole repulsive interaction increases with the hole density. In fact the plot of the electronic specific-heat coefficient (γ), which indicates the degree of hole-hole correlation, versus the hole density n_h for Yb compounds shows a positively correlated trend.[15] In the lower hole density region of $n_h \lesssim 0.7$ ($\nu \lesssim 2.7$), γ is still suppressed within $\sim 10^2$ mJ/(mol K^2). In this weak correlation region, the $4f$ system is situated in a valence fluctuation regime and the $4f$ holes move itinerantly. In contrast, in the higher hole density region near the trivalent state, $n_h \gtrsim 0.7 (\nu \gtrsim 2.7)$, γ exceeds $\sim 10^2$ mJ/(mol K^2), i.e., the ratio of the effective mass to a free electron $m^*/m_0 > \sim 10^2$ where the strongly correlated $4f$ holes should be treated as heavy fermions. In this region, $4f$ holes tend to be localized and spontaneous charge separation may occur. Herein the criterion value of 0.7 contains an ambiguity of 0.1–0.2, depending on the case. A similar classification has also been employed in Ref. 8. Because the present case with a maximum valence of 2.33 is assigned to the lower hole density region, *i*Cd-Yb is judged to be in a valence fluctuation state in the pressure region of this study.

Thus, every Yb site is considered to have a homogeneous mean valence that assumes a valence fluctuation state under pressure. Another case of charge separation would be the random distribution of divalent and trivalent sites caused by an entropic effect but this is unrealistic because this implies that one site becomes trivalent at the beginning of compression while another site turns to trivalent at the maximum pressure. This means there is a large local pressure difference over 30 GPa. However, such a difference cannot be balanced with the entropic gain at 300 K. The homogeneous valence picture is consistent with a monotonic linear valence change upon compression. It is also in agreement with our structural study on *i*Cd-Yb. The powder x-ray diffraction experiments up to 40 GPa have shown a monotonic volume compression behavior and the structural stability under pressure.[16] Although all the above investigations support the homogeneous valence rather than distinct charge separation, the possibility of a slight deviation at each site from the mean valence value remains.

The continuous valence increase upon compression is interpreted as follows. According to the impurity Anderson model, the Yb $4f$ level should be broadened slightly due to the conduction (c)-f electron hybridization. Actually, a theoretical calculation on this material indicates that the $4f$ level has an energy width of about 1 eV.[17] The $4f$ level gradually rises upon compression because the initial $4f^{14}$ state with a large ionic radius becomes less stable under pressure. Then the slightly broadened $4f$ level partially exceeds the Fermi level, which generates $4f$ holes. As the $4f$ level shifts gradually, n_h increases, indicating a continuous valence increase. Here, the $4f$ state can be described as a quantum superposition of the $4f^{14}$ and $4f^{13}$ state, $a|4f^{14}\rangle + b|4f^{13}\rangle$, and the increase in the valence upon compression is interpreted as an increase in the b/a ratio. In our study, the valence changed from the initial divalent state just at the beginning of compression, suggesting that the $4f$ state is located just below the Fermi level at ambient pressure. This is consistent with a theoretical study.[17] Upon applying pressure, the electrons squeezed out of the $4f$ state should be transferred to the conduction electron state, that is, mainly the $5p$ band of the Cd ions that surround the Yb sites.[17]

Future studies of quasiperiodic IV systems should investigate the physical properties of *i*Cd-Yb with scanning n_h or strength of hole-hole correlation by compression and compare the results to the periodic IV system of *c*Cd-Yb. Further compression should shift *i*Cd-Yb into a heavy-fermion system. In this region ($\nu \gtrsim 2.7$), a valence transition with charge disproportionation accompanied by a changing $4f$-hole character may occur due to the conversion from a delocalized state to a localized one. Additionally, the magnetic properties at low temperature should be interesting because the localized $4f$ hole or the $4f^{13}$ state possesses a localized magnetic moment. Another attractive topic for this system is the coupling of charge and the orientational degrees of freedom. Specifically, the Cd_4 tetrahedron in the Tsai-type atomic cluster in *i*Cd-Yb possesses an orientational degree of freedom. As for *c*Cd-Yb, various types of orientationally ordered phases have been observed at low temperature in the experimental pressure range of 0–5 GPa.[18] Coupling these two degrees of freedom should lead to new ordered states in *i*Cd-Yb.

In summary, a quasiperiodic IV system has been demonstrated by applying pressure to *i*Cd-Yb. The Yb L_{III}-edge XANES experiments demonstrate that the Yb valence increases continuously upon compression from the divalent state at ambient pressure to reach a valence of 2.33 at 31.7 GPa, indicating that one-third of the divalent component is replaced by the trivalent one. A comparison study on the crystalline approximant suggests that the quasiperiodically arranged Yb ions have a homogeneous intermediate valence, which assumes a valence fluctuation state under pressure. Moreover, further compression is expected to shift *i*Cd-Yb into a heavy-fermion system.

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