Comparative studies of positron annihilation lifetime and coincident Doppler broadening spectra for a binary Cd-based quasicrystal and 1/1-approximant crystal

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We performed the positron annihilation lifetime and coincident Doppler broadening measurements for binary icosahedral quasicrystal $Cd_{5.7}Ca$ and its 1/1-cubic Cd_6Ca and Cd_6Yb approximants. Since the obtained positron lifetimes are quite similar to one another, it is likely that the same type of structural vacancies exists in quasicrystal $Cd_{5.7}Ca$ and 1/1-cubic Cd_6Ca and Cd_6Yb approximants. The vacancy-type defects are concluded to be surrounded mostly by Cd atoms in both quasicrystal $Cd_{5.7}Ca$ and its 1/1-cubic approximant Cd_6Ca from the high-momentum Doppler broadening spectra. In addition, we studied the temperature dependence of the positron annihilation lifetime in the low temperature region from 10 to 300 K for 1/1-cubic approximant Cd_6Ca and Cd_6Yb crystals. As a whole, in both 1/1-cubic Cd_6Ca and Cd_6Yb approximants the positron lifetime τ_1 gradually increases with increasing temperature due to isotropic thermal expansion. However, the positron lifetime τ_1 does not change at the order-disorder transition temperature, namely, 100 and 110 K for 1/1-cubic Cd_6Ca and Cd_6Yb approximants, respectively. These results suggest that the size of the structural vacancies and local electron density do not change with the ordering.

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I. INTRODUCTION

Recently discovered Cd-based binary icosahedral phases, Cd-Yb and Cd-Ca, have provided a new field of quasicrystal research.[1,2] These binary quasicrystals have drawn a large amount of attention because they are the first examples of stable binary icosahedral phases and are considered to be a new type of icosahedral shell structure with an atomic cluster that is different from the Mackay icosahedron type (MI cluster)[3] and Bergman type.[4] Takakura *et al.*[5] proposed the structure models of the Cd_6Yb[6] and Cd_6Ca[7] approximants, in close relation to those of Cd-Yb and Cd-Ca quasicrystals. This new kind of atomic cluster contains a 4 Cd tetrahedron inside a 20 Cd dodecahedron cluster that is surrounded by a 12 Yb icosahedral cluster[6] in a 1/1-cubic Cd_6Yb approximant. While the atomic structures of 1/1-cubic approximant Cd_6M(M=Pr, Nb, Sm, Eu, Gd, Dy, Yb, Y, and Ca) have been well examined by Gómez and Lidin,[8] the exact structures of their quasicrystals have not been determined because of the lack of atomic periodicity. Based on the results of single-crystal x-ray diffraction measurements, they pointed out that different types of disorder exist in the central 4 Cd tetrahedron for approximant Cd_6M. In the case of 1/1-cubic Cd_6Yb and Cd_6Ca approximants, the same type of disorder is found in the 4 Cd tetrahedron. The disordered 4 Cd tetrahedron yields a cubic symmetry in the icosahedral three layered cluster. Moreover, according to Tamura *et al.*,[9] an order-disorder transition occurs at 100 and 110 K for 1/1-cubic Cd_6Ca and Cd_6Yb approximants, respectively, from the data of the low-temperature specific heat measurements, powder x-ray diffraction spectra, and electron diffraction patterns above and below the transition temperatures.

Positron annihilation lifetime measurement is a powerful method for detecting vacancy-type defects. This is due to the fact that positrons are trapped at open volume defects, resulting in an increase of the positron lifetime. One of the outstanding features of the positron annihilation methods is that the positron lifetime is sensitive only to the local atomic structure and is independent of whether the structure of the sample has long range periodicity or not. Comparing with the positron lifetimes of approximant crystals, we can clarify the existence of the structural vacancies in quasicrystals that have no periodic atomic order.

Furthermore, we can clarify the local chemical environment around the positron trapping sites by performing the coincident Doppler broadening spectroscopy. Our group has already reported the comparative study of binary quasicrystal $Cd_{5.7}Yb$ and its 1/1-cubic Cd_6Yb approximant. We have suggested that the same type of the structural vacancies exists in both quasicrystal $Cd_{5.7}Yb$ and 1/1-cubic approximant Cd_6Yb, and these vacancies are surrounded mostly by Cd atoms.[10,11] We have previously reported the temperature dependence of the positron annihilation lifetime of $Cd_{5.7}Ca$ quasicrystals prepared by different thermal treatments: one annealed at

773 K followed by water quenching and the other furnace cooled from the melt. We have observed a marked difference between them in both the absolute value and the temperature gradient of the positron lifetime. The result indicates that the size of the positron trapping site is different for the two quasicrystalline samples.[12]

In this study we investigated the local atomic environment around the positron trapping sites by the coincident Doppler broadening measurements at 300 K for a different quasicrystal $Cd_{5.7}Ca$ and its 1/1-cubic approximant Cd_6Ca. Moreover, we discuss the different temperature dependence of the positron lifetime in the low temperature region from 10 to 300 K for 1/1-cubic Cd_6Ca and Cd_6Yb approximants. In particular, we will discuss how their temperature variations of the positron lifetime are influenced by the order-disorder transition because local atomic density may change electronic states.

II. EXPERIMENT

Alloys of icosahedral quasicrystal and its 1/1-cubic approximant with nominal compositions $Cd_{5.7}Ca$ and Cd_6Ca were prepared by the following procedure. Flakes of high purity elements of Cd (99.9999%) and Ca (99.99%) with the compositions of $Cd_{5.7}Ca$ for the quasicrystal and Cd_6Ca for its 1/1-cubic approximant were wrapped tightly inside molybdenum foil and sealed in a quartz tube under an argon atmosphere. The elements were heated to 973 K to react each other, annealed at 773 K for 50 h, and then quenched into chilly water to obtain a homogeneous, equilibrium phase. The 1/1-cubic approximant with nominal compositions Cd_6Yb was prepared by the procedure described in detail elsewhere.[10] The characterization of the samples was performed by powder x-ray diffraction measurements with Cu$K\alpha$ radiation.

The positron annihilation measurements were carried out at 300 K, and then in the low temperature region from 10 to 300 K. The positron source ^{22}Na (activity about 10 μCi) sealed in a thin foil of Kapton was mounted with a sample-source-sample sandwich. The sample/source sandwich was maintained in vacuum at the desired temperature. The measurement temperatures were automatically set by a computer. The positron annihilation lifetime spectra were recorded with a Fast-Fast coincidence system employing H2431 photomultiplier by HAMAMATSU with 1×1 in.^{2} BaF_2 scintillators. Positron annihilation lifetimes were analyzed with the POSITRONFIT program,[13] using reference spectra for well-annealed Al to determine the time resolution and the source correction. The time resolution function was assumed to be composed of one Gaussian function. The time resolution of this system was about 250 ps full width at half-maximum (FWHM). Using this time resolution function, the positron lifetimes were measured for each sample after subtraction of the background and source component. The variance of the fit was below 1.2.

The coincident Doppler broadening spectra were measured using two high-purity Ge detectors with 1.0 keV (FWHM) energy resolution. The energies of the annihilating γ-ray pairs denoted by E_1 and E_2 were simultaneously recorded by the two detectors. The difference in energies of the two γ rays, $\Delta E=E_1-E_2$, is expressed as cP_L and the total energy, $E_T=E_1+E_2$, is expressed as $2m_0c^2-E_B$, where m_0 is the electron rest mass, c is the velocity of the light, E_B is the electron binding energy, and P_L is the longitudinal component of the positron-electron momentum. The Doppler broadening spectra were obtained by cutting the E_1, E_2 spectra along the energy conservation line $E_1+E_2=(1022\pm1)$ keV, taking into account the annihilation events within a strip of ±2.0 keV. More details on the coincident Doppler broadening spectroscopy have been reported by Asoka-Kumar *et al.*.[14] Since the pure element Ca is easy to be oxidized in the ambient atmosphere, the sample was placed into a SiO_2 tube, where Ar gas continuously flowed through in order to avoid from oxidization of the samples.

TABLE I. Positron annihilation lifetimes τ_1 of quasicrystal $Cd_{5.7}Ca$ and 1/1-cubic Cd_6Ca and Cd_6Yb approximants at 300 K, together with the positron lifetimes τ_f in the defect-free state for pure elements Cd,[a] Ca,[b] and Yb.[c] Averaged positron lifetimes in the defect-free state for quasicrystal $Cd_{5.7}Ca$ and approximant crystal, Cd_6Ca and Cd_6Yb, are listed below.

Sample	Lifetime τ_1 (ps)	Lifetime τ_f (ps)
QC-$Cd_{5.7}Ca$	280	205
Cubic-Cd_6Ca	277	205
Cubic-Cd_6Yb	278	200
Pure element		Lifetime τ_f (ps)
Pure Cd	–	190[a]
Pure Ca	–	297[b]
Pure Yb	–	260[c]

[a]Pure Cd, Ref. 15;
[b]Pure Ca, Ref. 16;
[c]Pure Yb, Ref. 17.

III. RESULTS AND DISCUSSION

The previous results of the positron annihilation lifetime measurements have shown that the same type of structural vacancies exists in both quasicrystal $Cd_{5.7}Ca$ and 1/1-cubic approximant Cd_6Ca.[12] The observed positron annihilation lifetime spectra are composed of single component, and the positron lifetimes τ_1 are 280 and 277 ps for $Cd_{5.7}Ca$ quasicrystal and 1/1-cubic approximant Cd_6Ca, respectively. Table I lists the positron lifetimes together with those of pure elements, Cd, Ca, and Yb. Comparing the positron lifetimes of quasicrystal $Cd_{5.7}Ca$, 1/1-cubic approximant crystal Cd_6Ca, and Cd_6Yb, the following picture can be drawn: we have estimated the positron lifetimes in the defect-free state for quasicrystal $Cd_{5.7}Ca$ and its 1/1-cubic approximants Cd_6Ca and Cd_6Yb by compositionally weighting the constituent element values, $\tau_{Cd}=190$ ps,[15] $\tau_{Ca}=297$ ps,[16] and $\tau_{Yb}=260$ ps.[17] Estimated values are 205 ps for Cd-Ca system and 200 ps for Cd_6Yb approximant crystal, which are significantly shorter than the measured ones. Considering that the measured positron lifetimes are significantly longer than the positron lifetime of monovacancy in pure Cd, namely,

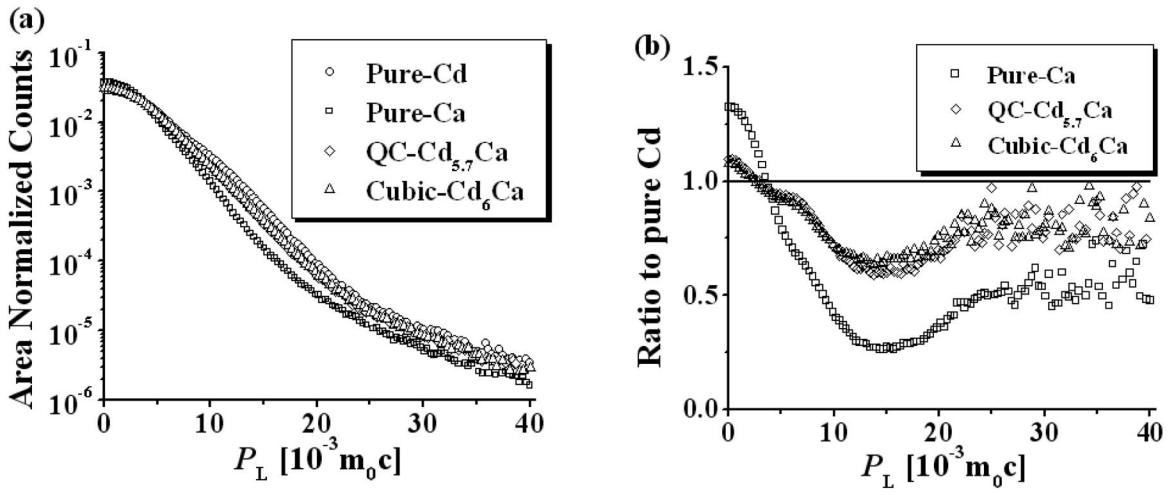

FIG. 1. (a) Coincident Doppler broadening raw spectra of icosahedral quasicrystal $Cd_{5.7}Ca$ (open diamonds) and its 1/1-cubic approximant Cd_6Ca (open triangles), together with those of pure Cd (open circles) and pure Ca (open squares). Each spectrum is normalized to the total number of counts. (b) Doppler broadening ratio curves normalized to that of pure Cd (horizontal line).

250 ps,[15] we concluded that the observed positron lifetimes are due to annihilations in the structural vacancy-type sites.

In order to investigate the local chemical environment around the positron trapping sites, we carried out the coincident Doppler broadening measurements for quasicrystal $Cd_{5.7}Ca$ and its 1/1-cubic approximant Cd_6Ca. Figure 1 shows (a) the high-momentum Doppler broadening raw spectra of the quasicrystal $Cd_{5.7}Ca$ and its 1/1-cubic approximant Cd_6Ca, together with those of pure elements, Cd and Ca, and (b) the ratio curves normalized to that of pure Cd. The Doppler spectra of the quasicrystal $Cd_{5.7}Ca$ and its 1/1-cubic approximant Cd_6Ca are quite similar to each other. Such close similarity between them in the core electron region, above 25×10^{-3} (m_0c), indicates that the local chemical surrounding of the positron trapping sites can be the same for both samples (see Fig. 1(a)). In the core electron region, the ratio curves of both quasicrystal $Cd_{5.7}Ca$ and 1/1-cubic approximant Cd_6Ca (see Fig. 1(b)) differ from the ratio curve of pure Ca, and are parallel to the horizontal line, which corresponds to pure Cd. We found that the trapping sites are surrounded mostly by Cd atoms in both quasicrystal $Cd_{5.7}Ca$ and approximant crystal Cd_6Ca.

Concerning the cubic approximant crystal Cd_6Ca and Cd_6Yb, it is well known that their structures are composed of atomic clusters of icosahedral symmetry with four-layered shell. A core of the cluster is an atomic shell of non-icosahedral symmetry. Four Cd atoms are placed at vertices of a small cube with occupancy 0.5. The second and the third shells are a dodecahedron of 20 Cd and an icosahedron of 12 Ca, respectively. The fourth shell is a Cd icosidodecahedron obtained by placing 30 Cd atoms on the edge of the Ca icosahedron. Thus, the most plausible candidate for the positron trapping sites will be an open space inside the second shell of the 20 Cd dodecahedron. Through the results of the positron annihilation lifetime and coincident Doppler broadening measurements, the following picture can be reasonably drawn: The quasicrystal $Cd_{5.7}Ca$ will be composed of the same local atomic cluster units as the 1/1-cubic approximant Cd_6Ca. After the thermalization, positrons will be localized in an open space with Cd-rich surroundings, that is, the open-space inside the second-shell of 20 Cd dodecahedron, as mentioned above. Then positrons are annihilated therein. The same picture will be applicable to the Cd-Yb system.[10]

Next, we studied the temperature dependence of the positron lifetime τ_1 in the low-temperature region from 10 to 300 K. According to Tamura *et al.*,[9] an order-disorder transition occurs at 100 and 110 K for 1/1-cubic Cd_6Ca and Cd_6Yb approximants, respectively, as probed by electrical resistivity and specific heat measurements, x-ray diffraction, and electron diffraction at low temperatures. They reported that the ordered structure possesses a noncubic lattice of a doubled unit cell and the transition is reasonably attributed to the orientation ordering of the 4 Cd tetrahedron located at the center of the icosahedral three layered cluster. We can examine approximate local electron density of the trapping site inside the second-shell of a 20 Cd dodecahedron by tracking the temperature variations of the positron lifetime τ_1 related to the annihilations in the structural vacancies.

Figure 2 shows the positron lifetimes as a function of temperature in the low-temperature region for 1/1-cubic approximant crystal Cd_6Ca and Cd_6Yb. We measured the positron annihilation lifetimes from 300 to 10 K (cooling run; inverse-triangles) and from 10 to 300 K (heating run; triangles). As a whole, both 1/1-cubic Cd_6Ca and Cd_6Yb approximants have a tendency that the positron annihilation lifetime τ_1 gradually decreases (increases) with decreasing (increasing) temperatures. Since the temperature variations are almost the same in both cooling and heating runs, the trend is considered to be a reversible change.

Then we focus on the variations of positron lifetime τ_1 around the order-disorder transition temperature, namely, 100 and 110 K for 1/1-cubic approximants Cd_6Ca and Cd_6Yb, respectively. It seems that the positron lifetime τ_1 does not change at the transition temperature and remains a constant value below the phase transition temperature for both approximant crystals. As far as the positron annihilation

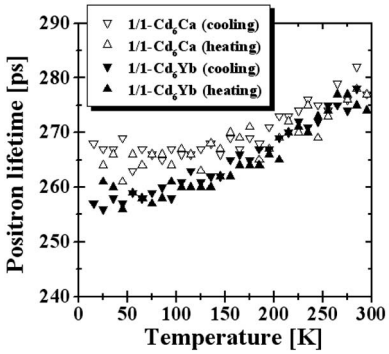

FIG. 2. Temperature dependence of the positron annihilation lifetime τ_1 for a 1/1-cubic Cd_6Ca approximant (open triangles) and 1/1-cubic approximant Cd_6Yb (full triangles). The data are plotted every 10 K. The data of cooling run (from 300 to 10 K) and heating run (from 10 to 300 K) are plotted by inverse triangles and triangles, respectively. Each data is plotted every 10 K for both samples.

spectroscopy is concerned, we cannot say that the electronic environment is affected by its orientation with respect to the larger cluster shells, but it is rather reasonable to conclude that the local electron density at the trapping site does not appreciably change by the ordering of the 4 Cd tetrahedron located at the center of the icosahedral cluster. This implies that the atomic configuration around the trapping site is unchanged with the transition. This indicates that the occupancy 0.5 at the disordered state is not due to the random occupation of four atoms at eight sites but due to the random orientation of two tetrahedral configurations. Namely, except for the relative orientation of the innermost Cd clusters, the atomic configuration of each first and second shell is essentially unchanged with the transition. The same conclusion was reached in the previous papers by Tamura *et al.*.[9] The approximant crystal Cd_6Ca has about 10 ps longer positron lifetimes than the Cd_6Yb approximant crystal at low temperature, indicating the slightly larger open space and the lower local electron density inside the 20 Cd dodecahedron in Cd_6Ca.

IV. CONCLUSIONS

We previously reported that the same structural vacancies exist in binary icosahedral quasicrystal $Cd_{5.7}Ca$ and its 1/1-cubic approximant Cd_6Ca based on the results of positron annihilation lifetime measurements.[12] The local chemical environment around the positron trapping sites was clarified by the coincident Doppler broadening measurements. Essentially the same type of annihilation sites with Cd-rich chemical environment were identified for the two phases. These results imply that quasicrystal $Cd_{5.7}Ca$ is composed of the same clusters as the 1/1-cubic approximant Cd_6Ca. The temperature dependence of the positron lifetime τ_1 in the temperature region from 10 to 300 K for 1/1-cubic approximant crystals Cd_6Ca and Cd_6Yb were measured, and we have found that the local electron density at the trapping site is unchanged with the order-disorder transition. This indicates that the occupancy 0.5 at the disordered state is not due to the random occupation of four atoms at eight sites but due to the random orientation of two tetrahedral configurations. Finally, we found that the size of the open space inside the 20 Cd dodecahedron of Cd_6Ca approximant will be slightly larger than that of the Cd_6Yb approximant below about 150 K.

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