

Stable icosahedral quasicrystals in binary Cd-Ca and Cd-Yb systems

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Stable icosahedral quasicrystals have been found in binary Cd-Ca and Cd-Yb systems in an as-solidified state as well as an annealed state. The icosahedral quasicrystals are identified to form at the composition of $\text{Cd}_{85}\text{Ca}_{15}$ and $\text{Cd}_{84}\text{Yb}_{16}$. An electron diffraction study confirmed that the icosahedral quasicrystals have a primitive lattice. Quasilattice parameters are 0.5731 nm for $\text{Cd}_{85}\text{Ca}_{15}$ and 0.5681 nm for $\text{Cd}_{84}\text{Yb}_{16}$.

Stable quasicrystals have been found in a small number of systems.^{1–10} Recently, Guo *et al.*^{11–12} had reported a group of stable icosahedral quasicrystals in the Cd-Mg-RE (RE=rare earth element) system, which is the largest group of quasicrystalline alloys, with 11 different RE elements. The Cd-Mg-RE quasicrystals are especially interesting from the viewpoint of physical properties since they contain rare-earth elements.

Until now, except for binary Ta-Te dodecagonal quasicrystal,¹⁰ no example of a two-component stable icosahedral quasicrystal was found. If a two-component icosahedral quasicrystal could exist, using the two-component quasicrystal would simplify experimental and theoretical investigation. In a detailed study on Cd-Mg-Yb quasicrystals, we have found the two-component stable icosahedral quasicrystals in Cd-Yb (Ref. 13) and Cd-Ca alloys. In this paper, we report formation of these binary quasicrystals.

The alloys were prepared from pure elements of Cd (99.99 wt %), Yb (99.9 wt %), and Ca (99.5 wt %) using an induction furnace in Al_2O_3 crucibles sealed in quartz tubes under Ar atmosphere, followed by annealing at 673 K for 100 h in an Ar atmosphere. Phase identification of the samples was performed by x-ray diffraction with Cu- $K\alpha$ radiation. Structure characterization of the quasicrystals was carried out by transmission electron microscopy (TEM). The specimens for TEM observations were powdered in alcohol and then transferred on to holed film.

Among the ternary Cd-Mg-RE systems, the quasicrystal is most stable in the Cd-Mg-Yb system, which formed in an as-solidified state as well as in an annealed state. In the Cd-Mg binary phase diagram, Cd and Mg form a mutual continuous solid solution in a wide temperature range, implying that Cd and Mg can replace each other. In a systematic investigation, we ignored Mg and revisited the phase diagram of Cd-Yb. It is striking that there is an unknown phase with a congruent melting point of 909 K at the composition of $\text{Cd}_{85.1}\text{Yb}_{14.9}$ ($\text{Cd}_{5.7}\text{Yb}$), whose Yb content is the same as that of the ternary Cd-Mg-Yb quasicrystal. Structure of the $\text{Cd}_{85.1}\text{Yb}_{14.9}$ had been studied by single grained x-ray diffraction, but could not correspond to any crystalline structure. Empirically, some stable quasicrystals were discovered by identifying unknown compounds. Thus, we suspected that the unknown $\text{Cd}_{85.1}\text{Yb}_{14.9}$ phase might be a quasicrystal.

Figure 1(a) shows a powder x-ray diffraction pattern of an as-solidified $\text{Cd}_{85.1}\text{Yb}_{14.9}$ alloy. Most of the strong diffraction

peaks can be assigned to be those of an icosahedral quasicrystal using the Elser's indexing method.¹⁴ Selected area electron diffraction patterns obtained from the $\text{Cd}_{85.1}\text{Yb}_{14.9}$ along five- and twofold axes are shown in Fig. 2, suggesting that the $\text{Cd}_{85.1}\text{Yb}_{14.9}$ compound is indeed an icosahedral quasicrystal. All the diffraction spots in the fivefold pattern have the characteristic tenfold symmetry. According to the array of the spots along the fivefold axis directions in the twofold patterns, the icosahedral quasicrystal is recognized to have a primitive lattice in six-dimensional space. The $\text{Cd}_{85.1}\text{Yb}_{14.9}$

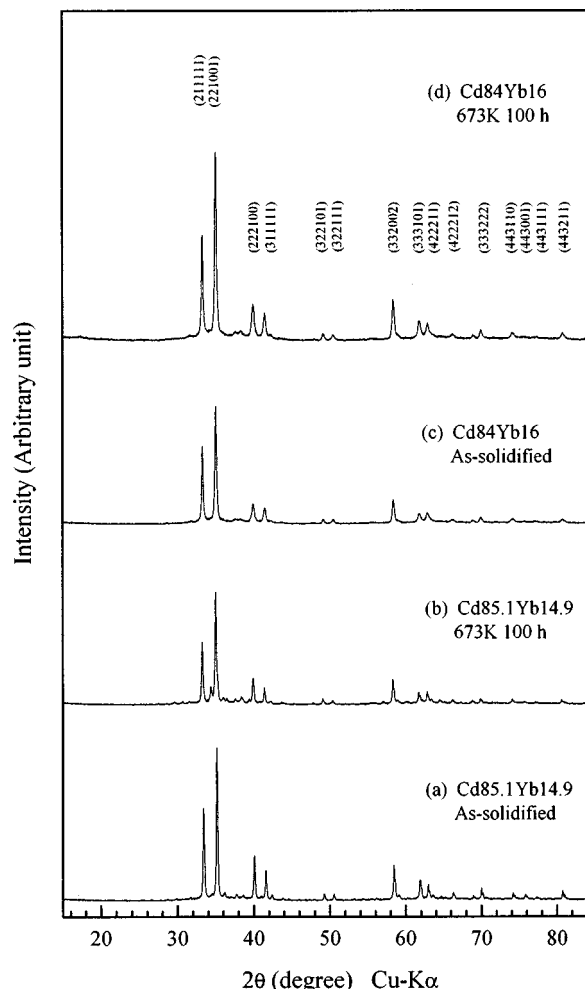


FIG. 1. Powder x-ray diffraction patterns of the Cd-Yb alloys.

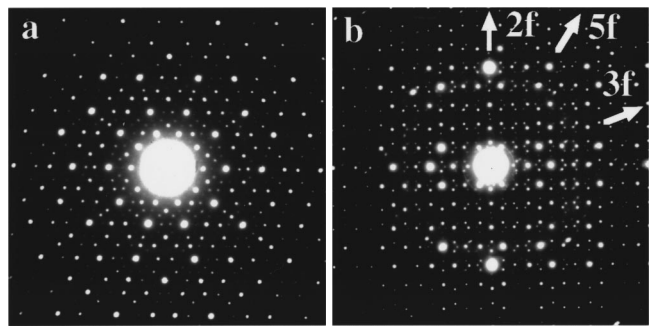


FIG. 2. Electron diffraction patterns of the $\text{Cd}_{85.1}\text{Yb}_{14.9}$ alloy. (a) Fivefold symmetry pattern. (b) Twofold symmetry pattern.

quasicrystal annealed at 673 K for 100 h partly transformed to a crystalline phase, as shown in Fig. 1(b). To make sure whether or not the thermodynamically stable quasicrystal exists in the Cd-Yb system, we changed the composition of the samples and investigated their stability, finding that the two-component Cd-Yb quasicrystal is thermodynamically stable, but the existence region of the stable quasicrystal has a relation to temperature. As shown in Figs. 1(c) and 1(d), Yb slightly enriched Cd-Yb samples, for example, $\text{Cd}_{84}\text{Yb}_{16}$, are composed of a single phase of the quasicrystal in the as-solidified state as well as in the annealed state. X-ray diffraction data of the annealed $\text{Cd}_{84}\text{Yb}_{16}$ is shown in Table I. All of the diffraction peaks can be indexed as the icosahedral phase with a quasilattice parameter of 0.5681 nm, which was estimated from the (211111) peak.

According to the similarity in the phase diagram and crystal structure, we further found another binary quasicrystal of $\text{Cd}_{85}\text{Ca}_{15}$. Figures 3(a) and 3(b) show the powder x-ray diffraction patterns of the $\text{Cd}_{85}\text{Ca}_{15}$ alloy. Both the as-solidified and annealed $\text{Cd}_{85}\text{Ca}_{15}$ samples reveal diffraction peaks that can be identified as an icosahedral quasicrystal, although intensity of the x-ray diffraction peaks changes relatively after annealed at 673 K for 100 h. This indicates that the $\text{Cd}_{85}\text{Ca}_{15}$

TABLE I. Peak position (Q, d), the normalized peak intensity (I), and half width at half maximum (ΔQ) of the $\text{Cd}_{84}\text{Yb}_{16}$ icosahedral quasicrystal determined from the x-ray diffraction data. The lattice parameter of the icosahedral quasicrystal $a_R = 0.5681$ nm.

Index	Q (nm^{-1})	d (nm)	I	ΔQ (nm^{-1})
(211111)	23.43	0.2682	57	0.15
(221001)	24.64	0.2550	100	0.13
(222100)	27.93	0.2250	19	0.14
(311111)	28.95	0.2170	15	0.13
(322101)	33.97	0.1850	5	0.14
(322111)	34.81	0.1805	5	0.13
(332002)	39.81	0.1578	26	0.14
(333101)	41.95	0.1498	12	0.18
(422211)	42.61	0.1475	10	0.13
(422212)	44.61	0.1409	5	0.14
(333222)	46.80	0.1343	7	0.13
(443110)	49.20	0.1277	6	0.15
(443001)	50.12	0.1254	5	0.17
(443111)	50.93	0.1234	3	0.19
(443211)	52.86	0.1189	6	0.15

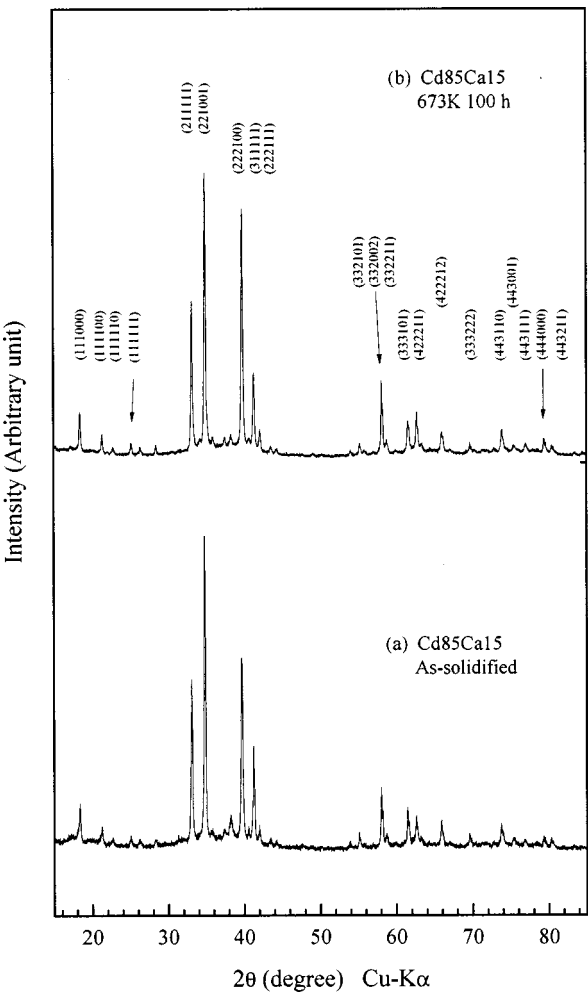


FIG. 3. Powder x-ray diffraction patterns of the $\text{Cd}_{85}\text{Ca}_{15}$ alloy.

icosahedral quasicrystal is thermodynamically stable. X-ray diffraction data of the annealed $\text{Cd}_{85}\text{Ca}_{15}$ icosahedral quasicrystal is shown in Table II and its quasilattice parameter estimated from the (211111) peak is 0.5731 nm. Selected area electron diffraction patterns obtained from the $\text{Cd}_{85}\text{Ca}_{15}$ along five- and twofold axes are shown in Fig. 4, confirming that the $\text{Cd}_{85}\text{Ca}_{15}$ is really the icosahedral quasicrystal. According to the array of the spots along the fivefold axis directions in the twofold patterns, it is known that the stable icosahedral quasicrystal has a primitive lattice in six-dimensional space.

In the Cd-Yb and Cd-Ca phase diagrams,¹⁶ there exist cubic phases of Cd_6Yb and Cd_6Ca just adjacent to the stable icosahedral quasicrystals. Cd_6Yb has a cubic structure with a lattice parameter of 1.564 nm and a space group of $Im\bar{3}$, consisting of 168 atoms. Cd_6Ca also has the same cubic structure with a lattice parameter of 1.568 nm and 168 atoms. The compositions of Cd_6Yb and Cd_6Ca are slightly different from those of the $\text{Cd}_{84}\text{Yb}_{16}$ and $\text{Cd}_{85}\text{Ca}_{15}$ stable quasicrystals by about 1 at. %, small enough to be negligible. Since $Im\bar{3}$ is a subgroup of the icosahedral symmetry group, the cubic phases are the candidate for the approximant of the quasicrystal. By confirming the relation $a = (4 + 8/\sqrt{5})^{1/2}a_R$, where a is the lattice parameter of an 1/1 approximant and a_R is the lattice constant of the icosahedral quasicrystal corresponding to the edge length of rhombohe-

TABLE II. Peak position (Q, d), the normalized peak intensity (I), and half width at half maximum (ΔQ) of the $\text{Cd}_{85}\text{Ca}_{15}$ icosahedral quasicrystal determined from the x-ray diffraction data. The lattice parameter of the icosahedral quasicrystal $a_R = 0.5731$ nm.

Index	Q (nm^{-1})	d (nm)	I	ΔQ (nm^{-1})
(111000)	13.00	0.4834	15	0.14
(111100)	15.05	0.4176	9	0.15
(111110)	16.03	0.3921	6	0.15
(111111)	17.65	0.3559	6	0.15
(211111)	23.22	0.2706	52	0.15
(221001)	24.41	0.2574	100	0.15
(311110)	26.69	0.2354	13	0.20
(222100)	27.68	0.2270	64	0.17
(311111)	28.71	0.2188	35	0.14
(222111)	29.23	0.2149	9	0.13
(222121)	30.20	0.2081	6	0.20
(332101)	37.73	0.1665	7	0.13
(332002)	39.57	0.1588	23	0.14
(332211)	39.99	0.1571	7	0.20
(333101)	41.68	0.1507	17	0.15
(422211)	42.37	0.1483	14	0.16
(422212)	44.35	0.1417	12	0.15
(333222)	46.54	0.1350	8	0.16
(443110)	48.93	0.1284	10	0.16
(443001)	49.83	0.1261	6	0.20
(443111)	50.65	0.1240	6	0.21
(444000)	52.06	0.1207	7	0.19
(443211)	52.60	0.1195	7	0.18

dra in three-dimensional Penrose tiling, the present cubic phases are sure to be the 1/1 approximants of the icosahedral quasicrystals. Structure of the cubic phases can be described by a different kind of packing of icosahedral clusters with internal symmetry breaking.¹⁵

Up to date, Al-Li-Cu is the only example in which both the icosahedral phase and its approximant exist as equilibrium phases and their compositions are very close. The Cd-Yb and Cd-Ca should be the second ones, so they will be available to study the difference in the structure and physical properties between the icosahedral phases and approximants. In addition, unlike all the known quasicrystals that are incongruent melting phases, according to the Cd-Yb phase diagram,¹⁶ the present stable $\text{Cd}_{84}\text{Yb}_{16}$ quasicrystal is a congruent melting phase. Therefore, its single grain would be easily grown.

The stable icosahedral phase has been treated as a Hume-Rothery electron compound, i.e., all the stable icosahedral

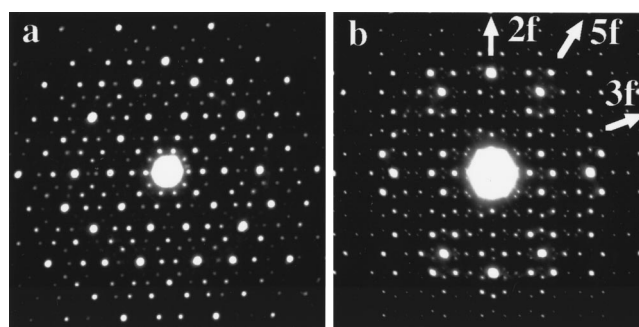


FIG. 4. Electron diffraction patterns of the $\text{Cd}_{85}\text{Ca}_{15}$ alloy. (a) Fivefold symmetry pattern. (b) Twofold symmetry pattern.

phases have a common valence concentration (e/a). The e/a is 1.75 for the Al-transition metal group and 2.1 for the Al-Zn-Mg group. As the valences of Cd and Ca are +2, the e/a of the binary stable icosahedral phase $\text{Cd}_{85}\text{Ca}_{15}$ is 2.0. Magnetic susceptibility measurements verified that Yb is almost divalent in the $\text{Cd}_{84}\text{Yb}_{16}$ icosahedral quasicrystal,¹⁷ hence we believe that the Yb should be divalent in the icosahedral phase. Consequently, the e/a of the binary stable $\text{Cd}_{84}\text{Yb}_{16}$ icosahedral phase is also 2.0. Among 15 rare-earth elements, most of them form the Cd_6RE (RE=rare-earth element) cubic phase, while only Yb forms a quasicrystal phase with Cd. The reason may be that all the rare-earth elements except divalent Yb and Eu are trivalent, so that the e/a of Cd-RE compounds deviates from 2.0. This implies that the electron structure may play an important role in the formation of the binary quasicrystals. For the Cd-Ca system, the e/a of any composition is always 2.0, while the icosahedral quasicrystal forms only at the composition of $\text{Cd}_{85}\text{Ca}_{15}$. This is a signal that the quasicrystal formation is also dominated by atomic size and ratio of atom number. This is further supported by the Cd-Yb system. The atomic radius of Yb, 0.194 nm, is quite close to that of Ca, 0.198 nm, so that the $\text{Cd}_{84}\text{Yb}_{16}$ quasicrystal has almost the same composition as that of the $\text{Cd}_{85}\text{Ca}_{15}$ quasicrystal. On the other hand, although Eu may be divalent, the atomic radius of Eu, 0.204 nm, is a little larger than those of Yb and Ca, resulting in the conclusion that quasicrystal does not form in the Cd-Eu system. On the basis of the above discussion, we conclude that the valence concentration and atom size dominate formation of the Cd-Ca and Cd-Yb icosahedral quasicrystals.

In summary, we have described the stable icosahedral quasicrystals in Cd-Yb and Cd-Ca binary systems. They are examples of stable icosahedral quasicrystals in binary alloys.

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