Hybridization Mechanism for Cohesion of Cd-based Quasicrystals

Yasushi Ishii
Department of Physics, Chuo University, Kasuga, Tokyo 112-8551, Japan

Takeo Fujiwara
Department of Applied Physics, University of Tokyo, Hongo, Tokyo 113-8654, Japan

Cohesion mechanism of cubic approximant crystals of newly discovered binary quasicrystals, Cd₆M (M=Yb and Ca), are studied theoretically. It is found that stabilization due to alloying is obtained if M is an element with low-lying unoccupied d states. This leads to conclusion that the cohesion of the Cd-based compounds is due to the hybridization of the d states of Yb and Ca with a wide sp band. Although a diameter of the Fermi sphere coincides with the strong Bragg peaks for Cd-Yb and Cd-Ca, the Hume-Rothery mechanism does not play a principal role in the stability because neither distinct pseudogap nor stabilization due to alloying is obtained for isostructural Cd-Mg. In addition to the electronic origin, matching of the atomic size is very crucial for the quasicrystal formation of the Cd-based compounds. It is suggested that the glue atoms, which do not participate in the icosahedral cluster, play an important role in stabilization of the compound.

Electronic structures of aluminum-based quasicrystals (QC) have been studied so far for many kinds of approximant crystals [1]. The most characteristic feature in the electronic structures of approximant crystals and probably QC is a pseudogap in the density of states (DOS) at the Fermi level. It is believed that origin of the pseudogap is mainly due to the Brillouin-zone (BZ)-Fermi-sphere (FS) interaction (the Hume-Rothery mechanism), and presumably secondly due to the s-d hybridization [2]. In the Hume-Rothery mechanism, a strong interference of electronic waves at \( k + G \) induces the pseudogap near the Fermi level where \( G \) is the reciprocal lattice vector giving strong Bragg scattering and satisfying \( |G| \approx 2k_F \). This interference effect is more efficient in QC than in approximant crystals because of sphericity of distribution of \( G \). It is empirically known that stable QC is obtained if the average number of valence electrons per atom, which is usually denoted as \( e/a \), is close to either 1.7 or 2.1. The QC without transition elements, such as Al-Li-Cu and Zn-Mg-RE (RE: rare earth), belong to a family of QC with \( e/a = 2.1 \), for which a diameter of the FS, \( 2k_F \), calculated from the electron density is close to the (222100) and (311111) reciprocal lattice vectors.

Very recently stable icosahedral QC have been found in binary Cd-Yb and Cd-Ca systems [3, 4]. The quasicrystalline phases are identified as unknown phases in the phase diagrams, Cd₅.7Yb and Cd₁₇Ca₃ [5]. Cubic crystalline phases, Cd₆M (M=Yb, Ca), are obtained in the composition near the quasicrystalline one. The isostructural cubic alloys are also obtained for other systems with M=Sr [6], Y [7] and most of rare-earth elements [10] although the icosahedral QC is realized only for M=Yb and Ca.

The Cd-based QC is not only the first stable binary QC but also a unique system in many aspects. First, the local atomic structure conjectured from that in the cubic phase is similar to the Al-Mn family of QC with \( e/a = 1.7 \) although it contains no transition elements as is discussed by Takakura et al [8]. The core structure of an icosahedral cluster is also very unique as explained below. Secondly, unlike the conventional QC without transition elements, \( e/a \) for Cd-Yb and Cd-Ca alloys is exactly 2 and the icosahedral phase is not obtained for Cd-M with trivalent metals, M [9]. Finally, although \( 2k_F \) calculated from the electron density is close to the (222100) and (311111) reciprocal lattice vectors, only Cd-Yb and Cd-Ca forms QC among the isostructural Cd-based alloys. It is important to examine the mechanisms other than the BZ-FS interaction, such as the \( sp-d \) hybridization effects and the atomic diameter effects. In this article we shall investigate the electronic structures of the cubic Cd₆Yb and Cd₆Ca crystals to study mechanism for cohesion of the newly discovered QC. We also present the electronic structures of isostructural compounds Cd₆Sr and Cd₆Mg although Cd₆Mg is hypothetical.

Cd₆Yb is a body centered cubic crystal with space group \( Im3 \), which contains 168 atoms (176 sites) in a cubic cell with lattice parameter \( a = 15.638 \) Å [11]. Although detailed structural analysis for Cd₆Ca has not been made, Cd₆Ca is believed to be isostructural to Cd₆Yb with a lattice parameter \( a = 15.680 \) Å [8]. In Cd₆Yb, the cluster is placed at the corner and the body center of a cubic cell [3]. A core of the cluster is an atomic shell of non-icosahedral symmetry as in a pseudo-Mackay cluster in Al-Pd-Mn [12]. Four Cd atoms are placed at vertices of a small cube with occupancy probability 0.5. Because Cd atom is not small enough to occupy neighboring vertices, the central shell of Cd atoms may be of a tetrahedral shape. The tetrahedral symmetry is a subgroup symmetry of the icosahedral one and the symmetry axes of the tetrahedral core coincide with those of outer icosahedral shells. Therefore, we presume that the
tetrahedral core is very probable. The second and third atomic spheres are a dodecahedron of 20 Cd atoms and an icosahedron of twelve Yb atoms, respectively. The fourth shell is a Cd icosidodecahedron obtained by placing 30 Cd atoms on the edge of the Yb icosahedron.

To avoid the fractional occupation of cadmium atoms in the electronic structure calculations, a tetrahedral cluster of four Cd atoms, instead of a cubic one, is placed at the corner and the body-center of the cubic unit cell. We assume the same atomic positions as those obtained for Cd$_6$Yb for all the compounds with an appropriate lattice constant shown in Table I. Calculation is done with the tight-binding linear muffin-tin orbitals (TB-LMTO) method in the atomic-sphere approximation (ASA) [13].

In Fig. 1(a), we show the total DOS for Cd$_6$Yb. A narrow band at about $-0.8$ [Ryd] is the Cd-4$d$ band and does not contribute to cohesion. Another narrow peak just below the Fermi level is attributed to the Yb-4$f$ states. Since the narrow 4$f$ band is almost filled, Yb is divalent as is Ca. This is consistent with measurements of magnetic susceptibility.

A shallow dip in the DOS is seen between the 4$f$ band and an unoccupied peak at 0.0-0.1 [Ryd], which is made from the Yb-5$d$ states. By checking decomposition of the DOS to partial waves, we find that the occupied states below the dip are predominantly made from the Cd-5$p$ states except for the narrow 4$f$ band. This is a qualitatively different feature from pure Cd metal, in which the s and p states contribute equally to the states near the Fermi Level. We speculate that hybridization of the Cd-5$p$ and Yb-5$d$ orbitals makes the bonding orbitals below the Fermi level leading to the dip (or the pseudogap) in the DOS.

The total DOS for Cd$_6$Ca, Cd$_6$Sr and Cd$_6$Mg are shown in Fig. 1(b)-(d). Band width, position of the 4$d$-band and other characteristics of Cd$_6$Yb are also found in Cd$_6$Ca and Cd$_6$Sr except for the narrow 4$f$ band in Cd$_6$Yb. For Cd$_6$Mg where magnesium has no low-lying unoccupied d state near the Fermi level, on the other hand, the shallow dip near the Fermi level vanishes. Therefore we can say that hybridization of the d states near the Fermi level is essential for the dip formation in the Cd-based compounds. This should be contrasted with the cases of Al-Li-Cu [2] and Zn-Mg-Y [14], where the sp-$d$ hybridization is rather minor in the pseudogap formation. This fact was confirmed by checking that the pseudogap does not vanish even if Cu in Al-Li-Cu and Y in Zn-Mg-Y are replaced with the elements without the d states, Al and Mg, respectively.

Calculated cohesive energies per atom at a fixed lattice constant are shown in Table II. The cohesive energy for Cd$_6$Mg at the optimal lattice parameter is similar to that for pure Cd [1.48 [eV/atom] for fcc with $a=4.45$ [Å]] and smaller by about 15% than those for the other Cd$_6$M compounds with the low-lying d band near the Fermi level. Therefore the hybridization of the d state with a wide sp band certainly contributes to stabilizing the Cd$_6$M compounds. Although there have been a lot of conjectures that the sp-$d$ hybridization is important for stabilizing the QC [12], the present calculation is the direct demonstration that the sp-$d$ hybridization induces the pseudogap or the dip in the DOS and lowers the structural energy of approximant crystals of QC.

A diameter of the FS is calculated from the electron density as $2k_F = 2.75$ [Å$^{-1}$], which is very close to the (222100) and (311111) Bragg scatterings at 2.79 and 2.90 [Å$^{-1}$], respectively, for the icosahedral Cd-Yb [5]. This seems to support the Hume-Rothery mechanism, in which the BZ-FS interaction induces the pseudogap near the Fermi energy. However, there is neither distinct dip (or pseudogap) in the DOS nor additional stabilization due to alloying for isostructural and isovalent Cd$_6$Mg, which has a similar structure factor to the other Cd$_6$M compounds. Thus we should say that the interference effect associated with the strong peaks in the structure factor is not of primary importance for the stability of the Cd-based compounds.

For the stable QC without transition elements, $e/a$ is usually close to 2.1. This empirical rule for $e/a$ is not satisfied for the present Cd-based compounds because all the elements are divalent and hence $e/a$ is exactly 2 [5]. Although a quantitative argument is difficult in the ASA, a ratio of the d-symmetric state to the sp-symmetric one in the Yb/Ca atomic sphere increases by alloying in comparison with pure Yb and Ca. This reminds us of the negative valence trend of transition elements in the Al-Mn family of QC [11,12]. The electron transfer to the d state together with the strong hybridization effects implies that the electronic structure of the Cd-based compounds is very different from that of the conventional QC without transition elements.

The Fermi levels of Cd$_6$Yb and Cd$_6$Ca are pinned at the shoulder of the occupied band, not at the minimum of the DOS. Nevertheless reasonable amount of energetic stabilization is obtained for the cubic Cd$_6$M compounds as shown above. This is because the occupied states just below the dip are bonding orbitals, whose levels are lowered by alloy formation. One expects, however, that the Fermi level is shifted to the minimum of the DOS, yielding the larger cohesive energy by substituting trivalent atoms for Yb and Ca. In fact, we have checked that the Fermi level for the isostructural Cd$_6$Y is located at the minimum of the DOS and the cohesive energy per atom is as large as 2.15 [eV/atom].

So far we have seen that the cubic Cd$_6$M compounds are stabilized if M is an element with low-lying unoccupied d states. It is reasonable to believe that the same mechanism works also in QC because the local atomic structure would be similar. Nevertheless, no quasicrystalline phase is obtained for Cd-Sr at the composition close to Cd$_6$M. As Guo et al. [6] have already pointed out, the atomic radius of Yb and Ca may be more suitable for
quasiperiodic arrangements of atoms. The atomic radii calculated from the lattice constants of pure systems are listed in Table I. The atomic radius of Sr is larger by 10% than those of Yb and Ca. It may be rather surprising that the Cd-Sr compound has the isostructural cubic phase with Cd₆Yb and Cd₆Ca in spite of such difference.

Guo et al. also argued that alloying of Cd with trivalent elements may not favor the QC formation because \( e/a \) shifts apart from 2. The electronic energy could, however, gain by the substitution of trivalent elements as mentioned above. The atomic radii of the trivalent rare-earth elements and Y are considerably small (1.75-1.87 [Å]) in comparison with the divalent elements, Yb and Ca. Matching of the atomic size is certainly important for the QC formation in the binary systems. We should point out here that only europium is exceptional in this context: Although Eu is divalent and the atomic radius is similar to Ca and Yb, the QC is not obtained for the Cd-Eu alloy. This is an open question to be answered in the future.

Finally, to observe the electronic structure in connection with the shell structure of the icosahedral cluster, we calculate the local density of states (LDOS) for atoms in the individual atomic shells in the cluster. In Fig. 2, we show the LDOS for the central Cd₄ tetrahedron and that for the glue Cd atoms, which do not participate in the icosahedral cluster. A midgap peak appears at around \(-0.1\) [Ryd] for the LDOS at the central Cd₄ tetrahedron and the hybridization effect is not remarkable at the center of the cluster. On the other hand, the dip above the Fermi level is clearly seen in the LDOS at the glue-atom sites and the DOS below the dip is enhanced. We speculate that the Cd-3p states on the glue atoms are strongly hybridized with the Yb-5d states to favor the cluster packing.

We have studied the electronic structures of the cubic Cd₆M approximant crystals of the newly discovered binary QC. It is found that stabilization due to alloying is obtained if M is an element with low-lying unoccupied d states. This leads to conclusion that the cohesion of the Cd-based compounds is certainly due to the hybridization of the d states of Yb and Ca with a wide sp band. Although a shallow dip in the DOS appears near the Fermi level and a diameter of the FS coincides with the strong Bragg peaks for Cd-Yb and Cd-Ca, the BZ-FS interaction does not play a principal role in the Cd-based systems because neither distinct dip nor additional stabilization due to alloying is obtained for isostructural Cd-Mg. In order to exclude definitely the Hume-Rothery mechanism, further studies are obviously needed, however. In spite of similar electronic structures for the cubic Cd₆M (except Mg), only Cd-Yb and Cd-Ca form QC. It is conjectured that matching of the atomic size is crucial for long-range quasiperiodic packing of the clusters.

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TABLE I. Cohesive energies per atom \( \Delta E \) and lattice constants \( a \) for cubic Cd₆M together with atomic radii of M (M=Yb, Ca, Sr and Mg). The lattice parameter for hypothetical Cd₆Mg is calculated a optimal one.

| M   | Yb | Ca | Sr | Mg |
|-----|----|----|----|----|
| \( \Delta E \) [eV/atom] | 1.68 | 1.75 | 1.69 | 1.47 |
| \( a \) [Å]           | 15.638 | 15.680 | 16.040 | 15.22 |
| atomic radius [Å]     | 1.94  | 1.97  | 2.15  | 1.60  |

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FIG. 1. Total (black) and partial (green: $p$-wave, red: $d$-wave) density of states for (a) Cd$_6$Yb, (b) Cd$_6$Ca, (c) Cd$_6$Sr and (d) Cd$_6$Mg.

FIG. 2. Local density of states (LDOS) for Cd$_6$Yb at the central Cd$_4$ tetrahedron (a) and that at the glue Cd atoms (b). The Cd-3$d$ components are eliminated from the LDOS.
(a) tetrahedral Cd

(b) glue Cd