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Approximant phase of an icosahedral quasicrystal in a boron-carbon semiconducting system

M. Takeda, K. Kimura,* A. Hori, H. Yamashita, and H. Ino

Department of Materials Science, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113, Japan

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The possibility of a semiconducting quasicrystal in boron-rich solids made of B_{12} icosahedra is investigated. On the basis of crystallographic data and a molecular-orbital calculation, we predict the existence of a semiconducting quasicrystal, based on α-rhombohedral units of boron icosahedra, and its boron-carbon composition. We have experimentally discovered a new 1/0-1/0-0/1 orthorhombic approximant phase of an icosahedral quasicrystal by annealing amorphous phase $B_{100-x}C_x$ ($x=3, 5, 7$) above 1200 °C for 10 min. It must be a semiconductor like other boron-rich compounds.

Quasicrystalline structures have only been found to exist in numerous metallic alloy systems,[1] and therefore it is of special research interest to discover such a structure that is stable in a covalent bonding system.[2,3] Although several studies have been directed at investigating semiconducting quasicrystals in clathrate compounds,[4,5] Ge,[6] BN,[7] and C_{60} (Ref. 8) materials, no suitable system has yet been established. Boron-rich solids are excellent candidates for this purpose because they possess a variety of semiconducting crystalline structures having icosahedral B_{12} clusters.[9] In addition, some of them have a unit cell that is quite similar to the prolate rhombohedron, one of the building blocks of the three-dimensional (3D) Penrose pattern,[2,3] i.e., the icosahedral quasicrystal.

The present study predicts the structure and composition of the icosahedral quasicrystal in boron-rich solids using crystallographic data and a molecular-orbital total-energy calculation. To estimate the cohesive energy of boron's crystalline and quasicrystalline structures, we performed the above calculation using the modified neglect of diatomic overlap (MNDO) method with the MOPAC program.[10] Detailed procedures of the calculation are published elsewhere.[11] An experimental search was also carried out to find the quasicrystalline or its approximant phase using a nonequilibrium state, because the formation range of quasicrystals by melt-quenching (nonequilibrium) is inherently wider than that by conventional solidification (near equilibrium). Briefly, amorphous films were prepared by electron-beam evaporation of a mixed powder of B and B_4C, with the resultant films being deposited and then removed from glass substrates. The amorphous powder was heated to 1400 °C in a BN crucible held in an Ar-sealed quartz tube. Their phases and compositions were subsequently determined via transmission electron microscopy (TEM), powder x-ray diffraction (XRD), an electron probe microanalyzer (EPMA), and electron spectroscopy for chemical analysis (ESCA).

The unit cell of α-rhombohedral boron has an icosahedral B_{12} cluster at each vertex as shown in Fig. 1(a).[12] Each icosahedron is directly bonded to six neighboring icosahedra along the rhombohedral axes and along nearly the fivefold axes of the icosahedra. When the directions of these two axes exactly coincide, the rhombohedral unit cell is the same as a prolate rhombohedron, which is one of two units cells comprising an icosahedral quasicrystal. The structure of α-rhombohedral boron is therefore considered to be the 0/1-2/0 rhombohedral crystalline approximant ($\tau=0/1$, $\tau^3=2/0$) of the icosahedral quasicrystal. If this unit cell is considered to be a prolate rhombohedron, then the corresponding structure of the oblate rhombohedron can be constructed as shown in Fig. 1(b). However, a problem occurs with this oblate structure because the distance is too short between two icosahedra located at the ends of the short body diagonal, and consequently, to achieve structure stability the three interfacing atoms must be removed and the remaining three atoms must relax. To evaluate the stability of these structures and their crystalline/quasicrystalline arrangements, we estimated their associated cohesive energies using a molecular-orbital total-energy calculation, with the results summarized in Table I. Note the cohesive energy of α-rhombohedral boron agrees well with the experimental value reported previously,[13] as well as being larger than that of the β-rhombohedral boron. This is consistent with the fact that α-rhombohedral boron is more stable than β-rhombohedral boron below 1200 °C. The "α-rhombohedral-type quasicrystal," which is constructed with the unit cells of Figs. 1(a) and (b), has a cohesive energy falling between that of α- and β-rhombohedral boron. Thus, based on these energy results it is hy-

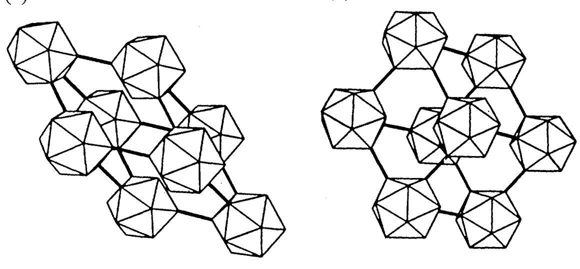

FIG. 1. Atomic structures of the two unit cells of the α-rhombohedral-type icosahedral quasicrystal; (a) prolate and (b) oblate rhombohedra. The former is also a unit cell of α-rhombohedral boron.

TABLE I. Cohesive energy of boron structures.

Structure	Cohesive energy (eV/atom) Calculation	Cohesive energy (eV/atom) Experiment
α-rhombohedral boron	5.99	5.81 (Ref. 13)
β-rhombohedral boron	5.31	
α-rhombohedral-type quasicrystal	5.64–5.84	

pothesized that this structure can be realized.

In the actual α-rhombohedral boron (α-B) crystalline structure, the B_{12} icosahedra are distorted and the angle between the rhombohedral axes is considerably smaller than the one between the icosahedral basic vectors of $\phi_{\rm icos}=63.43°$. The amount of distortion and the axis angle can be adjusted by adding another element to α-B. In the α-rhombohedral-type structures of B_6O, $B_{100-x}C_x$ ($9<x<19$), and $B_{13}P_2$; atoms of O, C, and P are, respectively, located on the unit-cell body diagonal of α-B. For O, P, and C, two- and three-atom chains are, respectively, formed there. As shown in Fig. 2(a), the distortion of B_{12} in these particular structures correlates with the angle between the rhombohedral axes. In the B-C system, the distortion is smallest and the axis angle rather close to $\phi_{\rm icos}$, and therefore this system was selected for our experimental search for a quasicrystal.

The composition of the B_4C structure in the equilibrium phase diagram of the B-C system ranges from 9 to 19 at. % C, and the distortion of B_{12} decreases with decreasing C concentration as shown in Fig. 2(b). Because the oblate rhombohedron of Fig. 1(b) has no inner C site, whereas the prolate one, i.e., the B_4C unit cell, has corresponding chain sites, the composition of its quasicrystalline structure is postulated to be comparatively C poor. Therefore, the corresponding quasicrystalline composition is expected to range from 0 to 9 at. % C.

On the other hand, all boron-rich solids constructed of B_{12} are semiconducting, with both α-B and B_4C having a fully occupied valence band. At a composition less than 20 at. % C, B_4C's valence band is not fully occupied, yet this material retains its semiconducting properties. The origin of this unique behavior has been suggested to be bipolaron formation of holes in the valence band[14] or the existence of localized states originating from one of the intramolecular orbitals at the top of the valence band.[15] Based on this, our hypothesized quasicrystal within the B-C system is expected to be semiconducting.

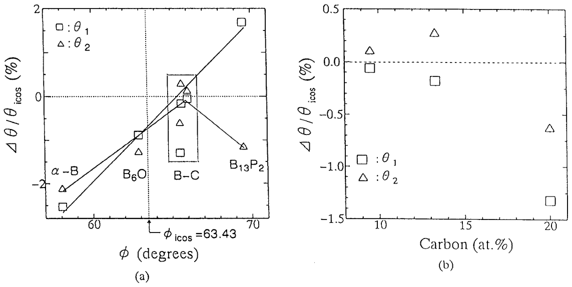

FIG. 2. (a) Distortion variations of the B_{12} icosahedron ($\Delta\theta_1$ and $\Delta\theta_2$) and rhombohedral axis angle (ϕ) in α-rhombohedral-type crystalline structures. θ_1 and θ_2 are the two measured angles between three of the six icosahedral basic vectors and the icosahedron's threefold axis. (b) Carbon concentration dependence of the distortion.

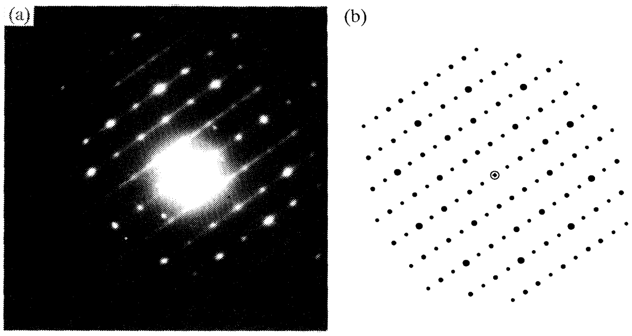

FIG. 3. (a) Electron-diffraction pattern of the transformation phase of $B_{97}C_3$ amorphous film after being heated for 10 min at 1400 °C. (b) Calculated pseudo-tenfold diffraction pattern of the 1/0-1/0-0/1 orthorhombic approximant phase.

Using EPMA and ESCA results, we verified the composition of a prepared amorphous film of $B_{81}C_{19}$ to be the same as that of the initial mixed powder. The powder XRD spectra for B-C system evaporated films have broad maxima characteristics in their amorphous phase.[2,3] Films with nominal composition $B_{100-x}C_x$ ($x=0$, 3, 5, 7, 10) were subsequently produced and then annealed between 800 and 1400 °C.

The amorphous phase for $x=10$ starts to crystallize at 1200 °C into the B_4C structure, whereas that for $x=3$, 5, and 7 starts at 1150 °C. In the latter case, we observed the appearance of diffraction peaks which cannot be indexed by any phase in the equilibrium phase diagram, as well as those which can be indexed by the B_4C structure. Figure 3(a) shows the electron-diffraction pattern of $B_{97}C_3$ amorphous film after being heated 10 min at 1400 °C, where a pseudo-tenfold electron-diffraction pattern is apparent. The XRD pattern of the $B_{95}C_5$ amorphous film after being heated 10 min at 1360 °C is shown in Fig. 4(a). Both diffraction patterns were analyzed and identified as belonging to the newly discovered 1/0-1/0-0/1 orthorhombic aproximant phase of the icosahedral quasicrystal. The orthorhombic lattice parameters *a*, *b*, and *c* are, respectively, 0.56, 0.88, and 0.90 nm, being close to those of the $B_{25}C$ tetragonal phase. The structure of this approximant phase is believed to be constructed with stacked prolate rhombohedra (Fig. 5), and can be considered as being a structure having a twin boundary at every interface of the rhombohedral unit cell along one of the twofold axes. It should be noted that this is a completely different structure from that of the $B_{25}C$ tetragonal phase. Figures 3(b) and 4(b) show the calculated patterns for this approximant phase using a B_4C unit cell in place of each prolate rhombohedron, where the results fairly well reproduce the experimental patterns [Figs. 3(a) and 4(a)]. Figures 4(c) and 4(d), respectively, show American Society for Testing Materials (ASTM) data for the B_4C and $B_{25}C$ phases. The observed

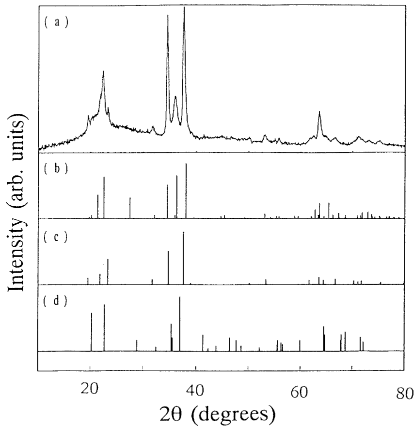

FIG. 4. (a) Powder x-ray-diffraction spectrum from Cu-$K\alpha$ radiation of the transformation phase of $B_{95}C_5$ amorphous film after being heated for 10 min at 1360 °C. (b) Calculated spectrum of the 1/0-1/0-0/1 orthorhombic approximant phase. (c) ASTM data of B_4C phase and (d) ASTM data of $B_{25}C$ phase.

pattern of Fig. 4(a) is notably different from these phases, although slight traces of the B_4C phase are evident. The streaks present in Fig. 3(a) and the broadness of peaks in Fig. 4(a), which do not appear in the B_4C structure, indicate a stacking disorder of the prolate rhombohedra, i.e., the existence of a stacking arrangement similar to that in the B_4C structure.

In summary, the existence of an icosahedral quasicrystalline structure constructed with the prolate rhombohedron (the unit cell of α-rhombohedral boron) and oblate rhombohedron (a hypothetical structure) is considered theoretically possible, at least as a metastable phase, based on the results of our molecular-orbital calculations.

We discover a type of 1/0-1/0-0/1 orthorhombic approximant phase in the quasicrystalline range of carbon composition in the B-C system, which was estimated using the crystallographic data of the α-rhombohedral boron type crystal (0-9 at. % C). However, since this structure is only constructed with the prolate rhombohedron, our theoretical prediction cannot be validated.

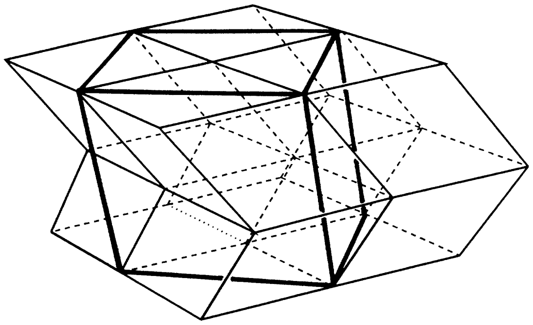

FIG. 5. Unit-cell structure of the 1/0-1/0-0/1 orthorhombic approximant phase showing the stacking of prolate rhombohedra.

This 1/0-1/0-0/1 orthorhombic phase is a higher approximant than the 0/1-2/0 rhombohedral phase, i.e., the B_4C structure, because the unit-cell volume of the former is four times greater than that of the latter. Moreover, the rhombohedral axis angle of the former (64.5°) is closer to the icosahedral angle ($\phi_{\text{icos}} = 63.43°$) than that of the latter (65.5–66.0°). It is realized that our search for a truly semiconducting quasicrystal was not actually realized since no oblate rhombohedron was contained in the discovered approximant phase. Nevertheless, we consider our approach to be a valuable step in the right direction.

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[*] FAX: +81-3-3815-8363.

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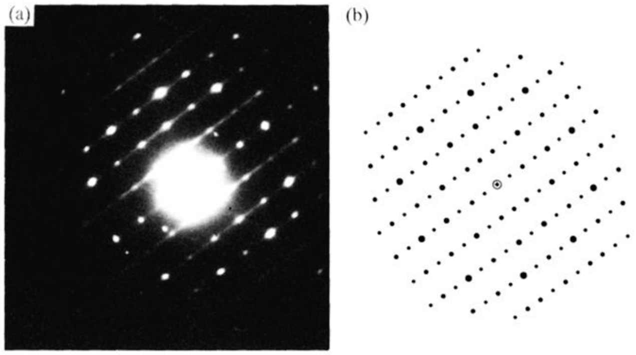

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