

A Unified Picture for Icosahedral Cluster Solids of Third Group Elements

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Some discussions are presented to get the unified picture for the aluminum-based and the boron-based compounds constructed of icosahedral clusters. Twelve atoms icosahedra, Al_{12} and B_{12} , have a covalent bonding nature, commonly, though thirteen atoms ones, Al_{13} and B_{13} , are metallic. There are vacant sites in the second shell of the multi-shell structure for boron ones. When these sites are occupied by dopant metal atoms, the cluster structure, DC conductivity and optical conductivity of the boron compound approach to those of the aluminum ones. Photocurrent is observed in aluminum compounds as well as in boron ones. It is considered that the photocurrent arises from carrier excitation across the pseudogap.

1. INTRODUCTION

Both the aluminum and the boron belong to the third group of the periodic table and have some solid state structures which are constructed of icosahedral clusters. In aluminum-based systems, we know several kinds of icosahedral quasicrystal and approximant, and in boron-based systems, icosahedral boron-rich solids are known [1,2]. Figure 1 shows the conductivity at 0K and the periodic length of the crystalline structure for some aluminum- and boron-based systems. The conductivity at 0K is finite for metals and zero for semiconductors. The periodic length is finite for crystalline approximants and infinite for quasicrystals. The aluminum-based icosahedral

compounds, which can produce the quasicrystalline structure and is originally metallic, approaches to a semiconductor, i.e., the electrical conductivity at 0K is decreasing to 0 with increasing the structural order [3,4]. The boron-based one, which produce the crystalline structure and is semiconducting, approaches to a quasicrystal, i.e., the unit cell size is increasing by tuning the composition [5].

In this paper, some discussions are presented to get the unified picture for the above two groups of materials constructed of the icosahedral cluster.

2. CLUSTER STRUCTURE

Both the compounds have the multiple shell structure of clusters with the icosahedral symmetry. Table 1 compares the multiple shell structures in the aluminum- and the boron-based systems. For aluminum-based systems, there are two types of icosahedral alloys, the Frank-Kasper- (FK-) type and the Mackay-Icosahedral- (MI-) type. As for the Al-Li-Cu Frank-Kasper phase (the 1/1 cubic approximant phase) [6], the first shell is an icosahedron, the second is a triacontahedron, which is constructed of a dodecahedron and an icosahedron, and the third is a truncated triacontahedron (a soccer-ball cluster). In the case of the Al-Mn-Si MI-type 1/1 cubic approximant [7], the second shell is constructed of an icosahedron and a truncated icosahedron instead of an dodecahedron, and the third shell is absent. In both

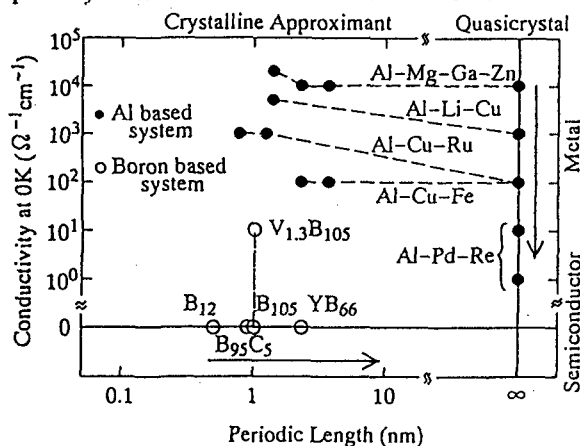


Fig. 1. DC conductivity at 0K and periodic length of structure for some icosahedral aluminum-based and boron-based systems.

Table 1. Multiple shell structures in aluminum-based and boron-based systems.

	first shell	second shell	third shell
FK-type Al-Li-Cu	icosahedron	triacontahedron (=icosahedron +dodecahedron)	truncated icosahedron (=soccer-ball cluster)
MI-type Al-Mn-Si	icosahedron	icosahedron +truncated icosahedron	—
β -rhombohedral YB ₆₆	icosahedron	icosahedron + <u>dodecahedral vacant sites</u>	truncated icosahedron (=soccer-ball cluster)

approximant structures, each multiple shell cluster is located at a vertex and a body centered site. The structures of both type quasicrystals are considered to be constructed of their respective multiple shell clusters.

In the β -rhombohedral boron structure, B₈₄ cluster is located at each vertex of the rhombohedral unit cell [8]. The cluster is constructed by connecting twelve B₆ half icosahedra to the center B₁₂ along the five fold axes. This structure is considered to be the 0/1-2/0 rhombohedral approximant. For the B₈₄ cluster, as shown in Fig. 5, the first shell is an icosahedron, the second is an icosahedron, and the third is a soccer-ball cluster.

Commonly in both compounds, the first shell is the icosahedron and the third shell is the soccer ball cluster (this is missing in the MI-type). Although the second shell is constructed of the icosahedron and the dodecahedron (FK-type) or the truncated-icosahedron (MI-type) in the aluminum compounds, the latter is missing in the boron compounds. The atom density in the second shell in the boron compounds is low, and it is considered that there are vacant sites in the second shell. A part of the dodecahedral vacant sites are known as the doping sites described in the section 4.

The fact mentioned above is the origin of difference in coordination number for the both compounds. In aluminum-based systems, the coordination number of most atoms is 11 or 12 like usual metallic systems. In boron-based systems, it is usually 6, which is smaller than that of metallic systems but is larger than 2, 3 or 4, that of usual covalent bonding systems.

3. ELECTRONIC STATES OF ICOSAHEDRAL CLUSTER

There are two types icosahedral cluster, thirteen atoms (with the center atom) and twelve

atoms (without the center atom) ones. Packing fraction of the thirteen atoms icosahedron is 0.727, which is smaller than 0.756, that of thirteen atoms close packed structure, but is greater than 0.680, that of body centered cubic structure. The thirteen atoms icosahedron must be stable under metallic bonding and may be called to be a metallic cluster. On the other hand, packing fraction of the twelve atoms icosahedron is 0.520, which is much smaller than those of metallic clusters and approaches to 0.340 that of the diamond structure. The twelve atoms icosahedron can not be stable under metallic bonding.

The twelve atoms icosahedron is one or only one solution to produce covalent bonding structure for the third group elements with three valence electrons. Typical covalent bonds in semiconductors are sp³ for the fourth group elements (Si, Ge and Sn), sp² for also the fourth one (C), p³ for the fifth one (P) and p² for the sixth ones (Se and Te). These bonds are two-centered ones, in which each of two atoms provides one electron and they share two electrons. When an atom produce one bond, number of its owned electrons increases by one. The fourth, fifth and sixth group elements can construct apparently the closed shell of s and p orbitals by producing four, three and two bonds, respectively. However, the third group elements can not construct the closed shell in the same way. Since they are electron deficient to complete the covalent bonding, they must construct the multi-centered covalent bonds to save electrons. For example, in the simple three centered bond, each of three atoms provides two thirds electron and they share two electrons. This bonding is realized in the inter-icosahedral bonds in the α -rhombohedral boron [9]. The intra-icosahedral bonding of twelve boron atoms icosahedron (B₁₂) is considered to be multi-centered one. Each atom of the B₁₂ has one outer bond, which is usual two-centered bond, along the five-fold axis. Each atom provide one electron to

Table 2. The stable position outside of the icosahedral clusters of aluminum and boron for some elements.

clusters	elements (X)		
	H	Li	Al or B
Al ₁₂ +X B ₁₂ +X	v	v	ec
Al ₁₃ +X B ₁₃ +X	f	f	f

this outer bond and two electrons to the intra-icosahedral bonds. Number of the electrons distributed to each triangle of the B₁₂ is $2 \times 12 / 20 = 1.2$. Since each atom has one outer bond and five neighbors of the triangle, it shares $2 + 1.2 \times 5 = 8$ electrons and can produce a closed shell.

Electronic states of the twelve atoms icosahedron of boron and aluminum were calculated using the *ab initio* molecular orbital method [10]. The B₁₂ cluster is the most stable at the B-B distance of 0.175 nm, which is consistent with the experimental value, and can be stable at the distance shorter than 0.2 nm. The Al₁₂ cluster can be stable at the Al-Al distance shorter than 0.255 nm, which is similar to those in the icosahedral aluminum compounds and shorter than 0.28 nm, that in fcc Al structure. Under the condition of the shorter atom-atom distance, the electronic states of the B₁₂ and Al₁₂ icosahedral clusters are exactly the same.

Table 2 shows the stable position outside of the icosahedral clusters of aluminum and boron for some elements. They are the results of structural optimization using the MOPAC program [11]. Three positions described by v, ec and f are shown in Fig. 2. As for the thirteen atoms icosahedron, Al₁₃ or B₁₃, all of three elements is stabilized at the position of f, which is the stable one for the rigid sphere packing. On the other hand, for the twelve atoms clusters, Al₁₂ or B₁₂, H and Li are stabilized at the position of v and terminate the dangling bond of the B₁₂, and Al or B is stabilized at the position of ec and looks like constructing the three-centered bond with two atoms in the Al₁₂ or B₁₂. These situation shows also that the Al₁₃ and B₁₃ are metallic and the Al₁₂ and B₁₂ have a covalent bonding nature.

These situations show the Al₁₂ with Al-Al distances shorter than 0.255 nm has the covalent bonding nature. It is interesting to mention that electronic transport properties [12] are rather metallic in Mg-Al-Zn quasicrystals constructed of the Al₁₃, and are far from that of usual metals in Al-

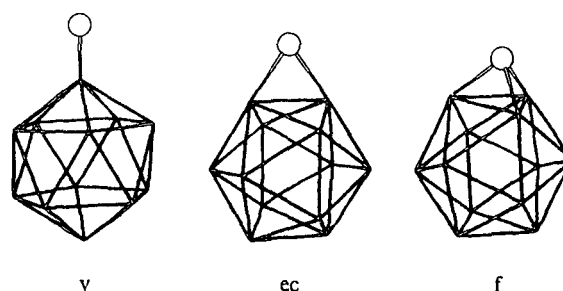


Fig. 2. Three stable atom positions outside of icosahedral clusters of boron

Li-Cu and MI-type quasicrystals constructed of the Al₁₂.

4. ELECTRONIC TRANSPORT

Figure 3 (a) shows the temperature dependence of DC conductivity, σ , for some aluminum-based icosahedral quasicrystals [12,13]. Electrical conductivity of the quasicrystal is extremely low as compared with usual metals because of the pseudogap and the localization tendency of electrons near the Fermi level [12]. Up to now all the discussions concerning an interpretation of the conduction mechanism of quasicrystals seem to be clarified mainly into two pictures [13]. In one of them, it is considered that temperature variation of the carrier density, n , plays an essential role in that of conductivity, $\sigma = ne\mu$. On the other hand in the other, it is supposed that temperature dependence of the mobility, μ , is responsible for that of σ . Band structure effect, which is based on spiky band and narrow gap in the density of states both with the width of about 10 meV, plays an significant role in the former. In the latter, localization effects such as weak-localization effect are considered to explain electronic transport of quasicrystals and even hopping conduction of electrons in rather strongly localized states has been proposed by several authors. The value of σ of the quasicrystals is comparable with that of doped semiconductor as shown in Fig. 3, and above two pictures for conduction mechanism are not metallic but semiconductor-like already.

Figure 3 (b) shows the temperature dependence of DC conductivity for Li- and some transition metals-doped β -rhombohedral boron crystals (B_{10s}) [14,15]. It shows that σ increases by several orders of magnitude after metals-doping of several at.% and has the variable range hopping

(VRH) type behavior. According to Mott's law of VRH conduction [16], σ is expressed as

$$\sigma = \sigma_0 \exp[-(T_0/T)^{1/4}], \quad T_0 = 60\alpha^3/\pi N(E_F)k_F, \quad (1)$$

where α^{-1} is the localization length of the wave function of the carrier and $N(E_F)$ is the density of states at the Fermi energy. Figure 4 shows the metal concentration, x , dependence of T_0^{-1} . In the case of usual doping, e.g., an impurity element in silicon or an alkali metal in C_{60} , T_0^{-1} increases monotonously with increasing dopant concentration. First, $N(E_F)$ increases, then α^{-1} increases near the metal-insulator transition, and it becomes infinite at the transition. As shown in Fig. 4, in the case of Li, Cu and Ni, unusually, T_0^{-1} increases, reaches at the maximum and decreases with further increasing x .

This unusual behavior can be explained as follows [14,15]. Since the B_{12} is two electrons deficient, one of the highest four-fold degenerated intra-icosahedral orbitals is empty and separate from the occupied ones by the distortion of the B_{12} . It is thought that this unoccupied orbital leads to an intrinsic acceptor band above the valence band edge in the β -rhombohedral boron [17]. Doped electrons from metal atoms occupy this band and show VRH conduction between localized states of the band. In this case, when number of electrons in this band exceeds half of all states in it, T_0^{-1} may change from increase to decrease with increasing x . Since the maximum values of T_0^{-1} in Fig. 4 depend on the kind of dopant metals, the rigid band model can not be applicable. This situation can be explained by considering the hybridization of the impurity levels of the dopant metals and the intrinsic acceptor band of β -rhombohedral boron. Table 3 and Fig. 5 shows the doping sites and their occupancy for each metal atom in the rhombohedral unit cell of β -rhombohedral boron. The structure of the unit cell can be viewed in two ways as shown in Fig. 5 (a) and (b). As shown in (a), the A_1 -hole is the nearest to the B_{12} and has four neighbors of them, thus, the level of the metal occupying the A_1 -hole must be hybridized with the intrinsic acceptor level of the B_{12} . It is found that the greater the occupancy of the A_1 -hole in Table 3 is, the greater the maximum value of T_0^{-1} in Fig. 4 is. As for V-doping, the metal-insulator transition may occur at the highest concentration.

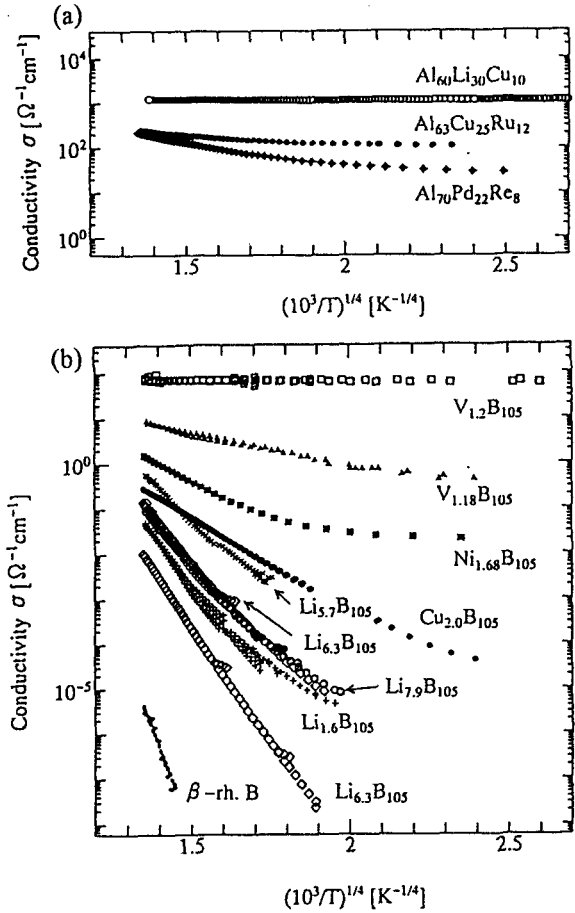


Fig. 3. Temperature dependence of DC conductivity for some (a) icosahedral aluminum-based quasicrystals and (b) metal-doped β -rhombohedral boron crystals.

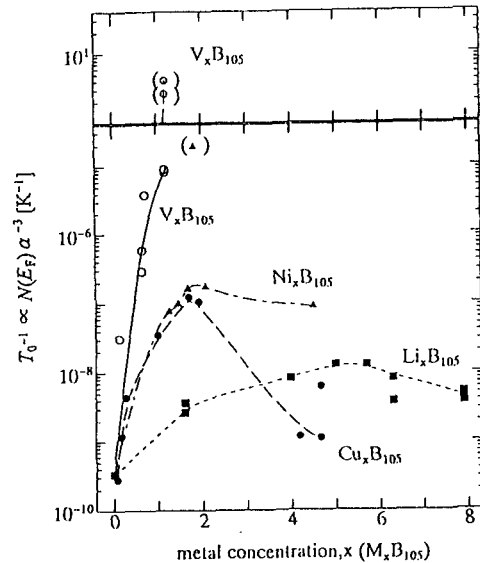


Fig. 4. Metal concentration dependence of T_0^{-1} of the variable range hopping formula for some metal-doped β -rhombohedral boron crystals.

Table 3. Occupancy of doping sites in metal-doped β -rhombohedral boron.

composition	doping sites occupancy (%)		
	A ₁ -hole 2 sites/unit cell	E-hole 2 sites/unit cell	D-hole 6 sites/unit cell
Li _{7.9} B ₁₀₅	0.0	100.0	100.0
Cu _{4.2} B ₁₀₅	7.9	33.4	59.9
Ni _{2.16} B ₁₀₅	44.7	0.0	21.6
V _{1.62} B ₁₀₅	64.0	0.0	5.3

In Fig. 6 (a) and (b), the spectra of the optical conductivity of some boron-rich structures is compared with the according spectra of the Al-Pd-Re quasicrystals measured with the same equipment [18], and additionally for comparison with the spectra of Al-Cu-Fe [19] and Al-Mn-Pd [20] reported from literature. Characteristic features of optical conductivity in the aluminum-based quasicrystals has been considered to be a very small Drude contribution, which is not apparent in the spectra as shown in Fig. 6 (b), and a big contribution of interband transition across the pseudogap [19,20]. Although the spectra of the Al-Pd-Re quasicrystals in Fig. 6 (b) has the same features, the value of conductivity is one order smaller than those of the others and than even those reported previously for the same alloy system [21]. The optical conductivity of the same Al-Pd-Re sample in Fig. 6 (b) was determined by spectroscopic ellipsometry in the 2.5-7.5 eV range [22], which has no ambiguity of the Kramers-Kronig transformation. The value at the lowest energy, which corresponds to 20000 cm^{-1} , is consistent with that in Fig. 6 (b). Therefore, the origin of discrepancy between the conductivity values in Fig. 6 (b) and those reported previously in the same Al-Pd-Re system is considered to be the ambiguity of the Kramers-Kronig transformation or the large sample dependence of physical properties in this alloy systems.

It is interesting to mention that, as shown in Fig. 5 (b), the A₁-hole is a part of the dodecahedral vacant sites in Table 1 in section 2, which are missing in the second shell in the boron compounds compared in the FK-type aluminum compounds. Therefore, when the multiple shell cluster structure of the boron compound (β -rhombohedral boron) approaches to that of the aluminum compounds (especially FK-type Al-Li-Cu) by doping to A₁-hole, not only the behavior of

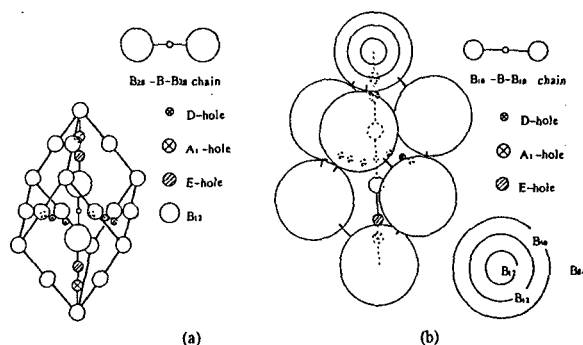


Fig. 5. Crystalline structure of β -rhombohedral boron shown in two different ways, (a) and (b).

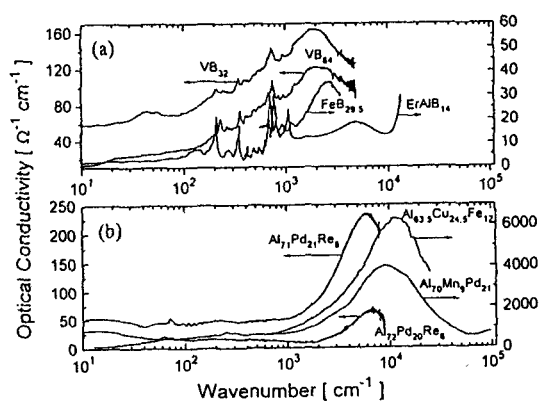


Fig. 6. Optical conductivity spectra for some (a) metal-doped β -rhombohedral boron crystals and (b) icosahedral aluminum-based quasicrystals.

DC conductivity but also that of optical conductivity of the former seem to approach to those of the latter.

5. PHOTOCONDUCTIVITY

Photoconductivity is widely used to investigate photocarrier generation process, localized states in a band gap and transport properties in semiconductor. We are applying this technique to both boron system and aluminum system. Modulated photocurrent method is very sensitive measurement. An intensity modulated monochromatic light is illuminated on a sample between two electrodes, and consequent photocurrent (the magnitude and the phase shift between the excitation light and the photocurrent) is measured with a lock-in amplifier. For a conventional semiconductor, the profile of localized states can be estimated by analyzing the frequency dependence of the phase shift on the basis of a simple model which assumes band-to-band excitation, unipolar photocurrent and trap-limited conduction in extended states [23].

Figure 7 (a) shows the frequency dependence of photocurrent for β -rhombohedral boron (solid circle). The data was analyzed by the above model. The photocurrent was calculated from the phase shift data (open circle in Fig. 7 (a)) and we found, however, that it is inconsistent with observed one. As a consequence, the photoconduction process in β -rhombohedral boron isn't so simple as assumed in the model, and it is considered that the intrinsic acceptor level plays an important role in the process. An analysis taking account of the acceptor level is now in progress.

As shown in Fig. 7 (b), we succeeded in measuring photocurrent in Al-Pd-Re quasicrystal for the first time. The fact that photocurrent is observed in quasicrystal is a direct evidence for existence of the pseudogap. The same analysis as done for β -rhombohedral boron was carried out, and we also found an inconsistency between observed and calculated photocurrent. Such a situation is a common feature for the both system.

6. CONCLUSION

The twelve atoms icosahedra, Al_{12} and B_{12} , have the same molecular orbitals, i.e., covalent bonding electronic structures, though the thirteen atoms ones, Al_{13} and B_{13} , are metallic. Both the aluminum- and the boron-based compounds have the multiple shell structure of clusters with the icosahedral symmetry. There are dodecahedral vacant sites in the second shell of the boron one. When a metal atom occupies a part of the dodecahedral vacant sites in β -rhombohedral boron, hybridization between a level of the metal atom and the intrinsic acceptor level occurs, and the electronic

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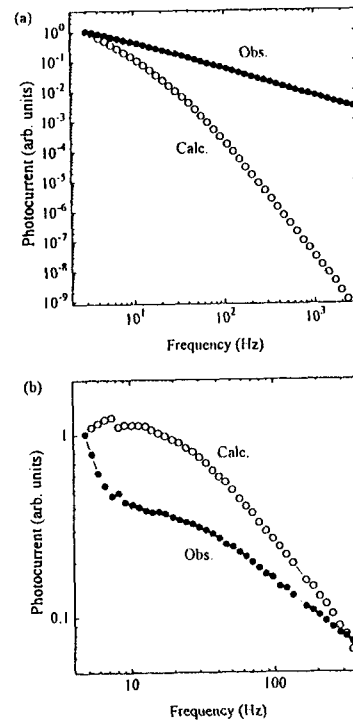


Fig. 7. Frequency dependence of photocurrent for (a) β -boron and (b) $Al_{70.5}-Pd_{21}-Re_{8.5}$. Open circles are calculated ones from phase shift data.

properties of the β -boron approaches to the metal-insulator transition. By this doping, the cluster structures, the behavior of DC conductivity and the optical conductivity spectra for the β -boron approach to those of the aluminum ones. Photocurrent was observed in Al-Pd-Re quasicrystal, and this result supports the existence of the pseudogap.

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