Metallic-covalent bonding conversion in boron icosahedral cluster solids studied using electron localizability indicator

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Abstract. The metallic-covalent bonding conversion of clusters in boron icosahedral cluster solids was studied using the electron density and electron localizability indicator (ELI). The comparison of B₁₂ and B₁₃ clusters revealed that the bonding conversion from covalent to metallic one involved a decrease in both the electron density and ELI between two boron atoms in the clusters. On the other hand, in the case of vanadium doping into the B₄₈ cluster surrounding the vanadium doping site in β-rhombohedral boron, the electron density increased in some parts of the cluster and decreased in other parts. This uncertainty regarding the bonding conversion was clarified by the use of the ELI. The ELI analysis clearly revealed that bonding conversion occurs in the cluster surrounding the vanadium doping site.

1. Introduction
Some of the solids based on group III elements are known to form icosahedral cluster solids (ICSs) consisting of clusters with icosahedral symmetry such as icosahedral clusters with 12 boron atoms (B₁₂) or aluminum atoms (Al₁₂) [1]. The icosahedral clusters as structural units impart peculiar characteristics to ICSs. β-rhombohedral boron (β-B) has been investigated extensively as the most typical ICS consisting of boron [2-4]. It has been revealed that metal doping into β-B can control the bonding nature in and between the clusters, which results in the variation of physical properties such as the electrical and thermal conductivities and the Seebeck coefficient [5-10]. Among the dopant metals, vanadium (V) has attracted much interest because doping of only about 1 at.% into β-B changes the temperature dependence of the electrical conductivity of β-B to an almost metallic dependence [5,7]. The origin of this sensitivity to doping has been considered to be the metallic-covalent bonding conversion (MCBC) of the clusters [1,11]. The MCBC may also be referred to as a multicenter – two-center bonding conversion.

The MCBC in ICSs has been considered as a conversion of the bonding nature of the bonds in and around the cluster that occurs as a result of the occupation of the cluster center by an atom. The MCBC has also been discussed in comparison with the metal-insulator transition (MIT) [1, 7, 8, 12-14]. The MCBC is commonly observed both in boron-rich ICSs (B-ICSs) and aluminum-rich ICSs (Al-ICSs) and can be clearly distinguished from the MIT. α-AlReSi and Al₁₂Re are typical Al-ICSs and have an Al₁₂ icosahedral cluster in the structure without and with an atom at the center of the
It has been suggested that the MCBC occurs in these ICSs on the basis of electron density analysis [12,13]. The above-described change in the electrical conductivity by doping a small amount of V in β-B as one of the B-ICS may also originate from the MCBC around the V doping site. The V atom is known to occupy the A1 site which is located at the center of the B_{48} cluster. The B_{48} cluster is located at the sharpest vertex among the rhombohedron and the tetrahedron made of four B_{12} clusters. Hosoi et al analyzed the electron density distribution in the B_{48} cluster upon V-doping [14] and discussed the MCBC on the basis of the decrease in the electron density at the midpoint of B-B bonds. Recent works on the MCBC in B- and Al-ICSs have focused on the comparison of electron density between clusters without and with an atom occupying the cluster center.

Recently, the electron localization function (ELF) and the electron localizability indicator (ELI) have been proposed as methods for analyzing the localization in chemical bonding. The ELF is a function proposed by Becke and Edgecombe in 1990 for analyzing the nature of chemical bonding [15] and has been used to analyze a wide range of materials from organic molecules to solids such as Li and V metals [16,17]. The ELF was also applied to analyze boron clusters to clarify the existence of bonding among more than two atoms [18-20]. The quantitative analysis of metallic and covalent bonding nature has also been performed on carbon-based solids with a diamond structure, as well as on silicon and β-tin [21], and on intermetallic compounds such as CaAl_{2} and BaAl_{4} [22]. Although the ELF has contributed to the investigation of the bonding nature, Kouhout has suggested that the use of the energy of a free electron gas causes the discussion of the localization of the electron to be unclear. He proposed the ELI by investigating the spatial distribution of same-spin electron pairs [23,24]. The ELI consists of the density function of the same-spin electrons.

The ELI in direct space is defined by the following three equations (1)-(3) [23-25]. Its major difference from the ELF is the exclusion of the free electron gas energy. The ELI takes a value greater than or equal to zero but is not limited to less than or equal to one as in the case of the ELF.

\[ \gamma(r) = \rho(r) \tilde{V}(r) \]  
\[ \tilde{V}(r) = \left[ \frac{12}{G(r)} \right]^{3/8} \]  
\[ G(r) = \sum_{i<j} \left| \phi_i \nabla \phi_j - \phi_j \nabla \phi_i \right|^2 \]

The ELI was defined to monitor the number of σ-spin electrons necessary to locally build a fixed fraction of a σ-spin electron pair [24,26], which is given in the continuous representation as the position where the Fermi hole curvature \( G \) for a time-independent single-determinant wave function from orbitals \( \phi \) leads (equations 2 and 3). Thus, the ELI distribution in position space can be represented as a product of two scalar fields in the position space (equation 1): the well-known σ-spin electron density \( \rho \) (a one-particle property), and the so-called pair-volume function \( \tilde{V} \) (a two-particle property), because it is proportional to the volume needed to locally encompass a fixed fraction of a same-spin electron pair of σ-spin electrons [27].

The larger the ELI value is, the more the electrons are localized. The ELI has also been applied to molecules and solids [24-26,28]. The objective of this paper is to discuss the MCBC of boron clusters in B-ICSs, on the basis of ELI analysis. Electronic-state calculations on the clusters extracted from B-ICSs were performed without and with the occupation of an atom at the center of the clusters.

2. Calculation method

Figure 1 shows clusters used for the analysis. The ELI analysis was first applied to quantitatively evaluate the bonding conversion using two clusters having typical covalent bonding (Si_{17}) and typical
metallic bonding (Al\textsubscript{19}) to clarify how the metallic and covalent bonding natures are revealed in the ELI distribution. Accordingly, we compared the ELI distributions of pairs of clusters without and with an atom at the cluster centers. The cluster pairs are boron clusters (B\textsubscript{12}\textsuperscript{2+} and B\textsubscript{13}\textsuperscript{-}) and boron clusters terminated by hydrogen atoms (B\textsubscript{12}H\textsubscript{12}\textsuperscript{2-} and B\textsubscript{13}H\textsubscript{12}\textsuperscript{+}; and B\textsubscript{48}H\textsubscript{36} and VB\textsubscript{48}H\textsubscript{36}). The B\textsubscript{48}H\textsubscript{36} cluster corresponds to the structure surrounding the A\textsubscript{1} site in β-B.

Electronic-state calculations were performed on all clusters using GAUSSIAN98. The structures of Si\textsubscript{17}, Al\textsubscript{19}, B\textsubscript{48} and VB\textsubscript{48} were extracted from the structures determined by X-ray powder diffraction. The electronic-state calculations of Si\textsubscript{17} and Al\textsubscript{19} were performed at the DFT-B3LYP theory level using the 6-31G(d) basis set. The dangling bonds of B\textsubscript{48} and VB\textsubscript{48} were terminated by hydrogen atoms and the electronic-state calculations were performed at the HF theory level using the 3-21G basis set. The optimized structures of B\textsubscript{12}\textsuperscript{2+}, B\textsubscript{12}H\textsubscript{12}\textsuperscript{2-} and B\textsubscript{13}H\textsubscript{12}\textsuperscript{-} were refined at the DFT-B3LYP theory level using the 6-31G(d) basis set. The structure of B\textsubscript{13}\textsuperscript{-} was determined by the radius between the atom at the cluster center and B\textsubscript{12} at the DFT-B3LYP theory level using the 6-31G(d) basis set because B\textsubscript{13}\textsuperscript{-} did not have a stable structure. The ELI was calculated using DGrid [29] in direct space.

3. Results and discussion
To evaluate how the metallic and covalent bonding natures are reflected in the ELI distribution, both the electron densities and the ELI values of the electrons in the Si\textsubscript{17} cluster with typical covalent bonding and in the Al\textsubscript{19} cluster with typical metallic bonding were compared. As shown in figure 2(a), the electrons in the Si\textsubscript{17} cluster are concentrated between pairs of Si atoms in the cluster, while figure 2(b) shows that there is no concentration of electrons between Al atoms in the Al\textsubscript{19} cluster, as expected from the nature of metallic bonding. According to the spatial distribution of ELI in figures 3(a) and (b), a clear two-center covalent bond between Si-Si pairs in the Si\textsubscript{17} cluster was observed and the maximum value of ELI between the cluster center and the nearest-neighbor atoms is 2.39, while ELI in the Al\textsubscript{19} cluster is 1.57, indicating as more metallic bonding than that in Si\textsubscript{17}.
The above discussion of metallic and covalent bonding appears to be reasonable. However, in the case of a smaller difference in the bonding nature, it is difficult to observe a difference between equidensity surfaces, and a more quantitative analysis is necessary. As preparation for a more difficult case, the following analysis is performed for the typical case of Si\textsubscript{17} and Al\textsubscript{19} clusters. Figure 4 shows ELI distribution histograms of the electrons in the Si\textsubscript{17} cluster (a), the Al\textsubscript{19} cluster (b) and the difference between them (c). The ELI values were obtained by integration from the position of the cluster center atom up to the distance corresponding to that between the center atom and the nearest neighbor atom. The histogram for the Si\textsubscript{17} cluster (figure 4(a)) indicates a relatively high ELI of approximately 2.0 with no concentration at a specific ELI level. This represents the covalent nature of the bonding electrons illustrated in figure 3(a). On the other hand, the histogram for the Al\textsubscript{19} cluster (figure 4(b)) is concentrated at an intermediate level of approximately 1.5, which corresponds to the metallic nature of the bonding electrons illustrated in figure 3(b). Accordingly, as shown in figure 4(c), the difference between the ELI for the Si\textsubscript{17} and Al\textsubscript{19} clusters is positive at the intermediate level and negative elsewhere, which represents the change in ELI due to the change in the bonding nature from covalent to metallic. Following this discussion, the change in the bonding nature of the cluster from covalent to metallic will be discussed on the basis of the increase in the frequency of the ELI at the intermediate level (approximately 1.5).

**Figure 2.** Equidensity surface (isosurface) at an electron density of 0.47 e/Å\textsuperscript{3} of in (a) Si\textsubscript{17} and (b) Al\textsubscript{19} clusters. The spheres in (a) and (b) denote the Si and Al atoms, respectively.

**Figure 3.** Spatial distribution of ELI at ELI=2.0 for (a) Si\textsubscript{17} and (b) Al\textsubscript{19} clusters. The spheres in (a) and (b) denote the Si and Al atoms, respectively. X: The position of maximum ELI between the atom at the cluster center and the nearest neighbor atom. The ELI value for Si\textsubscript{17} is 2.39 and that for Al\textsubscript{19} is 1.57.
Figure 4. Histogram of ELI values for (a) Si$_{17}$ and (b) Al$_{19}$ clusters. (c) shows the difference between the frequencies in (a) and (b).

Figure 5 shows a comparison of the spatial distribution of the electron density of the B$_{12}^{2+}$ (a) and B$_{13}^{-}$ (b) clusters. The electron distribution in the B$_{12}^{2+}$ cluster along the line connecting neighboring boron atoms suggests the existence of B-B covalent bonds. The equidensity surface at an electron density of 0.94 e/Å$^3$ disappears at the midpoint between the boron atoms in the B$_{13}^{-}$ cluster, implying weaker covalent bonding than that in the B$_{12}^{2+}$ cluster. As shown in figures 5(c) and (d), the electron distribution corresponding to B-B covalent bonds in the B$_{13}H_{12}^{2-}$ cluster also disappears in the B$_{13}H_{12}^{-}$ one, though the value of electron density is 0.78 e/Å$^3$ and lower than that for the B$_{12}^{2+}$ and B$_{13}^{-}$ clusters. However, the comparison between B$_{48}H_{36}$ (figure 5(e)) and VB$_{48}H_{36}$ (figure 5(f)) suggests that the electron density decreases in the bottom plane of the B$_{48}$ tetrahedron of B$_{12}$ clusters and increases on the ridge line of the tetrahedron (the rhombohedron of β-B) owing to the occupation of the center of the tetrahedron (the A$_1$ site) by the V atom. In contrast to the case of B$_{12}$ clusters, no overall decrease in the bonding electron densities among the B-B bonds surrounding the cluster center was observed in the B$_{48}$ clusters.

Figure 6(a) shows the ELI spatial distribution of the B$_{12}^{2+}$ cluster. It reveals the existence of a dodecahedral bonding frame in the cluster. On the other hand, no localized region is observed in the B$_{13}^{-}$ cluster (figure 6(b)) and the bonding nature in the cluster was found to be metallic. The B$_{12}H_{12}^{2-}$ and B$_{13}H_{12}$ clusters, shown in figures 6(c) and (d), respectively, had the same spatial distributions as the clusters without hydrogen termination in figures 6(a) and (b). The comparison of the B$_{48}H_{36}$ and VB$_{48}H_{36}$ clusters in figures 6(e) and (f), respectively, reveals that the region with localized electrons shrinks upon the occupation of the cluster center by a V atom. A difference of the change in the electron density from those in the previous two cluster pairs is that the more highly localized region does not grow along the ridge line of the tetrahedron (the rhombohedron of β-B).
Similarly to the quantitative discussion of the bonding nature of Al$_{19}$ and Si$_{17}$ clusters using the ELI histogram, the difference between the ELI histograms of the B-B bonds surrounding the cluster center for clusters without and with a cluster-center atom was calculated as shown in figure 7. For all cluster pairs -B$_{12}$H$_{12}^2$ and B$_{13}$H$_{12}^+$ clusters, B$_{12}$H$_{12}^2$ and B$_{13}$H$_{12}^+$ clusters, and B$_{48}$H$_{36}$ and VB$_{48}$H$_{36}$ clusters- the frequency of electrons with an intermediate ELI level of approximately 1.5 increased upon the occupation of the cluster center by an atom. This can be interpreted as a change in the bonding nature surrounding the cluster center from covalent to metallic upon the occupation of the cluster center. In particular, in the case of the bonding conversion from B$_{48}$H$_{36}$ to VB$_{48}$H$_{36}$ clusters, the change in the bonding nature is not clear from the spatial distribution of the electron density because electron density increased at some of the bonds and decreased at others. The reason for this change is the increase in the total electron density due to the supply of electrons from the V ion. The increased electron density of some of the bonds may be due to the electron supply, while the decrease in the electron density of others may be due to the bonding conversion. The ELI is not directly affected by the total electron density; thus, it is unaffected by the electron supply indicating an MCBC. In general the ELI analysis revealed that the bonding nature in the B-ICS changes from covalent to metallic owing to the occupation of the center of the clusters by an atom.
Figure 5. Equidensity surface of electron density for clusters (a) B_{12}^{2+}, (b) B_{13}^-, (c) B_{12}H_{12}^{2-}, (d) B_{13}H_{12}^+, (e) B_{48}H_{36} and (f) VB_{48}H_{36}. The sphere in (f) denotes the V atom.
Figure 6. Spatial distribution of ELI for clusters (a) $B_{12}^{2+}$, (b) $B_{13}^-$, (c) $B_{12}H_{12}^{2-}$, (d) $B_{13}H_{12}^+$, (e) $B_{48}H_{36}$ and (f) VB$_{48}H_{36}$. The sphere in (h) shows the V atom.
4. Conclusion

ELI distribution analysis was applied to clarify the MCBC in B-ICS. According to the ELI distribution analysis of an Al\textsubscript{19} cluster as a typical metallic bonding cluster and a Si\textsubscript{17} cluster as a typical cluster containing covalent bonding, the metallic bonding nature is reflected in the ELI distribution as a relative increase in the frequency of the intermediate level (an ELI of approximately 1.5). The occupation of the central site of the B\textsubscript{12} cluster by a boron atom resulted in both a decrease in the electron density and an increase in the frequency of the intermediate level in the ELI distribution. On the other hand, in the case of the occupation of the A\textsubscript{1} site in a B\textsubscript{48} cluster by a V atom, the electron density does not decrease as in the case of the B\textsubscript{12} cluster. On the basis of the change in electron density, the change in the bonding nature of the B\textsubscript{48} cluster is unclear. However, the frequency of the ELI distribution of the B-B bonds around the A\textsubscript{1} site atom clearly increased in the intermediate level upon the occupation of a V atom, which implies that the change in the bonding is reasonably isotropic. The histogram of the ELI revealed that its distribution changed from that of more covalent bonding to that of more metallic bonding upon the occupation of the A\textsubscript{1} site in the B\textsubscript{48} cluster. In conclusion, the ELI analysis revealed that the bonding nature in the B-ICS changes from more covalent to more metallic owing to the occupation of the center of the clusters by an atom.
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