Peculiar Covalent Bonds in α-Rhombohedral Boron

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A peculiar bonding feature of α-rhombohedral boron is found in the electron density distribution of the icosahedral B_{12} cluster. The electron density distribution is obtained by using the maximum entropy method with synchrotron radiation powder data. It clearly shows the characteristic two- and three-center covalent bond network which threads through atoms on the cluster surface. Besides, two kinds of covalent bonds in intercluster space are also shown in detail: a three-center trilaterally formed bond among the three clusters and a two-center bond with a remarkable feature of a bent bond between the clusters. The obtained covalent bonding features indicate the cluster-based nature of this material. [S0031-9007(99)09272-8]

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Owing to its vast variety of crystal structures, boron is one of the most fascinating elements. The most striking structure of boron is that boron atoms form a molecular-like icosahedral cluster in a crystalline state. Such a cluster is usually found in boron rich compounds as well. The simplest structure in which the icosahedron is recognized must be the elemental α-rhombohedral boron (α boron) or related compounds such as boron carbides. Even in such simple structures, lattice dynamics of the boron cluster is complicated and has been stimulatingly argued for a long time. This must be due to their unique structure and bonding nature as well as their transport properties and electronic structures [1–8].

The recent paper by Vast *et al.* settled one of the most controversial problems on the lattice vibrations of α boron [7] but revived the other problem, i.e., which bonds are stronger, intra- or intercluster bonds? They insisted the presence of a stiffer bond in the intracluster than that in the intercluster, which is opposed to previous results by Beckel *et al.* [3]. To explain the lattice dynamics of α boron, they concluded that the intercluster bond is much stronger than the intracluster bonds. In fact, all the structure analyses of α boron reveal that the atomic distance of the intercluster bond is shorter than the intraclusters [9–11].

In this Letter, the detailed electron density distribution of α boron obtained by the maximum entropy method (MEM) is given. The fine electron density distribution will give us an insight into bonds related to an icosahedral cluster of boron and, consequently, into lattice dynamics of boron compounds. Such information will also provide a new aspect of the problem concerned.

α boron is constructed from only one icosahedron in a unit cell (Fig. 1), comprised of crystallographically inequivalent two atomic sites, B1 and B2. The atoms in the B1 site are usually called *polar* atoms, which form upper and lower triangles of an icosahedron. The atoms in the B2 site are called *equatorial*, which form a waving hexagon along the equator of an icosahedron. In this letter, these atoms are abbreviated as p and e, respectively. α boron possesses some uncommon covalent bonds in addition to normal two-center ($2c$) two-electron ($2e$) covalent bonds between neighboring icosahedra. There are intracluster three-center ($3c$) bonds on the twenty triangular planes of an icosahedron and an intercluster $3c$ bond among three icosahedra on a (111) plane of rhombohedral lattice.

Conventional Fourier method and multipole analysis have been employed to obtained a deformation density of α boron [10,11]. A deformation density is the difference between an experimental density and a calculated density of noninteracting neutral atoms. In the calculated densities, no interaction between different atoms is assumed. These methods are necessarily model dependent. The MEM provides an alternative to study electron densities of crystalline materials as an imaging of x-ray diffraction data. In contrast to the conventional methods, the MEM is least biased with respect to unobserved structure factors and can produce a reliable electron density distribution in detail [12,13]. By using the MEM the electron density

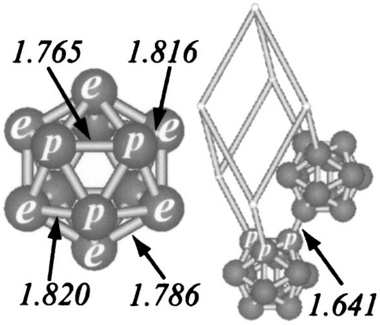

FIG. 1. Crystalline structure of α boron. 12-atom boron icosahedron (left) and rhombohedral lattice (right). Only two icosahedra are shown (right). "p" and "e" denote *polar* (B1) and *equatorial* (B2) atoms, respectively.

distribution can be obtained without any structure models. Furthermore no constraints are imposed except symmetry allowed from experimental structure factors. Assuming the experimental data used are accurate and reliable, the MEM can give a physically meaningful electron density distribution.

A powder sample prepared by chemical vapor deposition was sealed in a 0.3 mm int. diam. silica glass capillary. For good counting statistics, an x-ray powder diffraction pattern was measured using the synchrotron radiation x rays with imaging plates as detectors. The experiment was carried out at Photon Factory BL-6A$_2$, KEK. The wavelength of the incident x ray was fixed at 1.0 Å and exposure time was 1 h. The data were analyzed by a combination of the Rietveld analysis [14] and the MEM analysis [13,15]. First, the Rietveld analysis was done as a preliminary reference after subtracting the broad background of the capillary. The isotropic harmonic model was used for the temperature factors of each atom. The observed structure factors at each data point were evaluated by dividing the observed intensities at the corresponding data point according to the contributions of the individual reflections calculated by the modified Rietveld program [16]. A number of structure factors obtained from the experiment was 170. The reliability factors based on the Bragg intensities R_I and the weighted pattern R_wp were 4.4% and 1.1%, respectively. After the Rietveld analysis, the MEM analysis was done by the computer program, MEED [17], with $90 \times 90 \times 120$ pixels in a hexagonal lattice. For the initial electron density we used uniform electron density, so no information other than obtained structure factors was used in the analysis. The R factor based on the structure factors R_F and weighted R factor R_W were 2.1% and 1.5%, respectively.

To evaluate the strength of a certain bond, a number of electrons is calculated over the region suitably chosen for the bond. In the calculations, a cylinder and triangular prism are employed as the regions for 2c and 3c bonds, respectively. For the atoms, spheres with the same diameter are assumed. In this paper, only valence electron contribution to a bond will be discussed. Since the evaluated number of electrons in the present calculation still depends on the size of the calculated regions, one should consider those results as a criterion, which reflects the relative bond strength rather than the exact numbers of electrons for the bond.

The structural parameters obtained from the Rietveld analysis are listed in Table I. The bond lengths calculated from the structural parameters are shown in Fig. 1. Each bond length is in good agreement with previously reported experiments [9–11] and calculations [7,18]. In the process of the analysis, we included site occupancy parameters g_i for p and e sites as refined parameters in the Rietveld analysis. The parameters, g_i are usually fixed at 1.0 for elemental solids such as α boron, and never larger than 1.0, if the parameters represent occupation numbers of actual atoms. They should be regarded as the number of electrons accumulated at each site. Therefore it is not unphysical for one of the parameters to be over 1.0 and another one less than 1.0. Actually, the sum of the two parameters is equal to 2.0 within the standard deviations. This result is supported by the MEM analysis (see Table II) even if the occupancy parameters are fixed at 1.0. This means that a slight charge transfer occurs from the B2 site to the B1 site and consequently ionicity would take place.

TABLE I. Crystal data and refined structure parameters for α boron with space group $R\bar{3}m$ obtained by the Rietveld analysis. g_i means occupancy at each atomic site (see text). B is a thermal parameter. Parentheses refer to estimated standard deviations for the last digit.

	$a = 4.92396(5)$ Å,		$c = 12.6096(2)$ Å	
Site	g_i	x	z	B (Å^2)
B1	1.006(2)	0.11946(9)	−0.10995(9)	0.51(3)
B2	0.993(2)	0.1968(1)	0.0242(1)	0.50(3)

Figures 2(a)–2(c) show electron distributions of three inequivalent triangles on the icosahedron. The electron distribution obviously exhibits the 3c bond on a p-p-p triangle [Fig. 2(a)]. The highest electron density in this region occurs at the center of the triangle with 0.98 (e/Å^3). The 3c bond forms a trifurcate figure with three 2c bonds on p-p edges. The whole trifurcate 3c bond extending over the p-p-p plane contains 0.90 e. For the other two triangles in Figs. 2(b) and 2(c), the highest electron density point is not at the center of the triangles. For the p-p-e triangle, the highest point is at the center

TABLE II. Highest electron density and electron number in each atom and bond. Electron numbers were obtained by integration in a region suitably chosen. Some of the regions for 3c bonds and for 2c bonds are overlapping.

Site/bond		Highest Density (e/Å^3)	Electron numbers (e)
		Inequivalent atomic sites	
B1 (p)		⋯	2.69
B2 (e)		⋯	2.59
		Intercluster bonds	
2c	(p-p)	0.93	0.53
3c	(e-e-e)	0.64	0.77
		Intracluster bonds	
3c	(p-p-p)	0.98	0.69(0.90[a])
3c	(p-p-e)	0.72	0.71
3c	(p-e-e)	0.68	0.70
2c	(p-p)	0.93	0.13
2c	(p-e, short)	0.79	0.12
2c	(p-e, long)	0.89	0.12
2c	(e-e)	0.95	0.13

[a] The value for the whole of the trifurcate 3c bond.

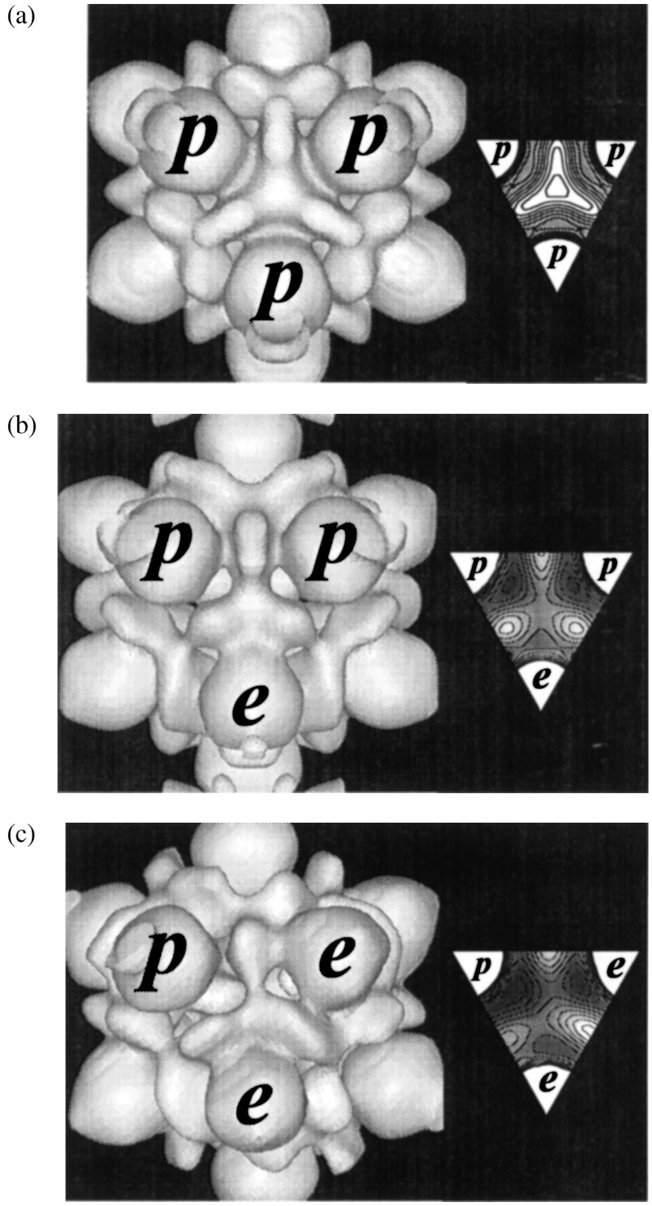

FIG. 2. Equidensity surfaces at 0.61 ($e/\text{Å}^3$) of electron density for intracluster bonds. Each figure is shown with a contour map for the triangular section formed by the lettered atoms. (a) p-p-p; (b) p-p-e; (c) p-e-e.

of the p-p edge and for the p-e-e triangle, it locates at the center of the e-e edge, respectively. Thus, strictly speaking, the bonds on these triangles (p-p-e and p-e-e) are not $3c$ bonds because the highest electron density region is not at the center of three atoms but at the center of one of the edges of the triangles, i.e., p-p or e-e atoms. In Fig. 2, it is clearly shown that all the triangle surface centers of an icosahedron are not maximum electron density points except for the two p-p-p triangles.

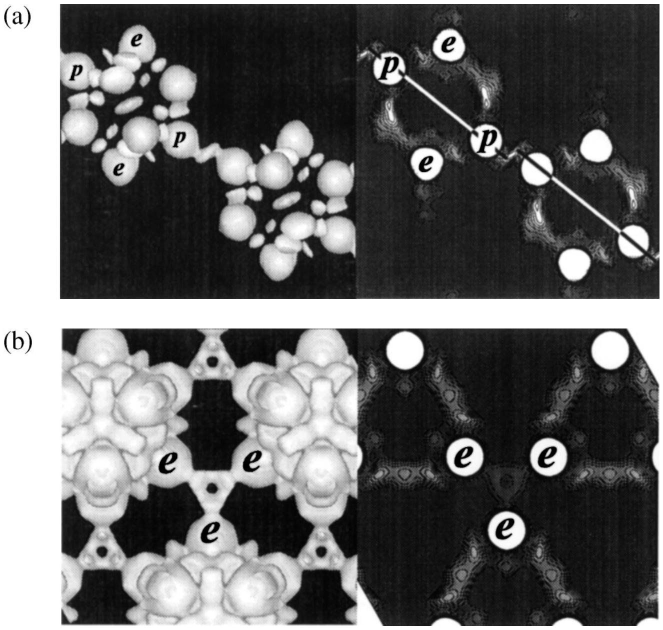

FIG. 3. Equidensity surfaces of electron density with the section contour maps for the intercluster bonds. The surfaces are at 0.73 ($e/\text{Å}^3$) for $2c$ and at 0.55 ($e/\text{Å}^3$) for $3c$ bonds, respectively. (a) $2c$ bond; (b) $3c$ bond.

An intericosahedral $2c$ bond, which is shown in Fig. 3(a), is rather different from a normal $2c$ covalent bond seen in, e.g., Si. A distorted, thick disklike electron distribution can be seen in the region between two atoms of neighboring icosahedra. Note that the bond goes off the B-B line. High electron concentration regions sticking out of two atoms lie on each line that passes through both the center of the icosahedron and the atoms. The regions overlap each other and form a bent bond. The bending occurs at two points of the covalent bond. This causes a short atomic distance which is incommensurate with its bond strength. That is, this short atomic distance does not mean a stronger bond than the others. Actually, a number of electrons in the bond is rather small, 0.53 e, whereas the highest electron density is 0.93 ($e/\text{Å}^3$) still at the center of the bond, which is high but comparable to that in the other bonds (see Table II). This suggests that this bond is probably weaker than predicted by Beckel *et al.* The reason why such an uncommon covalent bond is made is as follows: The angle between pseudo-five-fold axes which pass through the polar atoms and the center of the icosahedron is 61.7°, which is distorted from that of regular icosahedron (63.5°) possibly by the strong p-p-p bond. The $2c$ covalent bond between two icosahedra would be straight and normal if an angle between rhombohedral lattice vectors was identical with 61.7°. However, the angle of lattice vectors decreases to 58.0° owing to the attractive force of the intercluster $3c$ bond among three icosahedra (see below). Furthermore an icosahedral boron cluster has a strong nature of sticking out radial bonds along pseudo-five-fold axes [19]. Thus a gap between these two angles emerges and the intercluster $2c$ bond is bent.

The equidensity surface of the three-dimensional electron distribution of intercluster $3c$ bonds, which lies on the (001) layer of the hexagonal lattice, is shown in Fig. 3(b). This bond has a rather low electron density compared with the other intra- or intercluster bonds. There is a distinct difference from intracluster $3c$ bonds. In contrast to the intracluster $3c$ bond, this bond has a low electron density region at the center of the triangle and high electron density regions along the edges of the triangle. The maximum electron density in this bond, which appears near the corners of the triangle is 0.64 ($e/\text{Å}^3$). This value is lower than that of the intracluster $3c$ bonds and a value of the electron number of the bond is higher than that of the intercluster $2c$ bonds. This is due to a relatively large region of this bond. Thus one can expect that this bond is not very strong but not so weak, either. Vast *et al.* predicted by their first principle calculation that the angle between rhombohedral lattice vectors is unchanged under negative pressure [20]. It seems to support the bond strength described above.

Contrary to the result of lattice dynamics obtained by the classical model [3], the present results of electron density distribution reveal that the strength of the intercluster $2c$ bond is probably comparable to or less than the intracluster bonds. This discrepancy probably comes from the fact that the classical model does not employ enough variables of force constants to describe lattice vibrations adequately. In fact, a number of force constants used in Beckel's analysis seems to be insufficient, because uneven electron numbers of each bond in the icosahedron require a different force constant for each bond.

Our results indicate that the bonding in α boron is of the cluster-based nature. This may be true for icosahedral boron rich solids as well. In compounds with an α boronlike structure, an intercluster $2c$ bond would be stronger than that in α boron when the angle of the rhombohedral lattice corresponds to the angle of pseudo-five-fold axes in an icosahedron, because a bend in the bond is removed in such a case.

In conclusion, we have obtained details of electron density distribution of α boron by using the MEM. Noticeable differences among different bonds and the peculiarity of chemical bonds in α boron were clearly shown by three-dimensional electron density distributions. In an icosahedral cluster, a covalent bond network is constructed by high density regions of bonding electrons, which are spreading over the surface of the icosahedron. Strictly speaking, there are only two intracluster $3c$ bonds on the two triangle planes of the icosahedron. They are made of three *polar* atoms only. The other triangle planes are supported by two center bonds at the edges. The poles and the equator of an icosahedron are the higher electron density regions. It is reasonable to consider that the skeleton of the icosahedron comprises $3c$ bonds on the p-p-p plane, two kinds of p-p bonds, and e-e $2c$ bonds. An intercluster $2c$ bond is bent because of the deviation of two angles, i.e., one formed by rhombohedral lattice vectors and the other by pseudo-five-fold axes in an icosahedral cluster. This bond has a high electron density which is comparable to that of the bonds within an icosahedron cluster.

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