

## Ionicities of Boron-Boron Bonds in $B_{12}$ Icosahedra

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First-principles calculations are used to investigate ionicities of boron-boron bonds in  $B_{12}$  icosahedra. It is observed that the geometrical symmetry breaking of  $B_{12}$  icosahedra results in the spatial asymmetry of charge density on each boron-boron bond, and further in the ionicity of  $B_{12}$  icosahedra. The results calculated by a new ionicity scale, a population ionicity scale, indicate that the maximum ionicity among those boron-boron bonds is larger than that of boron-nitrogen bonds in the III-V compound cubic BN. It is of great importance that such an ionicity concept can be extended to boron-rich solids and identical atom clusters.

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Ionicity is an important, basic concept and exists only in chemical bonds between different atoms in general. In essence, it originates from the asymmetry of the spatial charge density distribution. Some scales have been defined to characterize the ionicity related to charge transfer [1–4], and successfully applied for understanding many basic properties [5–14] of solids and molecules in chemistry and physics. Based on these scales, however, all ionicities in chemical bonds between identical atoms are zero because of no charge transfer. Here we report the first observation of the existence of significant ionicity in chemical bonds between boron atoms in  $B_{12}$  icosahedron.

Boron and boron-rich solids [15] are part of the most important group of nonmetallic hard materials. In the past few years, boron-rich solids have received considerable attention [16–25], especially, boron suboxide  $B_6O$ , which was found to be a novel superhard material [20–23]. The hardness of boron-rich solids is related to the special structure of  $B_{12}$  icosahedron. By assuming that all the boron-boron bonds in the  $B_{12}$  icosahedron were pure covalent bonds in the calculation of hardness using our microscopic model [7], we found that the hardness of the  $\alpha$  boron or  $B_6O$  would be 50 GPa or 55 GPa, respectively, which is over 19% or 22% ~ 44% higher than the experimental value of 42 GPa [15] for  $\alpha$  boron or the value of 38 GPa [22] and 45 GPa [23] for  $B_6O$ . The microscopic model shows that the hardness of a polar covalent solid depends only on three factors of a bond, i.e., length, electronic density, and Phillips ionicity [7]. It should be noted that the accuracy for the microscopic model of hardness is within 10% [26]. Because bond length and electronic density are fixed for each bond, we speculate that ionicities of the boron-boron bonds in icosahedra are responsible for the decrease in hardness. However, the existence of ionicity for identical atom bonds is questionable in the theoretical framework of the common ionicity concept.

Our goal is to prove this speculation and to reveal the origin of the ionicity in the icosahedra of  $\alpha$ -boron. Specifically, we would like to quantitatively characterize the ionicity. In order to be able to calculate the ionicity, we shall define a new ionicity scale, and find the relationship between this new scale and the Phillips scale so as to calculate the ionicity of each boron-boron bond in the icosahedra using our hardness model [7]. This scale can be extended to boron-rich solids and identical atom clusters.

We have employed CASTEP [27] code within the local density approximation to perform first-principles calculations that explore the electronic structure of crystals. Norm-conserving pseudopotentials were used. The calculations were made using the plane-wave cutoff energy of 660 eV. The Brillouin zone sampling was performed using special  $k$  points generated by the Monkhorst-Pack scheme with parameters  $10 \times 10 \times 10$ . The technique [28] for the projection of plane-wave states onto a linear combination of atomic orbitals basis set was used to perform Mulliken population calculations.

We first analyze the types of boron-boron bonds in an  $\alpha$ -boron crystal consisting of only  $B_{12}$  icosahedra located at the vertices of a rhombohedral lattice ( $R-3m$ ) [16] as shown in Fig. 1(a). There are two inequivalent crystallographic sites, i.e., polar ( $B_p$ ) and equatorial ( $B_e$ ) sites, for boron atoms in Fig. 1(b) in an icosahedron. The  $B_p$  atoms, which form top and bottom triangular faces, are directly linked to the five neighboring atoms in the same icosahedron and to one polar atom in a neighboring icosahedra; the  $B_e$  atoms form a puckered hexagon in the plane perpendicular to the [111] axis. As shown in Fig. 1(a), three equatorial atoms are separate from the three neighboring icosahedra and are linked together by peculiar delocalized three-center bonds [19]. Therefore, 39 boron-boron bonds in one  $\alpha$ -boron unit cell can be divided into three different types. Type-I bonds are those linking two polar atoms

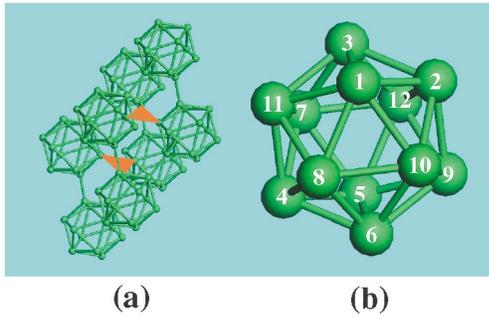


FIG. 1 (color). Structure of  $\alpha$ -rhombohedral boron: (a) the eight  $B_{12}$  icosahedra locate at the vertices of a rhombohedral unit cell with the lattice parameters of  $a = 4.974 \text{ \AA}$  and  $\alpha = 58.16^\circ$ . The peculiar delocalized three-center bonds are denoted with the red triangles; (b) the polar atoms are labeled with numbers of from 1 to 6, and the equatorial atoms with numbers of from 7 to 12 in  $B_{12}$  icosahedron.

between neighboring icosahedra, type-II bonds are the peculiar delocalized three-center bonds, and type-III bonds are those in  $B_{12}$  icosahedra.

To determine which types of bonds exhibit the ionicity, we explore the charge density of each bond. Figure 2 shows the charge densities in  $\alpha$ -boron by four color-contour maps. From the point of view of chemical bonding, type-I and -II bonds exhibiting symmetrical charge density distribution are purely covalent. Ideal icosahedron is a

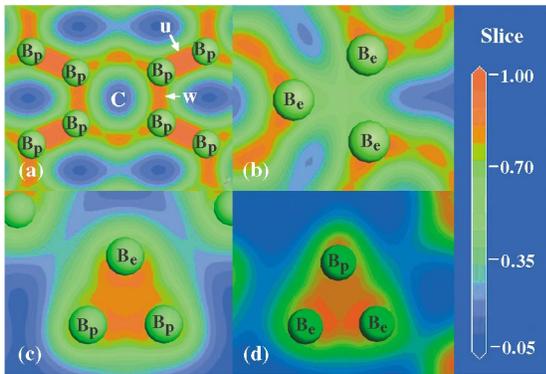


FIG. 2 (color). Typical color-contour maps of charge densities of chemical bonds in  $\alpha$ -rhombohedral boron: (a) on the color-contour map in (100) plane of  $\alpha$ -rhombohedral boron, the bright red  $B_p-B_p$  bonds (indicated by arrow u) in type-I are strong two-center covalent bonds, their charge density centers located at the middle of their bonds; the dark red  $B_p-B_p$  bonds (indicated by arrow w) are type-III bonds, their charge density weighted centers in (100) planes moving clearly from the bonding axis towards center C of icosahedron; (b) the charge densities of the peculiar delocalized three-center  $B_e-B_e$  bonds in type-II show threefold rotation symmetry because three  $B_e-B_e$  bond lengths are the same; (c) the charge densities of the bonds in type-III of  $B_p-B_p-B_e$  triangle exhibit the feature of asymmetry; (d) the charge densities of the bonds in type-III of  $B_p-B_e-B_e$  triangle also exhibit the feature of asymmetry.

quasicrystal structure with fivefold symmetry. While  $\alpha$ -boron maintains  $R-3m$  symmetry,  $B_{12}$  icosahedra on each lattice site distort and lose their fivefold rotation axis. Therefore, type-III bonds can be divided again into four subgroups by three slightly different types of 20 triangle faces of the icosahedron. The first subgroup has 12  $B_e-B_p$  bonds ( $B_{10}-B_1, B_{10}-B_2, B_{11}-B_1, \dots$ ) in six  $B_p-B_p-B_e$  types of triangle faces formed by one equatorial and two neighboring polar atoms. The second and third subgroups have six  $B_e-B_e$  ( $B_7-B_{11}, B_7-B_{12}, B_8-B_{10}, \dots$ ) and six  $B_p-B_e$  ( $B_1-B_8, B_2-B_9, B_3-B_7, \dots$ ) bonds in 12  $B_p-B_e-B_e$  types of triangle faces formed by one polar and two neighboring equatorial atoms, respectively. The fourth subgroup has six  $B_p-B_p$  ( $B_1-B_2, B_2-B_3, B_3-B_1, \dots$ ) bonds in two  $B_p-B_p-B_p$  types of triangle faces formed between two top (or bottom) polar atoms. The bond lengths of these four subgroups are slightly different (see Table II). The experimental measurement confirmed the difference in bond length in  $B_{12}$  icosahedron [29]. The broken geometrical symmetry of icosahedron due to the differences in bond lengths results in the asymmetrical distribution of charge density in the type-III bonds, such as the bonds in the  $B_p-B_p-B_e$  [see Fig. 2(c)] and  $B_p-B_e-B_e$  [see Fig. 2(d)] triangles. The asymmetrical distribution of charge density, caused from the broken geometrical symmetry, could also appear in other kinds of identical atom clusters. Garcia and Cohen [30] have attributed the existence of ionicity to the observed asymmetry of the charge density. We shall calculate this kind of ionicity later in this Letter.

In the conventional empirical ionicity scales of Pauling [1], Phillips [2], and Coulson [3], ionicity of a chemical bond is considered as zero for identical element solids. First-principles ionicity scales, here called as Garcia scale  $f_g$  [30], Zaoui scale  $f_z$  [31], and Christensen scale  $f_c$  [32], respectively, can be used to describe the spatial asymmetry of the charge distribution local on each bond where there is no electronic charge transfer along the bond axis in the  $\alpha$ -boron crystal. In Table I we compare the theoretical ionicity values of  $f_g$ ,  $f_z$ , and  $f_c$  to the Phillips ionicity  $f_i$ . We can obtain three linear relationships of  $f_g = 1.266f_i$  ( $R^2 = 0.75$ ),  $f_z = 1.098f_i$  ( $R^2 = 0.88$ ), and  $f_c = 1.195f_i$  ( $R^2 = 0.84$ ) as shown in Fig. 3. Zaoui scale tends to be better than Garcia and Christensen scales for the hardness calculations by using our microscopic model; however, the calculation error seems too large to be tolerated. Therefore, it is necessary to find a new ionicity scale for the characterization of ionicity in such crystals as  $\alpha$ -boron. We now shall construct this new scale.

Mulliken's bond overlap population [33] for nearest neighboring atoms, derived from first-principles calculations, is a measure of spatial charge density between bonding atoms, and this quantity does not totally depend on the valence charge transfer along the bond axis. Previous work [6,34] has indicated that the bond overlap population can reflect the trend of bond ionicity. For a

TABLE I. Comparison of  $f_h$  to  $f_g$ ,  $f_z$ ,  $f_c$ , and  $f_i$ . Calculating Mulliken population  $P$  from first-principles calculations using CASTEP code [27] and population ionicity  $f_h$  from Eq. (1).

Materials	$f_g^a$	$f_z^b$	$f_c^c$	$f_i^a$	$P$	$f_h$
Diamond	0	0	0	0	0.75	0
Si	0	0	0	0	0.75	0
BAs	0.116	...	0.002	0.002	0.74	0.013
BP	0.085	0.12	0.001	0.006	0.75	0
SiC	0.475	0.14	0.394	0.177	0.69	0.083
AlSb	0.230	0.245	0.163	0.250	0.65	0.143
c-BN	0.484	0.462	0.383	0.256	0.65	0.143
GaSb	0.169	0.264	0.108	0.261	0.63	0.174
AlAs	0.375	0.292	0.367	0.274	0.61	0.205
AlP	0.425	0.403	0.421	0.307	0.63	0.173
GaAs	0.316	0.312	0.310	0.310	0.61	0.205
InSb	0.294	0.301	0.303	0.321	0.57	0.271
GaP	0.371	0.377	0.361	0.327	0.63	0.174
InAs	0.450	0.357	0.553	0.357	0.53	0.340
InP	0.506	0.405	0.534	0.421	0.56	0.288
AlN	0.794	0.573	...	0.449	0.50	0.393
GaN	0.780	0.584	...	0.500	0.52	0.357
InN	0.853	...	...	0.578	0.45	0.487
ZnS	0.673	0.677	0.764	0.623	0.46	0.468
ZnSe	0.597	0.639	0.740	0.630	0.46	0.468

<sup>a</sup>Ref. [30].

<sup>b</sup>Ref. [31].

<sup>c</sup>Ref. [32].

specific crystal structure or cluster containing the same type of coordinates, we define here an ionicity scale  $f_h$  of a bond based on bond overlap population as

$$f_h = 1 - e^{-|P_c - P|/P}, \quad (1)$$

where  $P$  is the overlap population of a bond and  $P_c$  is the overlap population of the bond in a pure covalent crystal of that specific structure or cluster.  $f_h$  is equal to zero for a purely covalent bond and to unity for a purely ionic bond.

TABLE II. Bond parameters of  $\alpha$ -boron, ionicities of bonds in  $B_{12}$  icosahedron. Calculating the chemical bond parameters of the  $n^\mu$  and  $d^\mu$  from first-principles calculations using CASTEP code [27], and  $N_e^\mu$  from the Eq. (10)–(12) in Ref. [7] for  $\alpha$ -boron crystal. After deducing  $P_c$  value from Eq. (2), we obtain the population and Phillips ionicities for the four types of bonds in  $B_{12}$  icosahedra using Eq. (1) and the relationship of  $f_h = f_i^{1.36}$ .

Bond Type	Bond	$\alpha$ -boron			$B_{12}$ icosahedron		
		$n^\mu$	$d^\mu$ (Å)	$N_e^\mu$	$P$	$f_h$	$f_i$
I	$B_p$ - $B_p$	3	1.650	0.595	...	...	...
II	$B_e$ - $B_e$	6	1.984	0.323	...	...	...
	$B_e$ - $B_p$	12	1.773	0.480	0.53	0.019	0.054
III	$B_e$ - $B_e$	6	1.752	0.497	0.49	0.097	0.180
	$B_p$ - $B_e$	6	1.764	0.487	0.47	0.138	0.233
	$B_p$ - $B_p$	6	1.717	0.528	0.42	0.249	0.359

Usually the bonds in different types of structures would have different values of  $P_c$ .

To calculate the ionicity values of boron-boron bonds in  $B_{12}$  icosahedra using our model [7], we have to find a correlation between population ionicity  $f_h$  and Phillips ionicity  $f_i$ . Therefore, we compare  $f_h$  with  $f_i$  for a reference structure. We choose here the zinc blende structure and do a population analysis to determine  $f_h$ . The calculated overlap population of pure covalent C-C or Si-Si bonds is 0.75 in the diamond or silicon crystals. Thus we find that  $P_c = 0.75$  for the zinc blende structure. In order to further discern the relevance between different scales, we compare values (see Table I) of Phillips ionicity  $f_i$  and population ionicity  $f_h$  for 20 kinds of materials with zinc blende structure. A good fit to the relationship for  $f_h$  as a function of  $f_i$ ,  $f_h = f_i^m$ , yields  $m = 1.36$  with  $R^2 = 0.94$  (see Fig. 3).

The hardness of a polar covalent crystal exhibits an exponential relation with  $f_i$ . Based on the experimental value of hardness of 42 GPa [15] and the chemical bond data from the middle column in Table II for  $\alpha$ -boron crystal, we can derive  $P_c$  value for bonds in  $B_{12}$  icosahedra by employing our microscopic model of hardness from Eq. (2),

$$H_v = \left[ \prod^\mu (H_v^\mu)^{n^\mu} \right]^{1/\sum n^\mu}, \quad (2)$$

where  $H_v^\mu = 350(N_e^\mu)^{2/3} e^{-1.191f_i^\mu} / - (d^\mu)^{2.5}$  is the hardness of a crystal composed of  $\mu$ -type bonds,  $n^\mu$  is the number of  $\mu$ -type bonds in the actual crystal,  $f_i^\mu$  is the Phillips ionicity of a crystal composed of  $\mu$ -type bonds, and  $N_e^\mu$  is the number of valence electrons of  $\mu$ -type bond per cubic angstroms [7]. When introducing  $f_i = f_h^{1/m}$  and data in Table II to Eq. (2), we find that  $P_c = 0.54$  for bonds in the icosahedron. The corresponding Phillips ionicities

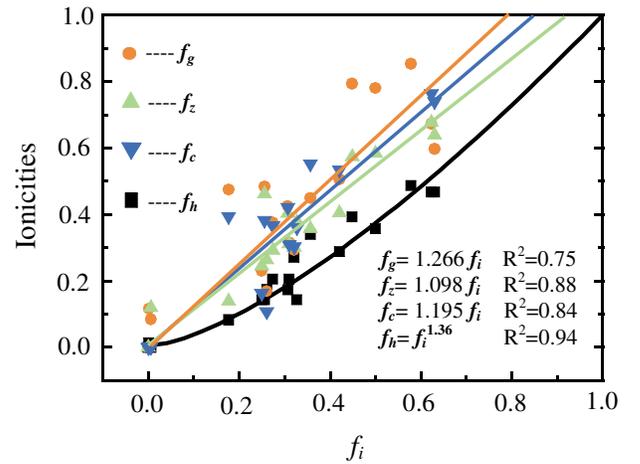


FIG. 3 (color). Plot of  $f_g$ ,  $f_z$ ,  $f_c$ , and  $f_h$  versus  $f_i$  values for zinc blende structure. Note that the  $f_h/f_i^{1.36}$  ratio for the chosen 20 materials lies on (or close to) the line of slope 1.

based on our relation between  $f_h$  and  $f_i$  for the four types of bonds in the  $B_{12}$  icosahedra are 0.054, 0.180, 0.233, and 0.359, and listed in the right column in Table II. The maximum ionicity 0.359 of boron-boron bonds occurs between two neighboring polar atoms, which is 40.2% larger than 0.256 of the boron-nitrogen bond in the III-V compound of cubic BN.

To test the validity of the population ionicity scale, we calculate the hardness of typical boron-rich solids  $B_6O$  and  $B_{13}C_2$ . The insertions of additional elements O and C between  $B_{12}$  icosahedra have obvious effects on the overlap populations of boron-boron bonds in the  $B_{12}$  icosahedra, but assessing the effects is beyond the scope of this work. Our calculated hardness of 42 GPa and 44 GPa agrees with the experimental values of 38 GPa [22] or 45 GPa [23] for  $B_6O$  and 45 GPa [15] for  $B_{13}C_2$ , respectively.

The investigations of ionicities of boron-boron bonds in  $B_{12}$  icosahedra that we report here reveal a fact that there can exist ionicity for identical atoms chemically bonded in a specific structure. The population ionicity scale is a very useful and universal tool for understanding the chemical bonding of boron-rich solids and identical atom clusters in chemistry and physics. More generally, the present results explode the common concept that ionicity only exists in chemical bonds formed between different elements, and offer a deeper understanding of the nature of a chemical bond.

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