Ionicity of bonding in elemental solids

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Abstract

Elemental solids are categorized into four classes based on the occupation of Wyckoff positions (WPs), to investigated their ionicities. In class I of elemental solids with only one WP occupied, such as diamond, the ionicities of all bonds are zero. In the other three classes of elemental solids with multiple equivalent or inequivalent WPs occupied, charge transfer can exist between atoms occupying different WPs, and hence have an ionic character. We identify some previously unrecognized elemental solids with partial ionicities using the method of Bader charge analysis. Especially, charge transfer in a boron-rich phase (ε-B) is comparable with that in oxides.

1. Introduction

Knowledge of the nature of chemical bonds is the foundation for understanding physical properties of solids [1]. It is conventionally believed that the ionicity can exist only in chemical bonds between atoms of different elements [2]. For example, ionicites of chemical bonds in binary crystals of the form A\textsuperscript{n}B\textsuperscript{m−n} (A in group-N and B in group-(8-N)) with rocksalt and zinc-blende structures are well known [3]. On the other hand, ionicities are zero for bonds in elemental solids such as elemental group-IV solids with a diamond structure. However, nonzero ionicites in boron-boron bonds have been predicted in α-B\textsubscript{12} crystal with the R-3\textit{m} structure containing B\textsubscript{12} icosahedra [4, 5]. Ionicities have also been found in γ-B\textsubscript{28} (space group \textit{Pnma}, No. 58) consisting of B\textsubscript{12} icosahedral and B\textsubscript{2} pairs at high-pressure experiments [6]. In 2011, the charge transfer and a polar-covalent bond have been reported in γ-B\textsubscript{28} based on detailed analyses of the experimental charge density [7, 8].

In this work, we investigate the origin of ionicity in elemental solids based on symmetry considerations. Our results can help one to determine whether an elemental solid may have ionic chemical bonds or not from occupied positions in the unit cell, without any calculations. Elemental solids are categorized into four classes (table 1 and see below). Charge transfer in each class of elemental solids is investigated based on the Bader charge analysis [9]. Calculated Bader charges can be compared with Bader charges obtained from experiments [7]. Finally, various elemental solids with ionic chemical bonds are presented.

2. Classification and computational methods

Knowledge of the space group (global symmetry) of elemental solids is not enough to characterize their bonding ionicites. Chemical bonding is related to the local symmetry (Wyckoff positions). We can categorize elemental solids into four classes according to occupied Wyckoff positions of atoms in unit cells, as listed in table 1. The class I of elemental solids is that only one Wyckoff position is occupied in the unit cell. For example, in elemental group-IV solids with a diamond structure (space group \textit{Fd}-3\textit{m}, No. 227), eight atoms in the unit cell occupy only one Wyckoff position \textit{8a} with coordinates (0, 0, 0) and (1/4, 1/4, 1/4). For elemental group-V solids with the space group \textit{R}-3\textit{m} (No. 166), six atoms in the unit cell (hexagonal axes) occupy only one Wyckoff position \textit{6c} with coordinates (0, 0, z). These elemental solids all belong to the class I. The class II of elemental solids is that multiple equivalent Wyckoff positions are occupied in the unit cell. The above mentioned α-B\textsubscript{12} crystal with the R-3\textit{m} structure, in which 36 boron atoms occupy two equivalent Wyckoff positions 18\textit{h} with coordinates...
We now analyze the ionicity of chemical bonds in the four classes of elemental solids as classified according to the occupied Wyckoff positions in their unit cells. For each class, the space group, occupied Wyckoff positions (WPs), and the existence of the ionicity, and a brief characterization of occupations for each class are shown. The numbers of multiple equivalent or inequivalent WPs are also given in parentheses.

| Class | Structures | WPs | Ionicity | Occupations |
|-------|------------|-----|----------|-------------|
| I     | diamond ($F\bar{d}$-3m) | 8a  | No       | one WP occupied |
| II    | $\alpha$-B$_2$ (R-3m) | 18h (2) | Yes | one WP multiply occupied |
|       | B (Pn-3) | 24d (2) | Yes | |
| III   | graphite (P6$_3$/mmc) | 2b, 2c | Yes | multiple inequivalent WP occupied |
|       | $\gamma$-La (P6$_3$/mmc) | 2a, 2c | Yes | |
|       | 4H-Ge (P6$_3$/mmc) | 4c, 4f | Yes | |
|       | As (P6$_3$/mc) | 2a, 2b | Yes | |
| IV    | $\beta$-B$_2$ (Pmmn) | 8h (2), 4g (3) | Yes | multiple inequivalent WP, and at least one of them multiply occupied |
|       | $\delta$-B (P4$_2$/nmm) | 2b, 8m(2), 16m(2) | Yes | |
|       | $\varepsilon$-B (R-3m) | 5b, 18h (2), 6c | Yes | |

(0.0103, 0.0103, 0.6540) and (0.2211, 0.2211, 0.6305) [6], respectively, belongs to the class II. The class III of elemental solids is that multiple inequivalent Wyckoff positions are occupied in the unit cell (such as graphite). The class IV of elemental solids is that multiple equivalent and inequivalent Wyckoff positions are occupied in the unit cell. The above mentioned $\gamma$-B$_2$ crystal belongs to the class IV since 28 boron atoms in the unit cell occupy two equivalent Wyckoff positions 8h and three equivalent Wyckoff positions 4g which is inequivalent to 8h. In table 1, we list various elemental solids belonging to these four classes. Ionicities of these systems will be investigated in the following.

The ionicity can be described in terms of charge transfer between atoms forming the chemical bond. In order to calculate the charge transfer, we use the Bader charge analysis to estimate the total charge on an atom [10]. In this approach, real space is divided into Bader regions based on topology of the electronic density. The total charge on an atom is obtained by integrating the electronic density within the Bader region in which an atom is located, and possibly adding the electronic charge in nearby regions that do not include a nucleus [11]. The Bader charge for an atom is defined as the difference between the number of its valence electrons and its total charge obtained from the Bader charge analysis. Nonzero Bader charges indicate nonzero ionicities of the corresponding bonding. Let us first consider the chemical bond between atoms of different elements A and B in crystals (e.g. ANB$_8$), as shown in figure 1(a). In this case, the Bader charge for A (B) is usually positive (negative) in unit of e. This reveals the existence of charge transfer between A and B. Thus the ionicity in chemical bonds between A and B is nonzero. For the typical ionic crystal NaCl, the Bader charge for Na is +0.866 e, which characterizes the ionicity of the Na–Cl bond [11]. This Bader charge analysis can be directly applied to elemental solids.

To calculate Bader charges and physical properties of solids, first-principles calculations were performed based on density functional theory (DFT) [12] with the local density approximation, as implemented in the Vienna Ab Initio Simulation Package (VASP) [13–15]. An energy cutoff of 500 eV was used for all calculations. A grid-based Bader analysis algorithm without lattice bias was adopted to make sure our calculated charge very accurate [16]. A fine fast Fourier transform (FFT) grid [11] was used to accurately reproduce the correct total core charge [17].

3. Results and discussion

We now analyze the ionicity of chemical bonds in the four classes of elemental solids as classified above. All chemical bonds in class I are formed between identical atoms (e.g. A atoms) occupying one Wyckoff position (e.g. WP1), as shown in figure 1(b). In this case, all A atoms in the unit cell have the same Bader region and the same electronic density within the Bader region, and thus have the same total charge and Bader charge. This implies that Bader charges for all A atoms should be zero. As a result, all ionicities of bonds in the class I of elemental solids are zero. For example, our first-principles calculations show that the total charge for all eight carbon atoms (see figure 2(a)) in the unit cell of diamond is 4.000 e, which means that Bader charges for all C atoms are zero as given in table 2. Thus ionicities of all C–C bonds in diamond are zero (purely covalent). This is a well-known result, and is the first step to present our classification, and also serves as the demonstration of the accuracy of our calculated Bader charge.

For the class II of elemental solids, we consider a bond between A1 and A2 atoms which occupy two equivalent Wyckoff positions (e.g. WP1 and WP1'), as shown in figure 1(c). In general, A1 and A2 atoms have different Bader regions and electronic densities within the Bader region, and thus have different total charges and Bader charges. This implies that the Bader charges for A1 and A2 should not be zero, which reveals the
existence of charge transfer between A1 and A2. As a result, the ionicity of A1-A2 bonds is not zero. In the unit cell of the \( \alpha \)-B\(_{12} \) crystal, 36 boron atoms can be divided into two groups denoted as B1 and B2, which occupy two equivalent Wyckoff positions \( 18h \) respectively. The calculated Bader charges for B1 and B2 are +0.0572 e and −0.0550 e, respectively, which are consistent with previously reported experimental Bader charges for B1.

**Figure 1.** The bond between (a) different elements (A and B), (b) the same element (A) occupying one Wyckoff position (WP1), (c) the same element (A1 and A2) occupying two equivalent Wyckoff positions (WP1 and WP1 \(^\prime\) ), (d) the same element (A1 and A2) occupying two inequivalent Wyckoff positions (WP1 and WP2). The existence of the charge transfer for each case is also indicated.

**Figure 2.** Crystal structures for (a) diamond, (b) graphite, (c) \( \alpha \)-La, and (d) As. Atoms occupying different Wyckoff positions are shown with different colors.
(+0.0668 e) and B2 (−0.0674 e) [8]. These Bader charges are small but cannot be ignored. The charge transfer between B1 and B2 is not significant. The ionicities of B1–B2 bonds are nonzero. However, ionicities of B1–B1 and B2–B2 bonds in α-B12 are all zero as the case in the class I of elemental solids. Recently, a new boron–rich phase with the space group $\text{Pn}a$–3 (No. 205) was obtained [18]. In its unit cell, 48 boron atoms occupy two equivalent Wyckoff positions $2d$. Our calculations show that Bader charges for B1 with coordinates (0.138 16, 0.452, 0.804 63) and B2 with coordinates (0.667 27, 0.042 42, 0.720 33) are $−0.174$ e and $+0.174$ e, respectively. The charge transfer between B1 and B2 is more significant that in $\alpha$-B12.

For class III of elemental solids, we consider a bond between A1 and A2 atoms occupying two inequivalent Wyckoff positions (e.g. WP1 and WP2), as shown in figure 1(d). In general, A1 and A2 atoms have different Bader regions and electronic densities within the Bader region, and thus have different total charges and Bader charges due to the inequivalence of WP1 and WP2. This implies that Bader charges for A1 and A2 should not be zero, which reveals the existence of charge transfer between A1 and A2. As a result, the ionicity of A1–A2 bonds is not zero.

Based on information on inequivalent Wyckoff positions for each space group, we can find out elemental solids belonging to the class III. We focus on Wyckoff sets of space group 194 ($P6_3$/$mmm$) and 186 ($P6_3mc$) [19]. Graphite has the symmetry of $P6_3$/$mmm$, in which four carbon atoms in the unit cell occupy 2b and 2c positions shown in figure 2(b) [20]. Since 2b (0, 0, 1/4) and 2c (1/3, 2/3, 1/4) are inequivalent Wyckoff positions, graphite belongs to the class III of elemental solids. Two carbon atoms occupying 2b (2c) positions are denoted by C1 (C2). In each atomic plane, C1 and C2 form chemical bonds. Total charges for C1 and C2 are 4.047 e and 3.953 e respectively. This indicates that about 0.01 e are transferred between C1 and C2, indicating a weak ionic character of C1–C2 bonds. Of course, the charge transfer is very small and thus bonding between C1 and C2 is predominantly covalent. The inequivalence of C1 and C2 can also be found in the difference between partial density of states for C1 and C2 as shown in figure 3(a). There exist other crystal structures with the space group $P6_3$/$mmm$ where multiple inequivalent Wyckoff positions are occupied. Four atoms in the unit cell can also occupy two inequivalent Wyckoff positions 2a (0, 0, 0) and 2c (1/3, 2/3, 1/4) shown in figure 2(c). This is the double hexagonal close packed ($dhcp$) structure ($\alpha$-La type) [21]. In addition, 8 atoms in the unit cell can occupy two inequivalent Wyckoff positions 4e (0, 0, z) and 4f (1/3, 2/3, z), which is the structure of 4H–Ge [22]. Bader charges for Ge1 (4e) and Ge2 (4f) are given in table 2. For the $P6_3mc$ (No. 186) space group, 2a (0, 0, z) and 2b (1/3, 2/3, z) are two inequivalent Wyckoff positions [19] as shown in figure 2(d). This crystal structure can be denoted as the distorted $\alpha$-La type structure. Our calculations for arsenic in this phase ($a = 3.633$ Å, $c = 7.680$ Å) indicate that Bader charges for As1 with coordinates (0, 0, 0) and As2 with coordinates (1/3, 2/3, 0.1761) are $+0.109$ e and $−0.109$ e, respectively. This reversals the bonding polarity of the As1–As2 bond. Partial density of states and atomic orbital ($p_z$) projected band structures shown in figures 3(b)–(d) also reveal the inequivalence of As1 and As2.

| Crystal | Atom | Charge | Crystal | Atom | Charge |
|---------|------|--------|---------|------|--------|
| diamond | C    | 0.000  | $\alpha$-B12 | B1   | +0.0572 (+0.0668) |
| graphite | C1   | −0.0465 | B2   | −0.0550 (−0.0674) |
|         | C2   | +0.0465 | 4H-Ge | Ge1  | −0.0372 |
| B ($\text{Pn}a$–3) | B1   | −0.1743 | Ge2  | +0.0439 |
|         | B2   | +0.1743 | $\gamma$-B28 | B1 | +0.0037 (+0.029) |
| As      | As1  | −0.1086 | B2   | +0.0523 (+0.0636) |
|         | As2  | +0.1094 | B3   | +0.0251 (+0.0255) |
| $\delta$-B | B1   | −0.2886 | B4   | −0.1650 (−0.1680) |
|         | B2   | +0.1203 | B5   | +0.2306 (+0.2418) |
|         | B3   | +0.1570 | $\epsilon$-B | B1 | −0.7036 |
|         | B4   | −0.1883 | B2   | −0.4344 |
|         | B5   | +0.0982 | B3   | +0.0297 |
|         |      |        | B4   | +1.5774 |

We now investigate the class IV of elemental solids. The Bader charges of boron atoms in $\gamma$-B28 crystal have been studied (see also table 2) [6]. Our results are consistent with previous data. Based on occupied positions of atoms in unit cells, we find that previously synthesized two boron–rich phases $\delta$-B and $\epsilon$-B [23] belong to the class IV. The space group of $\delta$-B is $P4_2/\text{mmm}$ (No. 134). There are 50 B atoms in the unit cell with one 2b (B1), two 8 m (B2 and B3), and two 16$\prime$ (B4 and B5) Wyckoff positions occupied [23]. Bader charges for B1 (0, 0, 1/2), B2 (0.1239, 0.1239, 0.3685), B3 (0.2458, 0.2458, 0.5897), B4 (0.3161, 0.1042, 0.3907), and B5 (0.2288, 0.0827, 0.0819) are $−0.2886$ e, $+0.1203$ e, $+0.1570$ e, $−0.1838$ e, and $+0.0982$ e respectively. Charge transfer in $\delta$-B is
notable. In $\varepsilon$-B ($R$-3$m$, No. 166), 45 B atoms occupy one $3b$ (B1), two $18h$ (B2 and B3), one $6c$ (B4) Wyckoff positions \[23]. Bader charges for B1 ($0, 0, 1/2$), B2 (0.1626, 0.8374, 0.6413), B3 (0.2255, 0.7745, 0.7805), and B4 (0, 0, 0.6192) are $-0.7036$ e, $-0.4344$ e, $+0.0297$ e, and $+1.5774$ e, respectively (see also table 2). The large charge transfer in $\varepsilon$-B is comparable with that of the typical ionic crystal MgO (1.72 e) \[11], indicating a significant ionicity.

According to above discussions, we can find that occupied Wyckoff positions determine the existence of the charge transfer in elemental solids. Most of well-known elemental solids belong to category I, in which the ionicity of bonding is zero. In boron-rich phases belonging to category II [$\alpha$-B$_{12}$ and B ($Pa$-3)], the amount of charge transfer per atom is smaller than that in other boron-rich phases belonging to categories III and IV. This indicates that multiple equivalent Wyckoff positions (e.g. two 18 $h$ positions in category II) may not provide very different local environments for bonding atoms. On the other hand, for different elements, more significant ionicity can occur in elemental solids formed with amphoteric elements (B and As) since they have good abilities of both electron gain and electron loss.

4. Summary

In summary, we have investigated the charge transfer between atoms in four classes of elemental solids classified with occupied Wyckoff positions. There is no charge transfer in the class I of elemental solids with only one occupied Wyckoff position. However, the charge transfer can exist in other three classes of elemental solids with multiple equivalent or inequivalent occupied Wyckoff positions. In elemental solids, the origin of the ionicity of the bond is that two atoms forming the bond should belong to two Wyckoff positions. Ionicities in some elemental solids have been demonstrated with first-principle calculations using the Bader charge analysis.

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