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Theory of two boron neutral pair defects in silicon

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Abstract. Using *ab initio* local density calculations, we consider the microscopic structures of two neutral pair defects of B in Si. The structures are closely related to proposed configurations of the 'B-interstitial-related defect' in Si, with a B atom substituted for a Si atom. The B-split substitutional configuration has two empty, symmetrically equivalent, p orbitals, and may undergo (pseudo-) Jahn–Teller distortions when negatively charged.

The B-interstitial-related defect (BIRD) in Si:B was the first negative-U defect to be identified [1]. It was discovered to be a peculiar defect because it would occupy sites of low symmetry [2]. Recently I made a theoretical calculation proposing microscopic structures of the defect in its various charged states [3, 4]. In its positively charged state it was found to be a combination of a Si interstitial and a B substitutional defect, and in its negatively charged state a symmetry breaking took place giving a structure reminiscent of a split substitutional [5].

In this paper we will study a related defect. We will consider the same microscopic structures, the substitutional–interstitial pair and the split substitutional for a neutral defect in which a B interstitial is substituted for the original Si interstitial, the *boron neutral pair defect* (BNPD). We hope to take advantage of the similarity to obtain a better theoretic understanding of both defects, and to verify experimentally—or refute—the theoretical model based upon parallel experiments for the two defect types. For example, the BIRD is created by irradiation of Si:B, and the theoretical suggestion is that the corresponding irradiation-induced Si interstitials are trapped by the B substitutional atoms. If this model is correct, we would expect the BNPD to be created in an experiment when we inject B interstitials in Si:B.

A neutral B pair defect in Si has been proposed earlier, in which the B atoms would share a substitutional site and bind to each other, as well as to the four surrounding Si atoms. The symmetry of this defect was thought to be lower than tetrahedral and possibly axial. It was concluded that the defect model could not be fully validated for the following reason: although the defect could be formed in p-type material by substitutional and interstitial B atoms attracting via the Coulomb interaction, it was thought unlikely to form in n-type material and this was contrary to observation [6]. A model for C–Si pairs similar to a split substitutional has also been proposed [7], and the model presented may be relevant to C-split substitutionals in Si, although it seems that pairs of C atoms pair up with a Si atom in between [8].

The calculations were performed in the local density approximation using Hamann–Schluter–Chiang pseudopotentials and the supercell approximation [9]. In an 8-atom unit cell, using 1–6 k-points in the irreducible Brillouin zone and a

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15 Ryd energy cut-off, the configuration was relaxed while keeping second-nearest-neighbouring Si atoms fixed. Thereafter, using a 32-atom cell, 1 k-point (0.25, 0.25, 0.25) and 7 Ryd, the energy gain resulting from second- and further nearest neighbours was calculated. Local mode frequencies were calculated at 15 Ryd using 1–2 k-points in the 8-atom cell, with tests for up to 6 k-points. The electronic states were obtained by studying the large 32-atom cell at 7 Ryd, and then approximately compensating for the low cut-off by adding on the relative change in band energy with respect to the valence or conduction bands of bulk Si going from 7 to 15 Ryd in the small 8-atom cell [10].

Let us study the two related defect configurations BIRD and BNPD. The relaxed structures obtained earlier for the BIRD are shown in figure 1, while the relaxed structures obtained in the present work for the BNPD are shown in figure 2. The Si atoms are represented by filled circles, and the B atoms by unfilled circles. Let us first look at figures 1(a) and 2(a). These represent the defects in their trigonally symmetric positions, C_{3v}. These configurations consist of a substitutional B atom paired with an interstitial Si or B atom, respectively. The substitutional–interstitial distance is shorter for the B–B pair than for the B–Si pair, because of the smaller size of the B interstitial. The bonds labelled 'd3' are shorter in the BNPD presumably because of the smaller steric repulsion of the B interstitial as compared to the Si interstitial. Note that the d1 distance is shorter for the BIRD. This could be due to stronger substitutional–interstitial bond formation for the B–B pair, which weakens the corresponding d1 bond.

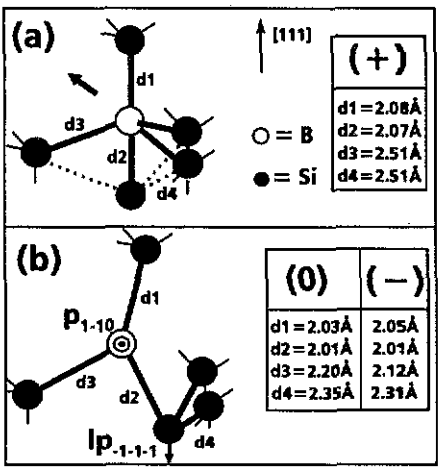

Figure 1. Charge-state-dependent configurations for the B-substitutional–Si-interstitial pair; see [3]. (a) The positive state. The arrow indicates the direction of distortion in the neutral and negative states that are shown in (b). Several interatomic distances are indicated. In (b) two of the electronic orbitals are indicated as well: p_{1-10} and lp_{-1-1-1} where p stands for a p orbital and lp for a lone pair sp^3 orbital; the subscripts indicate the direction of the orbital.

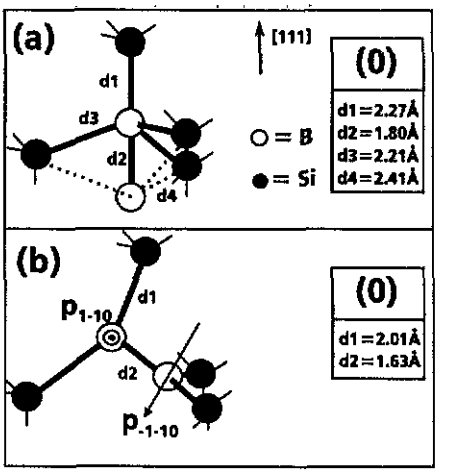

Figure 2. Similar configurations for the B neutral pair defect, both in their neutral charge states. (a) The substitutional B-interstitial B configuration (b) The split-substitutional configuration. Several interatomic distances are indicated. Two electronic orbitals are indicated: p_{1-10} and p_{-1-10} where p stands for a p orbital; the subscripts indicate the direction of the orbital.

In figures 1(b) and 2(b) we show the configurations in their split-substitutional

positions. Note that for the BIRD (figure 1(*b*)), the symmetry is very low, C_{1h}; this is caused by a distortion of the defect in the (1-1 0) plane [2]. The symmetry for the BNPD is much higher, D_{2d}, with the two B atoms taking equivalent positions. Let us consider the electronic states indicated in the figure. These are labelled p_{ijk} and lp_{ijk}, where p stands for p orbital and lp for lone pair. The indexes indicate the direction of the orbitals. For the BNPD, these are two symmetry-equivalent p orbitals on the B atoms. In the neutral charge state, these are empty. As we fill them, a Jahn–Teller distortion is possible, making the two B atoms symmetry inequivalent. Whether the distortion is actualized depends upon the energy of the p orbital. If it is below the bottom of the conduction band, there is a Jahn–Teller effect. If it is above the bottom of the conduction band, there is, at best, a pseudo-Jahn–Teller effect.

The geometry of the BNPD clarifies the large charge-induced relaxation of the B-interstitial-related defect. It is undergoing a Jahn–Teller distortion but, due to its large size, the positively charged state of lowest energy correponds to a substitutional–interstitial pair rather than a split substitutional (the energy difference between these configurations were found to be around 1.6 eV [3]). Note that instead of two equivalent p orbitals, the B-interstitial-related defect has one B p orbital and one Si lone pair. The former is near the bottom of the conduction band, while the latter is near the top of the valence band. The BIRD gap state consists of a p-like bonding state localized on the B atom and two nearby Si atoms [2, 3].

The total energy results on the BNPD are shown in table 1. The two configurations should have an energy difference within about 0.4 eV, and we cannot tell which is the lower. We tested for a barrier between the two configurations of the BNPD, by examining the energy of the configuration half-way between in the 8-atom unit cell and allowing for the B–B bond length relaxation. The result indicated the presence of a barrier of about 0.5 eV.

Table 1. Calculated contributions and error estimates to the total energies of the BNPD in its two configurations.

Energy correction	SIP (eV)	SS (eV)
Energy, 15 Ryd, 8-atom cell, 1–2 *k*-points	0	−0.15
ΔE, 15 Ryd, 8-atom cell, 1–6 *k*-points	0.35	−0.01
Second- and further neighbour relaxation energy in 32-atom cell	−0.08	−0.06
ΔE, 1–2 *k*-points in 32-atom cell	0.08	−0.13
Final energy	0 ± 0.35	−0.15 ± 0.14

To facilitate experimental identification of the BNPD configurations, we calculated approximate local mode frequencies. We assumed that for the split substitutional configuration the antisymmetric mode could be modelled with a single spring between the B-atoms. We calculated the corresponding spring constant (which also includes

the effects of the Si–B bonds) and we find a frequency of about 1100 ± 100 cm^{-1}. For the substitutional–interstitial pair, we used a two-spring model—one connected between the B atoms (bond d2) and one between the substitutional B atom and the Si atom bonded by d1. The latter atom was taken to be frozen. The corresponding antisymmetric mode is positioned at 800 ± 100 cm^{-1}.

Two sets of localized electronic states near the gap were found for the D_{2d} state of the BNPD. One is located near the top of the valence band (0.7 ± ≃ 0.2 eV below the valence band maximum—the error bar comes from the difference in estimates from one to two special-k-point calculations in the 32-atom cell; a 0.4 eV correction for the change in band energy from 7 to 15 Ryd in the small unit cell was added), corresponding to a single bonding state with about 50% of the charge density on the two B atoms (p character, with the orbitals pointing along the B–B bond) and 25% (mixed p and d character) on the four Si neighbours. A second is located near the bottom of the conduction band (0.2 ± ≃ 0.0 eV above the bottom of the conduction band; a −0.1 eV correction for the change in band energy from 7 to 15 Ryd in the small unit cell was added). This corresponds to the two degenerate p orbitals pointing in orthogonal directions. About 26% of the charge of one band is localized on either orbital. Note that the finite size of the supercell increases the kinetic energy of the defect states, and our estimates are accordingly upper bounds. A preliminary calculation of the doubly negative charge state at 7 Ryd in the 32-atom cell, indicated that the state near the top of the valence band moves up by about 0.6 eV, suggesting a correspondence between this state and the gap state of the BIRD. Furthermore, the previously degenerate states near the bottom of the conduction band split into two states with a separation of 0.4 eV.

Table 2. Calculated spring constants and approximate local mode frequencies for the two BNPD configurations. The error bars were obtained from a typical test of k-point convergence for the split substitutional configuration and assumed to be of the same ratio for the substitutional–interstitional pair configuration.

Force constants, 8-atom cell, 1 k-point, 15 Ryd	Substitutional -interstitial pair	Split substitutional
k_{B-B} (eV $Å^{-2}$)	11 ± 1.5	21 ± 3
k_{B-Si} (eV $Å^{-2}$)	5.0 ± 0.8	—
ν_1 (cm^{-1})	800 ± 100	1100 ± 100

In the BNPD C_{3V} configuration, there is a state near the top of the valence band (0.5 ± ≃ 0.3 eV below the valence band maximum, where the error bar comes from the difference in estimates from one to four special k-point calculations; a 0.2 eV correction for the change in band energy from 7 to 15 Ryd in the small unit cell was added) centred on the interstitial B atom, with a charge density of 26% of a band. It has roughly 17% s character and 9% p character; another 7% can be found on the substitutional B atom with mixed s, p and d character. There is also a set of less localized states near the bottom of the conduction band (0.3 ± ≃ 0.1 eV above the bottom of the conduction band; a −0.1 eV correction for the change in band energy from 7 to 15 Ryd in the small unit cell was added). They are centred on the B interstitial atom with 12% each in p orbitals perpendicular to the B–B bond.

Finally, let us summarize our predictions for the BNPD. It should be formed by

injection of B interstitials in Si:B material. There are two possible states of the neutral defect, one with a C_{3V} point group symmetry, and one with a D_{2d} point group symmetry; the two should have energies of within about 0.4 eV of each other. The presence of a 0.5 eV intermediate barrier was indicated. Local mode frequencies were calculated to be 1100 cm^{-1} for the D_{2d} state and 800 cm^{-1} for the C_{3V} state. As we add electrons to this defect, it may undergo a symmetry breaking to a C_{1h} point group symmetry, similar to that of the BIRD, where one of the B atoms moves out in a (110) plane. For the BIRD defect, as the symmetry-broken state is taken, the 'memory' of the (111) axis remains [2]. For the BNPD an axis may also be 'remembered'. The particular axis depends upon which defect configuration has the lowest energy. It would be either the (111) axis (for the C_{3V} configuration) or the (001) axis (for the D_{2d} configuration).

Acknowledgments

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Troxell J R and Watkins G D 1980 *Phys. Rev.* B **22** 921
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After completion of this work it was pointed out to the author that a similar result for the positive charge state can be found in a figure published as a private communication by C S Nichols in
Burns G and Glazer M 1990 *Space Groups for Solid State Scientists* (New York: Academic) p 193
In this result the interstitial Si atom was assumed to occupy a perfect tetrahedral site. It was also earlier suggested, but found unreasonable, that the substitutional B atom traps a Si interstitial, by
Bean A R, Morrison S R, Newman R C and Smith R S 1972 *J. Phys. C: Solid State Phys.* 5 379
The trapping of Si interstitials by B has also been discussed by, for example
Mayer W, Grasse D and Peisl J 1985 *Phys. Status Solidi* a **87** 583
and
Corbett J W, Bourgoin J C, Cheng L J, Corelli J C, Lee Y H, Mooney P M and Weigel C 1976 *Radiation Effects in Semiconductors (Inst. Phys. Conf. Ser. 31)* (Bristol: Institute of Physics) p 1
[4] Note that two similar systems, consisting of a pair of column III, IV or V first-row and second-row atoms, are the C interstitial–P substitutional pair in Si—for a recent paper see
Zhan X D and Watkins G D 1991 Appl. Phys. Lett. 58 2144
—and the C–Si interstitialcy in Si—see
Song L W and Watkins G D 1990 *Phys. Rev.* B **42** 5759
[5] This configuration is also commonly referred to as a split *interstitial.*
[6] Bean A R, Morrison S R, Newman R C and Smith R S 1972 *J. Phys. C: Solid State Phys.* 5 379
[7] See, for example,
Watkins G D and Brower K L 1976 *Phys. Rev. Lett.* **36** 1329
[8] Song L W, Zhan X D, Benson B W and Watkins G D 1990 *Phys. Rev.* B **42** 5765
[9] See, for example,
Joannopoulos J D 1985 *Physics of Disordered Materials* ed D Adler, H Fritsche and S R Ovshinsky (New York: Plenum) and references therein
[10] In table 1 we find the changes in the total energy as we vary the accuracy of our calculation. The *k*-point error is about 0.35 eV for the small unit cell (at a 15 Ryd cut-off) and 0.1 eV for the larger unit cell (at a 7 Ryd cut-off). We give a measure of the error due to the small

supercell size: the energy gained when relaxing the second- nearest-neighbour and further away Si atoms in the larger 32-atom cell is about 0.1 eV. The band gap error due to the local density approximation does not contribute to the total energy, since, for the neutral defects at hand, all occupied states are in the valence band. The positions of the electronic states are accurate to within about 0.5 eV, as has been reported by other authors—see, for example,

Yin M T and Cohen M L 1982 *Phys. Rev.* B 26 5668