

## Polarity inversion in the electron density of BP crystal

Paula Mori-Sánchez and A. Martín Pendás and Víctor Luña

*Departamento de Química Física y Analítica, Facultad de Química, Universidad de Oviedo, E-33006-Oviedo, Spain*

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A rigorous analysis of the electron density of the BP crystal in the light of the atoms in molecules theory reveals very unusual properties. The standard polarity  $B^{\delta+}P^{\delta-}$  found at the zinc-blende equilibrium geometry suffers a reversal under the application of hydrostatic pressure. The inversion occurs through an intermediate situation in which the P valence shell is transferred to a non-nuclear maximum before being caught by the B atom.

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A general consensus exists on the special properties of boron phosphide (and to a lesser extent boron arsenide) among the III-V semiconductors.<sup>1-6</sup> The nearly identical electronegativities of B and P make the BP crystal a candidate for almost perfect covalency. The unusual ordering of the  $X_1^c$  and  $X_3^c$  states in local-density approximations band structure calculations led Wentzcovitch *et al.*<sup>7,1</sup> to assume a strong B  $p$  character at the top of the conduction band due, perhaps, to an unusual  $B^{\delta-}P^{\delta+}$  polarity. This conclusion was in agreement with Harrison's tight-binding effective charges,<sup>8</sup> but reversed the relative B/P electronegativity of most scales but Phillip's. Further work by Wentzcovitch *et al.*<sup>2</sup> attempted to estimate the charge transfer by calculating the valence density enclosed by spheres around the nuclei with a radius defined by the last closed valence density contours in the (100) plane. The results were interpreted as showing the B atom to be more electronegative than P at the zinc-blende equilibrium geometry, and predicted an increasing P→B charge transfer as pressure increases. Despite the crude approach, these results help to explain, for instance, the boron preference for silicon at the SiC/BP interface,<sup>3</sup> thus reduced to an anion-to-cation best match, or the large and negative <sup>11</sup>B NMR shielding in BP, contrary to the behavior found in BN.<sup>9</sup> Furthermore, a similar picture emerges from the Mulliken analysis of Hartree-Fock and density functional theory (DFT) linear combination of atomic orbitals (LCAO) total electron densities,<sup>10,6</sup> though the low heteropolarity makes the Mulliken partition especially likely to fail in these cases.

The BP polarity problem, i.e., whether B or P is more electronegative in this crystal, and its possible change with pressure still remain open questions in our opinion. Our aim in this article is to shed light on the problem by means of an objective and rigorous analysis of the total electron density of BP provided by the theory of atoms in molecules (AIM).<sup>11</sup> Our use of the partitioning scheme required by nonrelativistic quantum mechanics<sup>12</sup> should let us avoid the methodological uncertainties of previous approaches.

Our analysis rests on the calculation of reliable total electron densities. This excludes, unfortunately, most of the pseudopotential techniques developed for the study of semiconductors. We have used the DFT-LCAO CRYSTAL method of Dovesi *et al.*,<sup>13,14</sup> with the Becke exchange<sup>15</sup> and the Perdew-Wang generalized gradient approximation correlation potential.<sup>16</sup> The Gaussian bases used in our calculations

are of triple  $\zeta$  valence plus polarization quality: (6211/211/1) on B and (88211/8211/1) on P. The core Gaussian exponents are obtained from atomic calculations, whereas the valence and polarization exponents have been taken from the values optimized by Paulus *et al.*<sup>17</sup> at the experimental geometry of the BP crystal. To check the reliability of our calculations we have determined the electronic and equilibrium properties of the crystal and we report them in Table I. The overall agreement with experiment is good and corresponds to what should be expected for the basis set and functionals chosen. Of particular relevance are the VBW and bulk properties, which are the ones most connected to the ground state electron density analyzed in this work.

The definition of a crystalline polarity is intimately bound to the possibility of splitting the crystal properties into atomic contributions. This is a fundamental achievement of the AIM theory. The molecular or crystalline space can be rigorously and uniquely partitioned into open quantum regions if some boundary conditions are enforced: only when these regions are separated by zero-flux surfaces (ZFS's) of the electron density gradient vector field,  $\vec{\nabla}\rho(\vec{r})$  can it be guaranteed that every quantum mechanical operator is locally well behaved and every quantum mechanical observable is made up of additive atomic contributions. The ZFS's divide the crystal into atomic basins, each containing a single electron density maximum (usually an atomic nucleus) plus the points contained in all the electron density gradient field lines attracted to it. Each ZFS itself is made up of the  $\vec{\nabla}\rho(\vec{r})$  field lines attracted to a first order saddle critical point of the electron density, called the *bond critical point* (BCP) in AIM's parlance. Two  $\vec{\nabla}\rho(\vec{r})$  field lines start at the BCP that

TABLE I. Calculated and experimental properties of BP.

| Property                     | This work | Expt. (Ref.)         |
|------------------------------|-----------|----------------------|
| $a$ (Å)                      | 4.554     | 4.543±0.001 (18)     |
| $B_0$ (GPa)                  | 175       | 173 (19), 152±5 (18) |
| $B'_0$                       | 3.51      | 4.3±0.5 (18)         |
| $B''_0$ (GPa <sup>-1</sup> ) | -0.023    |                      |
| Indirect gap (eV)            | 1.75      | 2.0 (20)             |
| Direct gap (eV)              | 3.38      | 5.0 (21)             |
| VBW <sup>a</sup> (eV)        | 15.64     | 16.5±0.5 (22)        |

<sup>a</sup>Valence band width.

climb to the two bonded nuclei and constitute the bond path. References 11 and 23, as well as others cited therein, provide an in-depth presentation of the AIM theory.

The electron density of BP presents, at the equilibrium geometry, a very simple topology. A single type of bond critical point appears along each B-P nearest neighbor line, 0.69 Å away from the B atom and 1.28 Å away from the P atom. The properties at the BCP show clear evidences of *shared shell* bonding:<sup>11,23</sup> large electron density ( $\rho_b=0.85 e/\text{Å}^3$ ), negative and large Laplacian ( $\nabla^2\rho_b=-5.09 e/\text{Å}^5$ ), and perpendicular to parallel curvature ratio greater than 1 ( $-\lambda_1/\lambda_3=1.830$ ). All these are signs of a predominantly covalent system. The charge transfer can be determined through the integration of the electron density within the atomic basins.<sup>23</sup> The result is a positive charge on B ( $+0.95e$ ) and, correspondingly, negative on P ( $-0.95e$ ). These charges are in agreement with the fact that the B basin appears much smaller than the P basin: 24% of the cell volume corresponds to B and the other 76% to P. On the other hand, these charges, even though far from negligible, are much smaller than those found in, for instance, the BN crystal:  $\pm 2.4e$ .

Our results show the  $B^{\delta+}P^{\delta-}$  polarity derived, for instance, from Pauling's empirical electronegativities. This contradicts Wentzcovitch's *et al.* results<sup>2</sup> and deserves further consideration. The strategy used in Ref. 2 to integrate the electron density, apart from being arbitrary, presents two important caveats: the atomic spheres do overlap and do not fill the crystal volume. Accordingly, some density is left out and some other is counted twice in the integration. The overlap is particularly important in the high density internuclear directions: the sum of the atomic sphere radii in Table IV of Ref. 2 is 2.318 Å compared to the internuclear distance  $R_{BP}=\sqrt{3}a/4=1.974$  Å. Our electron density, when analyzed with the same strategy, produces very similar results to that of Wentzcovitch *et al.*<sup>2</sup> The atomic basins in the AIM theory, however, rather than spheres, are polyhedra with curved edges and faces and they completely fill the crystal volume with no overlap.<sup>23</sup>

Hydrostatic compression, however, has a profound effect on the electron density of BP, which vindicates some of the conclusions of previous researchers.<sup>2,6</sup>

We have determined the total energy and electron density for a grid of 33 crystal volumes ranging from  $0.5V_0$  to  $1.4V_0$ , where  $V_0$  corresponds to the equilibrium geometry. The zinc blende crystal structure, experimentally known to be stable up to at least 110 GPa,<sup>18</sup> has been assumed at all volumes.

We have found that the BP crystal suffers a change in its topology at about  $V/V_0\approx 0.75$  and, again, a second change at about  $V/V_0\approx 0.57$ . This is a most unusual behavior, not found before among the many covalent or ionic crystals whose topology has been studied, to the best of our knowledge. The topological changes occur on the B-P nearest neighbor line and they will be described with the help of Fig. 1. The topology found at the equilibrium geometry is maintained for  $V>0.75V_0$ , the only effect of compression being the progressive increase of the electron density in the internuclear region (see curves A and B in Fig. 1). A single BCP occurs on the B-P line and the relative size of B and P atoms

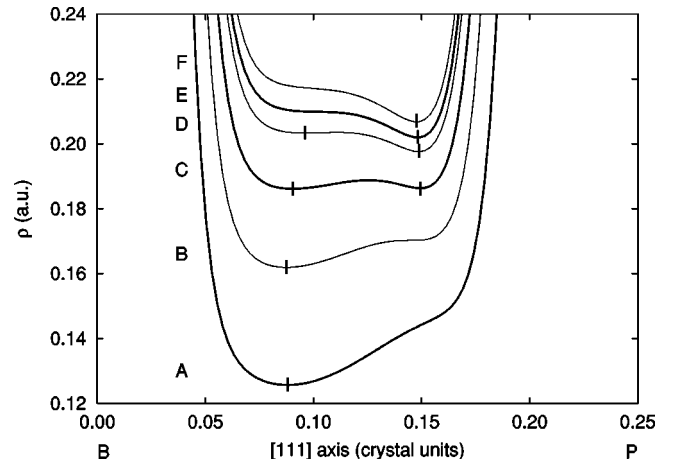


FIG. 1. Electron density along the B-P bond line for six different lattice parameters ( $a$ ): 4.55 (A), 4.14 (B), 3.99 (C), 3.80 (D), 3.75 (E), and 3.70 Å (F). Vertical lines mark the position and density of the bond critical points. The lines designed A, C, and E correspond to different prototypical topologies of the crystal electron density discussed in the text. The shallow maxima in the C and D curves are NNM's.

remains almost constant. When the volume descends below  $0.75V_0$ , this BCP splits, without leaving the B-P line, into a non-nuclear maximum (NNM) and two BCP's (curves C and D). This topology is maintained on compression until reaching  $0.57V_0$ . At this volume, the two BCP's coalesce onto the NNM and a single BCP is obtained as a result (lines E and F). The low and high pressure topologies are equivalent, except that B and P atoms exchange their relative size.

The occurrence of a NNM, albeit rare, is a phenomenon already known in, for instance, some metallic crystals and clusters. In fact, we have recently shown that NNM's are a normal step in the evolution of chemical bonding of many homonuclear groups as internuclear distances decrease.<sup>24</sup> According to our analysis, NNM's should be a most rare phenomenon in heteronuclear groups, the charge transfer associated with the heteropolarity preventing the conditions that favor the NNM's. The small difference in electronegativity between B and P atoms makes the BP crystal an ideal candidate to behave more like homonuclear systems in this respect. Interestingly enough, Wentzcovitch *et al.*<sup>1</sup> anticipated our search, even though their use of valence-only electron pseudo-density impeded a true analysis of NNM's.

In any case, the unusual idea of NNM's has led us to look for confirmation. First, we have checked that the electron density properties examined here are stable with respect to variations in the LCAO basis set or in the exchange and correlation functionals. Second, we have analyzed the electron density of the open shell BP diatomic and the saturated  $BH_2PH_2$  molecule. We have used a high quality basis set: triple  $\zeta$  valence plus diffuse functions, three  $d$  and one  $f$  polarization functions, TZV+(3 $d1f$ ), as implemented in the GAMESS molecular code.<sup>25</sup> Several levels of calculation have been examined, the best one being CISD (configuration interaction including single and double excitations). We have found NNM's in all calculations, the range of internuclear distances in which they appear depending, of course, on the

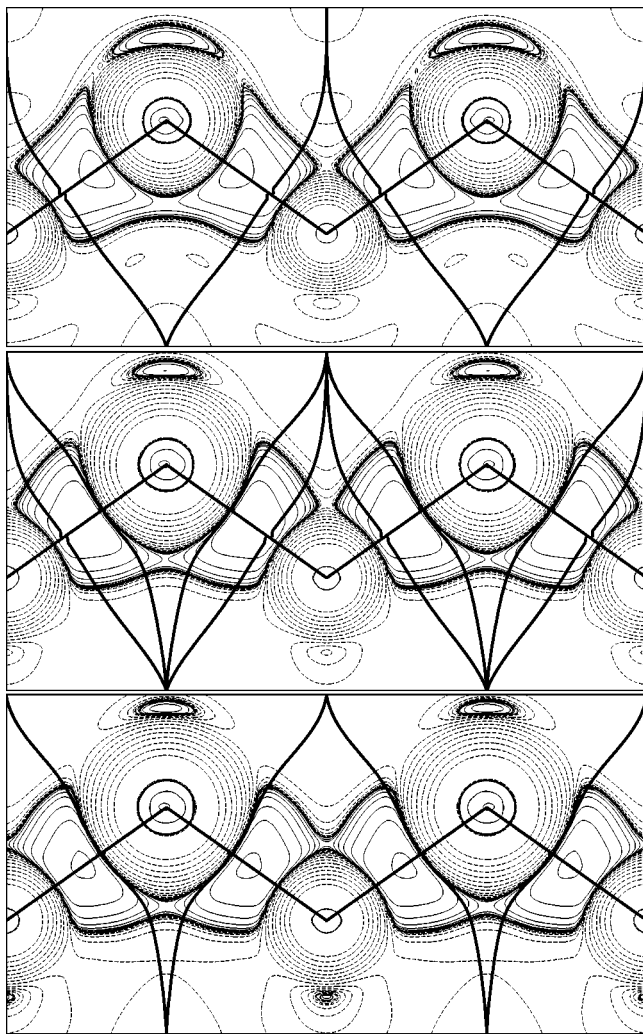


FIG. 2. [110] plane of the BP crystal, containing three B and two P nuclei. The plots correspond to lattice parameters of 4.55 (top), 3.93 (middle), and 3.75 Å (bottom). Thick solid lines show the bond paths and the atom basin boundaries. The contour lines depict the electron density Laplacian  $[\nabla^2\rho(\vec{r})]$ . Negative and positive contours are depicted as thin solid and dashed lines, respectively, according to the geometric scale  $\pm 0.001 \times 2^{n-1} e/\text{bohr}^5$  ( $n$  11–15).

electronic state and molecule as well as on the calculation technique. In the case of the  $X_c^{-3}\Pi$  BP ground state the CISD calculations predict the NNM's to occur for internuclear distances between 1.64 and 1.43 Å, slightly below the molecular equilibrium distance 1.73 Å, and also smaller than the range of NNM's in the crystal:  $R(\text{B,P})=1.64\text{--}1.79$  Å. These results exclude the possibility of the NNM's appearing as an artifact of the crystalline calculation.

We can gain further insight into the electron distribution in the BP crystal by examining closely the [110] plane, which contains a zigzag of nuclei plus the bond paths that connect them. Shown in Fig. 2 are the contour lines of the electron density Laplacian  $\nabla^2\rho(\vec{r})$ , together with the bond paths and the atomic basin boundaries in the plane. The value of the Laplacian at a point measures whether the electron density is locally concentrated ( $\nabla^2\rho < 0$ ) or depleted

( $\nabla^2\rho > 0$ ) there, thus providing a detailed map of the basic and acidic regions, respectively, in the crystal.<sup>26</sup> Large charge concentrations occur around the B-P line, which contains the bond critical points. In the low pressure regime the charge concentration region belongs to the P atom basin, surrounding its nucleus tetrahedrally. At higher pressures, the internuclear charge concentrations form the NNM's, with a lenticular shape, that appear separating the P from the B basin. At even higher pressures, the NNM's disappear and the charge concentration region is transferred to the B basin. Figure 2 faithfully maps the transition from a  $\text{P}^{\delta-}\text{B}^{\delta+}$  to a  $\text{P}^{\delta+}\text{B}^{\delta-}$  situation. The whole process can be described as the transfer of valence electrons from the P to the B atom.

Some interesting aspects of the density behavior under compression, apart from the NNM's and the polarity inversion, deserve to be exposed. First, the ionicity component in the B-P bonding increases with increasing pressure. This is observed in the value of  $\nabla^2\rho(\vec{r}_c)$  at the bond critical point ( $-5.09 e\text{Å}^{-5}$  for  $a=4.55$  Å but  $+0.93 e\text{Å}^{-5}$  for  $a=3.75$  Å) as well as in the value of the atom basin charges [ $Q(\text{B})=0.95e$  for  $a=4.55$  Å and  $Q(\text{B})=-2.74e$  for  $a=3.75$  Å]. Second, and more remarkable, three different but related phenomena occur simultaneously when the crystal volume decreases below  $0.57V_0$ : (a) the NNM's disappear and the B atoms adopt the anionic role; (b) the charge concentration regions associated with the P-B bond lines become connected and form a three dimensional network that extends to the whole crystal; and (c) the crystal becomes metallic, with the  $X_c^1$  state appearing under the Fermi level. The last two facts appear to be systematically connected in several metals that we have studied.

We have found clear evidence of the polarity changes in BP, but we still have an important question to answer. Is it possible to detect the phenomenon experimentally? According to our calculation, the range of existence of NNM's corresponds to the pressure range of 85–260 GPa. The zincblende structure is known to be stable up to at least 110 GPa, which corresponds to the highest pressure experimentally studied in this crystal.<sup>18</sup> The observation by Ito and Endo<sup>27</sup> of a cusp at around 40 GPa in the electrical resistance versus pressure curve might be related to the formation of NNM's. A direct confirmation of this suspicion could be gained by analyzing the electron density deduced from x-ray diffraction measurements. The electron density at the NNM's is rather large ( $1.27 e/\text{Å}^3$  for  $a=3.93$  Å) and easy to detect experimentally; it is, however, very similar to the densities of the near points along the B-P line, which converts the observation of the NNM density cusp into a delicate problem.

It would be far easier to notice the predicted high pressure metallic state. Wentzcovitch *et al.*<sup>2</sup> have predicted, however, a transition from the zinc-blende ( $B3$ ) to a rock-salt ( $B1$ ) structure at about 160 GPa, a pressure quite similar to our own estimation. Ozoliņš and Zunger<sup>28</sup> have recently shown, on the other hand, that the  $B1$  structure becomes unstable, probably by transformation to a  $Cmcm$  phase, in highly covalent materials like BP. In any case, our calculations predict that both the  $B1$  and  $Cmcm$  phases are metallic, lack



NNM's, and consist of a B anion bounded to a smaller cationic P atom, thus behaving similarly to the high pressure zinc-blende BP crystal.

To conclude, a polarity reversal occurs in the BP crystal upon application of hydrostatic pressure. When compressed, the large charge density accumulation around the B-P bond paths separates from the P basins to form NNM's. When these accumulations become connected in a three dimensional network extending to the whole crystal, a metallic phase is obtained. The metallization probably occurs, however, through a structural phase transition before the metallization onset of the zinc-blende phase is achieved.

Is BP a unique crystal in this behavior or, rather, are there other similar compounds? The best candidates would be heteronuclear crystals with a very small difference in electronegativity among the atomic components. As a proof of the

concept we have studied the electron density of some promising diatomic molecules. Several systems have been found that exhibit a large range of existence for NNM's: LiNa, LiCa, BAs, and BeAl. All these molecules have a difference in Pauling's electronegativity  $\chi_P$  smaller than 0.15. We also found, however, molecules with  $\Delta\chi_P \approx 0$  that show no signs of NNM's: CS, CSe, and BGe, for instance. Whether this is due to the use of Pauling's scale or because some further condition is required apart from  $\Delta\chi \approx 0$  remains to be seen. What looks clear to us is that important surprises still remain hidden in the electron density properties of very slightly heteropolar compounds.

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