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First approach to the band structure of α-rhombohedral boron

F. Perrot

Commissariat à l'Energie Atomique, Centre d'Etudes de Limeil, BP 27, 94190 Villeneuve St. Georges, France

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We report a calculation of the energy-band structure of α-rhombohedral boron. The lack of theoretical studies of solid B (a technologically interesting material) can be explained by the difficulties of a quantitative calculation: twelve atoms in the cell and a very open structure. The "muffin-tin-orbitals" method for atomic spheres having a large overlap has been used. The total potential is a superposition of individual potentials of finite range, built from the atomic charge density. The Kohn-Sham exchange potential is correctly calculated using the superposition of atomic densities and then numerically fitted with a superposition of individual functions. The results show a nonmetallic behavior of α-B with an indirect bandgap. But this agreement with experiment is not quantitative: The gap is significantly too large and the occupied band too narrow. The modifications required for improving this calculation are reviewed.

I. INTRODUCTION

Boron was the last common solid element to resist having any of its forms structurally elucidated, although most of its physical properties are surprising. For instance, solid boron is a nonmetal with low chemical reactivity, unlike aluminum which has the same electronic configuration s^2p^1 but is metallic. Its hardness and thermal stability are also quite exceptional.[1] Such interesting properties and others (neutron-stopping power, etc.) lead to various technological applications which will stimulate theoretical investigation of the electronic structure of solid boron. Two main questions have to be answered first: (i) Do band-structure calculations account for the nonmetallic behavior of solid B and (ii) what is the exact nature of the bond between atoms in this material?

In the present paper, we try to study the first point by proposing a crude band structure of B which, to our knowledge, has never been calculated up to now. We use the nonlinearized "muffin-tin orbitals" (MTO) method with a potential derived from a superposition of atomic potentials. Owing to the complexity of the crystalline structure (we have chosen the simplest one, that of α-B) and the importance of nonspherical effects, such a calculation is faced with considerable practical difficulties. Our results will show an insulating character of α-B, with an indirect band gap, a conclusion which agrees with experiment.

A short description of the α-B lattice is given in Sec. II. In Sec. III, the construction of the one-electron potential is described. The main features of the MTO method are presented in Sec. IV; a discussion of the removal of singularities due to the divergence of the structure coefficients at the center of the Brillouin zone is given in the Appendix. The results are reported and discussed in Sec. V, and the modifications of the model required for a self-consistent calculation are then examined as a conclusion.

II. ALPHA-RHOMBOHEDRAL BORON

The three well-known forms of crystalline boron are the following: alpha-rhombohedral boron (α-B) with 12 atoms in the unit cell, beta-rhombohedral boron (105 atoms), and tetragonal boron (49 atoms).[1] Of course, we shall focus our attention on α-B. The primitive arrangement of solid boron is the 12-atom icosahedron shown in Fig. 1. The atoms are located on a sphere of radius R and each of them has five nearest neighbors on the same icosahedron, at a distance

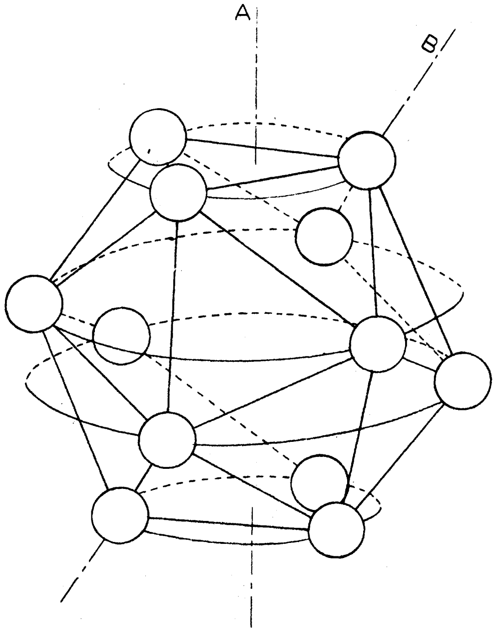

FIG. 1. 12-atom icosahedron of boron.

$d=[2(1-1/\sqrt{5})]^{1/2}R$. The center of the sphere is a center of inversion. The figure has three axes of symmetry: one of twofold rotational symmetry, one of threefold symmetry (A in Fig. 1), and one of fivefold symmetry (B in Fig. 1). In polar coordinates, with the z axis along A, the positions of the atoms are

$$z=z_1,\quad \rho=(1+\sqrt{5})z_2,\quad \phi=0,2\pi/3,4\pi/3,$$

$$z=-z_1,\quad \rho=(1+\sqrt{5})z_2,\quad \phi=\pi/3,\pi,5\pi/3,$$

$$z=-z_2,\quad \rho=(3+\sqrt{5})z_2,\quad \phi=0,2\pi/3,4\pi/3,$$

$$z=z_2,\quad \rho=(3+\sqrt{5})z_2,\quad \phi=\pi/3,\pi,5\pi/3,$$

with

$$z_1=\left(\frac{5+2\sqrt{5}}{15}\right)^{1/2}R$$

and

$$z_2=\left(\frac{5-2\sqrt{5}}{15}\right)^{1/2}R\,.$$

The structure of α-B is a close-packed array of rhombohedral unit cells, each of them containing one icosahedron. The angle α between any two of the primitive vectors of the lattice is $\alpha=58°$, instead of $\alpha=60°$ in the face-centered-cubic lattice. As the fivefold symmetry is incompatible with any crystal structure, the icosahedra are slightly distorted. Each atom has five nearest neighbors in its own cell, and another one in an adjacent cell, at a distance $1.016R$ (strong bond) or $1.213R$ (weak bond). This is the second reason for which the coordination polyhedron based on the six neighboring atoms is distorted.[2,3] The lattice of α-B is a very open structure: The fraction of the unit cell filled by 12 touching atomic spheres is only 0.399. Inserting an additional empty sphere at the center of the icosahedron would only slightly increase this fraction to 0.423. This clearly prevents the use of the "muffin-tin" approximation for the potential, as will be discussed in the next section. According to Slater's textbook,[4] the space group is D_{3d}^5, which includes 12 operations; the reciprocal lattice is rhombohedral too. The irreducible part of the Brillouin zone (BZ) is shown in Fig. 2.

III. OVERLAPPING ONE-ELECTRON POTENTIAL FOR α–B

In B at normal density, the radius of the touching "muffin-tin" (MT) spheres is $R_{\mathrm{MT}}=1.62$ a.u. and the radius of the Wigner-Seitz (WS) sphere is $R_{\mathrm{WS}}=2.27$ a.u., so that their ratio is $R_{\mathrm{MT}}/R_{\mathrm{WS}}=0.71$, instead of 0.90 as in fcc aluminum. The electronic charge outside the MT sphere is $1.7e$, compared with $0.73e$ in Al. The one-electron potential used in a band-structure calculation must take into account properly the strong overlap of individual potentials. This has been done in the following way.

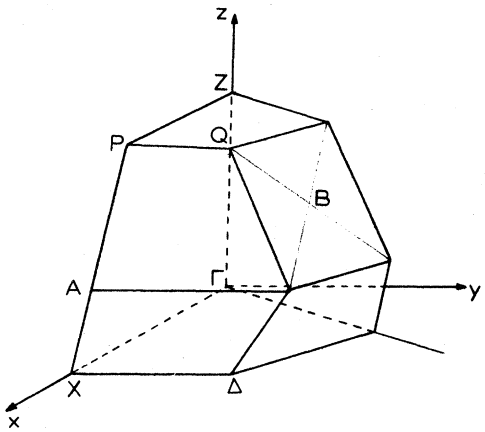

FIG. 2. Irreducible part of the Brillouin zone for the α-rhombohedral lattice.

A. Superposition of atomic charge densities

The charge density needed to construct the crystal potential is generated by a self-consistent free-atom calculation with Kohn-Sham (KS) exchange. This density $n(r)$ may be approximated rather accurately for $r\geqslant S$ by a Gaussian:

$$n(r)=Ae^{-\alpha r^2}\ \text{for}\ r\geqslant S \tag{1}$$

as shown in Fig. 3. S will be the range of the overlapping potential; the choice $S=3R_{\mathrm{mt}}/2$ appeared to be adequate. Let us define the function

$$f(r)=[n(r)-Ae^{-\alpha r^2}]\Theta(S-r) \tag{2}$$

[where $\Theta(r)$ is the Heaviside function], so that the superposed density for the crystal is

$$\rho(\vec{r})=\sum_{\vec{R},\vec{Q}}f(|\vec{r}-\vec{R}-\vec{Q}|)+\frac{1}{\Omega_0}A\left(\frac{\pi}{\alpha}\right)^{3/2}\sum_{\vec{K}}S(\vec{K})e^{-K^2/4\alpha}e^{i\vec{K}\cdot\vec{r}}\,, \tag{3}$$

where $\vec{R}$ is a lattice vector and $\vec{Q}$ the vector which fixes the position of one atom in the cell. $\vec{K}$ is a vector of the reciprocal lattice, $S(\vec{K})$ the structure factor, and Ω_0 the volume of the WS sphere. If α is small enough, the sum in (3) may be restricted to the term $\vec{K}=0$ so that

$$\rho(\vec{r})=\sum_{\vec{R},\vec{Q}}f(|\vec{r}-\vec{R}-\vec{Q}|)+n_0, \tag{4}$$

$$n_0\Omega_0=A\left(\frac{\pi}{\alpha}\right)^{3/2}. \tag{5}$$

The electrical neutrality requires that

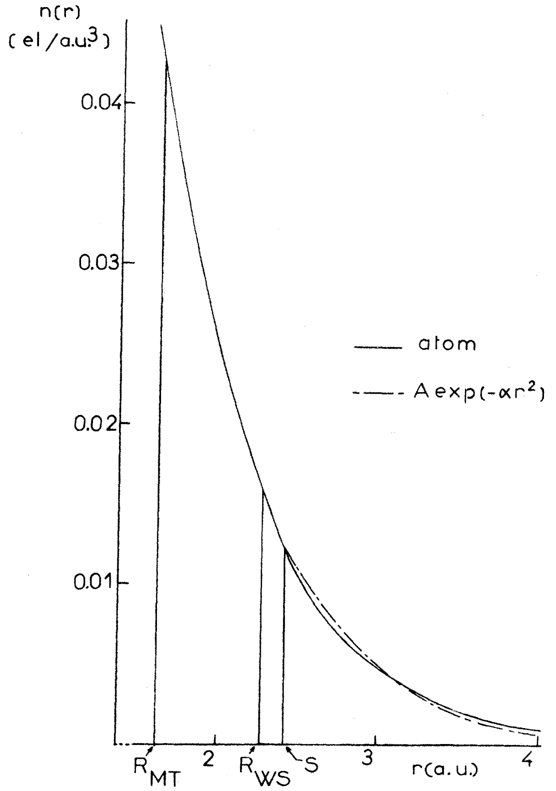

FIG. 3. Plot of the total electron density in atomic boron. The relative positions of the muffin-tin and Wigner-Seitz radii are shown. S is the range of the overlapping potential used in the calculation.

$$n_0\Omega_0 = Z - \int_0^S f(r)\,d\vec{r}, \tag{6}$$

and the comparison between the two values of n_0, given by either (5) or (6), indicates the accuracy of the approximation. In our calculation they agree within 5%. In the following, we shall use the value (6) in order to exactly preserve neutrality. Equation (4) expresses the total density as the sum of a uniform background plus finite-range contributions centered on each site.

B. Crystal Coulomb potential

Let $v(r)$ be the atomic Coulomb potential corresponding to the individual density $n(r)$. With the approximate form (1) of $n(r)$ for $r \geq S$, we obtain the approximate potential in the same domain:

$$v(r) = -\frac{2\pi A}{\alpha r}\int_r^\infty e^{-\alpha r^2} dr \quad \text{for } r \geq S. \tag{7}$$

We now define an auxiliary function $w(r)$:

$$w(r) = \begin{cases} Be^{-\beta r^2} & \text{for } r \leq S, \\ v(r) & \text{for } r > S, \end{cases} \tag{8}$$

where B and β are chosen in such a way that w and its derivative are continuous at $r = S$:

$$\beta S^2 = -\frac{\pi}{\alpha s}\frac{n(S)}{v(S)} + \frac{1}{2}, \tag{9}$$

$$B = v(S)e^{\beta S^2}. \tag{10}$$

Using the technique of the preceding paragraph, with

$$u(r) = [v(r) - Be^{-\beta r^2}]\Theta(S - r), \tag{11}$$

the superposed Coulomb potential is

$$V_C(\vec{r}) = \sum_{\vec{R},\vec{Q}} u(|\vec{r} - \vec{R} - \vec{Q}|) + V_{C0} \tag{12}$$

where V_{C0} is the average value of $w(r)$, given by

$$V_{C0} = \frac{2\pi S^3}{\Omega_0} v(S)\left(\frac{x^2}{y^2} - 1 + \frac{1}{2y^2} - \frac{1}{x^2} + \frac{\sqrt{\pi}}{2}\frac{e^{x^2}}{x^3}\operatorname{erf}(x)\right) \tag{13}$$

with $x^2 = \beta S^2$ and $y^2 = \alpha S^2$.

C. Exchange potential

The problem with exchange is approximating the potential for the solid, which is a nonlinear function of the total charge density, by a superposition of individual potentials of finite range. In the KS approximation, the "exact" potential is

$$V_X(\vec{r}) = -K[\rho(\vec{r})]^{1/3}, \tag{14}$$

where ρ is given by (4). K is a numerical constant equal to $(3/\pi)^{1/3}$. V_X can be numerically calculated at any point $\vec{r}$. We want to obtain an accurate representation of V_X in the form

$$V_X(\vec{r}) = \sum_{\vec{R},\vec{Q}} g(|\vec{r} - \vec{R} - \vec{Q}|) - Kn_0^{1/3}. \tag{15}$$

The function g is written

$$g(r) = K\{[f(r) + n_0]^{1/3} - n_0^{1/3}\}\Theta(s - r) + \sum_{n=0}^{N} a_n r^n e^{-\gamma r}\Theta(r - s)\Theta(S - r). \tag{16}$$

The range of the function f appearing in the density (4) is limited to S so that there is no overlap in the domain $r < s = 2R_{mt} - S$: In that region $g(r)$ is given by the first term of (16). In the overlapping region $s \leq r \leq S$, $g(r)$ is expanded according to the second part of (16). The coefficients of the expansion are determined by a least-squares fit of the numerical values of $V_X(\vec{r})$ given by (14) on a three-dimensional mesh of 132 points. The continuity of $g(r)$ for $r = s$ and the value $g(S) = 0$ are imposed. The value of γ is varied until the best fit is obtained. With five basis functions ($N = 4$) an accurate fit corresponding to a mean error of 0.0005 Ry in V_X is obtained.

IV. MTO BAND-STRUCTURE MODEL

The number of basis functions required to obtain a reasonable accuracy is a major aspect of the choice of the method adapted to an open-structure band calculation. In the case of $\alpha-\mathrm{B}$, the number of reciprocal-lattice vectors $\vec{K}$ with length smaller than $3k_F$ (k_F is the Fermi momentum) is 496. An augmented-plane-wave calculation (imperatively including a treatment of non-MT effects) would need, according to the criterion $K_{\max}R_{\mathrm{mt}}=6$ (p states),[5] about 500 basis functions. The Green's-function method is, from that point of view, the most suitable: The size of the secular determinant would be 106 for a full treatment of the $l=0$, 1, and 2 angular momenta and only 48 if the d component could be treated as a perturbation.

The MTO method without an "atomic-sphere approximation," as proposed by Andersen,[6] is equivalent to the Green's-function method where the structure coefficients are calculated at zero energy. The secular equation is in that case

$$\sum_{lm\vec{Q}}\left(-2(2l+1)\frac{D_1(E)+l+1}{D_1(E)-l}\right.$$
$$\left.\times\delta_{ll'}\delta_{mm'}\delta_{\vec{Q}\vec{Q}'}+S^{\vec{k}}_{l'm'\vec{Q}',\,lm\vec{Q}}\right)C_{lm\vec{Q}}=0. \tag{17}$$

$S^{\vec{k}}_{l'm'\vec{Q}',\,lm\vec{Q}}$ is the structure coefficient, the expression of which can be found in Ref. 6. This coefficient is independent of energy and does not change in a uniform scaling of the lattice. $D_l(E)$ is the logarithmic derivative (multiplied by r) of the l-momentum radial orbital at energy E, in principle, calculated at the MT radius. The very interesting point is that Ball has shown that the Green's-function equations, and consequently the MTO equation (17), remain valid for overlapping potentials,[7] with the single condition that there exists a region around each ion in which only the potential of that ion is nonzero (i.e., the range S of the potential is smaller than the nearest-neighbor distance). The fundamental reason why the band structure is correctly determined by Eq. (17) for overlapping potentials is that they can be derived not from a variational principle requiring knowledge of the wave function everywhere, but from a condition on the scattering amplitudes. So we shall use Eq. (17) for our overlapping potentials in α-B, with the structure coefficients corresponding to a sphere of radius S (the range of the potential) and $D_l(E)$ calculated at $r=S$ in the individual potential. A very important point of Ball's demonstration is that Eq. (17) does not determine the electron wave function entirely. As a consequence, it is impossible to perform self-consistent calculations for overlapping spheres based on Eq. (17) only: The use in whole space of wave functions calculated with the vectors $C_{lm\vec{Q}}$ determined by (17) is incorrect, especially when the amount of overlap is large.

Some difficulties are encountered in the calculation of the band structure at the center of the Brillouin zone that are due to divergence in $S^{\vec{k}}_{l'm'\vec{Q}',\,lm\vec{Q}}$ at $\vec{k}=0$. A particular study of the solution of Eq. (17) for this point is presented in Appendix A.

We mentioned that the $l=2$ momentum can be taken into account in Eq. (17) by perturbative techniques without increasing the size (48 at a given point $\vec{k}$ in the BZ) of the secular equation. This can be done using Löwdin's partitioning scheme.[8] The full matrix of the system including the $l=2$ terms is divided according to

$$M=\begin{pmatrix} N & Q \\ Q^t & P \end{pmatrix},$$

where P contains the $l=2$ elements only, so that the equation $\det M=0$ is equivalent to $\det(N-QP^{-1}Q^t)=0$. In the present case, the value of $F_l(E)$ for $l=2$ is always large compared with the structure coefficients so that the approximation which consists in replacing P^{-1} by a diagonal matrix with all elements equal to $1/F_2(E)$ is entirely justified. Finally, we obtain

$$M_{ij}=N_{ij}-\sum_k Q_{ik}Q_{jk}/F_2$$

with $1\leq i,j\leq 48$ and $49\leq k\leq 108$ (see the Appendix for F_l).

V. NUMERICAL RESULTS

Andersen has shown that an accurate fit of the logarithmic derivatives $D_l(E)$ in a particular branch is obtained from

$$\frac{1}{D_l(E)-D_l(E_\nu)}=-\frac{S\phi^2_{\nu l}}{E-E_\nu}-S\phi_{\nu l}\dot{\phi}_{\nu l}$$
$$+(E-E_\nu)S\phi^2_{\nu l}\langle\dot{\phi}^2_{\nu l}\rangle, \tag{18}$$

depending on a correctly chosen reference energy E_ν and four "potential parameters" $D_l(E_\nu)$, $\phi_{\nu l}$, $\dot{\phi}_{\nu l}$, and $\langle\dot{\phi}^2_{\nu l}\rangle$.[6] In Table I, we give the values of these parameters calculated in the potential described in Sec. III for the reference energy $E_\nu=-0.90$ Ry on the absolute scale (the

TABLE I. Potential parameters used for the band-structure calculation of α-B.

l	$\phi_{\nu l}$	$D_l(E_\nu)$	$\dot{\phi}_{\nu l}$	$\langle\dot{\phi}^2_{\nu l}\rangle$
0	−0.3253	−1.5445	0.2407	0.1072
1	0.4443	−0.0146	−0.1972	0.0803
2	0.6581	1.6137	−0.0779	0.0087

uniform constant potential is $V_0 = V_{CO} - Kn_0^{1/3} = -1.202$ Ry on that scale). The range of the potential is $S = 2.4243$ a.u. The lattice constants, as defined in Ref. 4 are $a = 9.5621$ a.u., $s/a = 0.5598$, and $r/a = 0.8286$.

The band structure has been calculated on a regular mesh with 14 points in four layers in the irreducible part of the BZ. Additional points on the faces have been also calculated. The energy levels for eight of these points are given in Tables II and III, and the energy bands along the direction ΓZ are shown, as an example, in Fig. 4. The origin of energies in the tables is the lowest level at Γ, the value of which is −1.442 Ry on the absolute scale. This calculation shows that the 18 bands fully occupied by the 36 electrons in one cell are well separated from the higher bands, leading to a nonmetallic behavior of α-B as indicated by experiment. This result is a consequence of the crystalline structure: A similar calculation for the fcc lattice gives a band structure entirely analogous to that of metallic Al. We find that the gap between valence and conduction bands in α-B is indirect from Γ to B. Its value is 2.88 eV (0.212 Ry). Unfortunately, we know the experimental gap for β-B only. However, the band-structure properties may be expected not to vary strongly from α-B to β-B.[9] Photoemission measurements on β-B show that this material is an indirect band-gap semiconduc-

TABLE II. Energy levels in α-B for some symmetry points. The origin of energies is the lowest state at the center of the zone. Units are rydbergs.

	Γ		Z		A		B
1	0.0	1	0.085	1	0.093	1	0.118
3	0.295	1	0.116	4	0.120	3	0.145
6	0.310	6	0.301	4	0.283	3	0.244
6	0.310	6	0.301	3	0.287	4	0.254
1	0.326	1	0.311	1	0.313	1	0.287
1	0.372	5	0.361	1	0.370	1	0.295
5	0.380	5	0.361	2	0.386	2	0.475
5	0.380	5	0.466	1	0.467	1	0.483
5	0.447	5	0.466	4	0.472	2	0.501
5	0.447	3	0.534	2	0.499	3	0.534
3	0.464	1	0.549	3	0.523	4	0.534
6	0.527	3	0.578	4	0.529	3	0.571
6	0.527	3	0.597	4	0.583	4	0.576
3	0.627	6	0.614	1	0.587	3	0.605
2	0.671	6	0.614	3	0.624	1	0.622
5	0.714	6	0.631	4	0.657	3	0.628
5	0.714	6	0.631	2	0.718	4	0.665
1	0.726	2	0.676	1	0.718	1	0.714
1	0.964	5	0.980	1	0.949	1	0.938
5	1.049	5	0.980	2	1.031	2	0.987
5	1.049	1	0.992	3	1.081	1	1.039
		2	1.072	1	1.100		

TABLE III. Energy levels in α-B for some symmetry points. The origin of energies is the lowest state at the center of the zone. Units are rydbergs.

	X		Δ		P		Q
+	0.102	1	0.119	+	0.118	1	0.125
+	0.134	2	0.162	+	0.160	2	0.176
+	0.228	1	0.176	+	0.178	2	0.179
−	0.277	2	0.255	−	0.263	2	0.206
+	0.332	1	0.305	+	0.308	2	0.370
+	0.378	1	0.389	+	0.369	1	0.387
−	0.408	2	0.438	−	0.444	2	0.404
+	0.430	2	0.454	+	0.444	1	0.412
−	0.483	1	0.460	−	0.470	1	0.486
+	0.512	1	0.495	+	0.535	1	0.533
−	0.545	2	0.571	−	0.570	1	0.567
+	0.554	1	0.573	+	0.577	1	0.569
+	0.574	2	0.593	+	0.581	2	0.595
+	0.600	2	0.622	−	0.601	1	0.610
−	0.620	1	0.631	+	0.621	2	0.622
+	0.658	2	0.640	+	0.639	1	0.646
−	0.699	1	0.649	−	0.688	2	0.660
+	0.706	1	0.699	+	0.693	2	0.692
+	0.945	1	0.987	+	0.944	2	0.963
−	1.029	2	0.989	−	1.008	1	1.029
+	1.080	1	1.035	+	1.042	2	1.029
		2	1.056	−	1.084	1	1.037

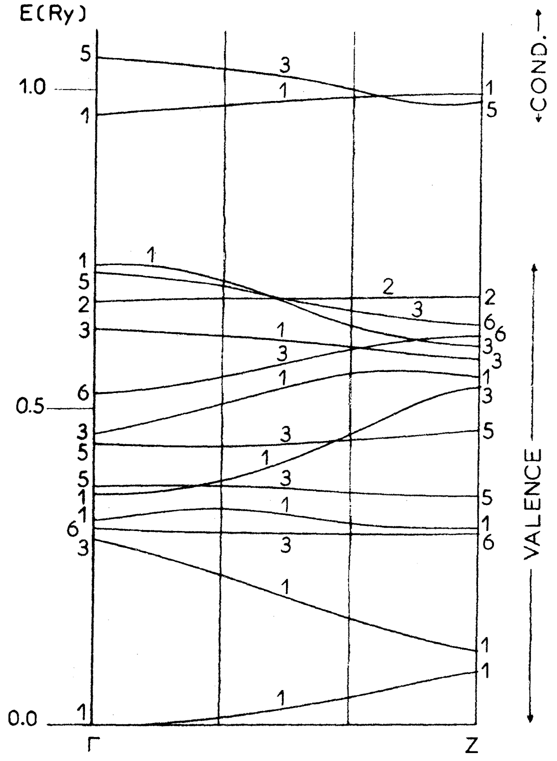

FIG. 4. Energy-band structure of α-B along the Γ–Z direction.

tor, with a gap of 1.5–1.6 eV/,[10,11] significantly smaller than our calculated value. Our theoretical model gives an occupied bandwidth of 0.726 Ry, which seems to be underestimated compared with the value of 1.14 Ry obtained for the $2p$ valence band of α-B from x-ray K-emission spectra.[9]

In order to prove the large influence of the strong potential overlap, we have made a similar calculation at Γ for a potential with a smaller range $S' = 1.25R_{\mathrm{MT}}$ (instead of $S = 1.50R_{\mathrm{MT}}$). The valence bandwidth in that potential is 1.186 Ry (instead of 0.726 Ry) and the band gap is 0.392 Ry (compared with 0.238 Ry), in much poorer agreement with experiment. These important variations are due to the tail of the potential itself, but also to the replacement of the radial solutions of the Schrödinger equation by the energy-independent MTO (of the form $r^{-(l+1)}$) when the atomic sphere radius is reduced from S to S'. Clearly, the use of the largest possible value of S is imperative.

V. CONCLUSION

We have presented a calculation of the energy bands of α-B using a method which is most likely the simplest of those expected to give a realistic description of such a complex structure. The results are in qualitative agreement with experiment: They explain that α-B is a nonmetal with an indirect band gap. The calculated gap is approximately twice the observed value and the estimated bandwidth is significantly too small. These numerical discrepancies may be attributed to the following shortcomings of this first approach: (i) use of a non-self-consistent potential and (ii) use of the KS exchange approximation without the correlation effects to which the gap is rather sensitive, particularly in nonmetals.[12]

As we are now sure that band models can give a relevant answer to the question of electronic structure of solid boron, the problem of self-consistency must be examined. To solve this problem, it is necessary to generate the wave functions. As shown previously, this is not possible in the MTO method with spheres having a large overlap. So, adjacent (i.e., MT) spheres should be used, raising the difficulties of band calculations with strong non-MT effects. A scheme allowing a fast computation of the matrix elements of the non-MT part of the potential is to be presently developed. We hope that a self-consistent calculation along these lines will be successful. The influence of various correlation potentials commonly used in solid-state theory could be easily tested in relation with these improvements of the present work.

APPENDIX

Here we present a particular treatment of Eq. (17) at the center of the BZ. According to their general form given in Ref. 6, the structure coefficients can be written

$$S^{\vec{k}}_{l'm\vec{Q}',\,lm\vec{Q}} = e^{i\vec{k}\cdot(\vec{Q}'-\vec{Q})}\,T^{\vec{k}}_{l'm\vec{Q}',\,lm\vec{Q}}$$

so that, after the appropriate unitary transformation, Eq. (17) becomes

$$\sum_{lm\vec{Q}} T^{\vec{k}}_{l'm\vec{Q}',\,lm\vec{Q}}\,a_{lm\vec{Q}} = -F_l(E)\,a_{l'm\vec{Q}'}\,, \tag{A1}$$

where the notation

$$F_l(E) = -2(2l+1)\frac{D_l(E)+l+1}{D_l(E)-l} \tag{A2}$$

has been used. We are interested in the solutions of (A1) for $\vec{k}\to 0$. The choice of $\vec{k}$ along the the z axis does not restrict the generality of the following study. With such a convention, the matrix T can be divided into regular and irregular parts:

$$T^{\vec{k}}_{l'm\vec{Q}',\,lm\vec{Q}} = R^{\vec{k}}_{l'm\vec{Q},\,lm\vec{Q}} + I^{\vec{k}}_{l'm\vec{Q}',\,lm\vec{Q}}\,, \tag{A3}$$

where $R^{\vec{k}}$ has a finite limit for $\vec{k}=(0,0,k)\to 0$ and

$$I^{\vec{k}}_{l'm\vec{Q}',\,lm\vec{Q}} = \begin{cases} Ak^{-2} + O(k^2) & \text{for } l'=l=0\,, \\ Bk^{-1}\delta_{m'0}\delta_{m0} + O(k^2) & \\ \quad\text{for } l'=0,\, l=1 \text{ or } l'=1,\, l=0, & \\ 0 + O(k^2) & \text{for } l'=l=1 \end{cases} \tag{A4}$$

A and B depend on geometrical quantities only, but neither depend on the particular values of $\vec{Q}'$ and $\vec{Q}$ nor on $\vec{k}$. As we search for eigenvalues

$$E = E_0 + E_1k^2 + \cdots \tag{A5}$$

the expansion of $F_l(E)$ near the center of the zone is

$$F_l(E) = -\left(\frac{U_l}{k^2} + V_l + \cdots\right). \tag{A6}$$

The form of the wave function inside the sphere $\vec{Q}(\vec{\rho} = \vec{r} - \vec{Q})$ is

$$\psi = \frac{1}{\phi_0'(E,S)}\,a_{00\vec{Q}}\,\phi_0(E,\rho)Y_0^0(\hat{\rho}) + \sum_m \frac{1}{\phi_1(E,S) - S\phi_1'(E,S)}\,a_{1m\vec{Q}}\phi_1(E,\rho)Y_1^m(\hat{\rho})\,, \tag{A7}$$

where $\phi_l(E,\rho)$ is the normalized radial part of the Schrödinger equation. The $l=2$ angular momentum is not included in (A7) for simplicity but can be added without difficulty since it does not contain any irregular term. Expanding the $a_{lm\vec{Q}}$ in powers of k and treating separately the successive orders appearing in Eq. (A1) leads to the following results:

(i) There exists a solution Γ_1 with full s symmetry, which satisfies

$$D_0(E_0)=0 \quad [U_0 \neq 0 \text{ in Eq. (A6)}], \tag{A8}$$

$$a_{00\vec{Q}}/\phi_0'(E_0,S)=\eta \quad (\text{independent of } \vec{Q}),$$

$$a_{1m\vec{Q}}=0 .$$

(ii) There are hybridized $s-p$ solutions for eigenvalues E_0 such that both U_0 and U_1 [Eq. (A6)] vanish. With the expansion

$$a_{lm\vec{Q}}=\alpha_{lm\vec{Q}}+k\beta_{lm\vec{Q}}+k^2\gamma_{lm\vec{Q}}+\cdots$$

these solutions are given by the following system:

$$\sum_{\vec{Q}} \alpha_{00\vec{Q}}=0 , \tag{A9}$$

$$\sum_{lm\vec{Q}} \left(R^0_{l'm'Q',lm\vec{Q}} - \frac{B^2}{A}\delta_{l'1}\delta_{l1}\delta_{m'0}\delta_{m0} - V_l\delta_{l'l}\delta_{m'm}\delta_{\vec{Q}'\vec{Q}}\right)\alpha_{lm\vec{Q}}+\mu\delta_{l0}=0 ,$$

where there are 48 unknown variables $\alpha_{lm\vec{Q}}$ and one unknown value of $\mu=\sum_{\vec{Q}}(A\gamma_{00\vec{Q}}+B\beta_{10\vec{Q}})$. The numerical quantities A and B are defined in (A4), and the expression of $-B^2/A$ is $2\pi S^3/\Omega_0=1.8212$. System (A9) in α and μ is homogeneous and there are particular values of E_0 for which its determinant vanishes.

The treatment of (A1) up to order k^0 also gives the following relations:

$$\beta_{1m\vec{Q}}=0 ,$$

$$\sum_{\vec{Q}}(A\beta_{00\vec{Q}}+B\alpha_{10\vec{Q}})=0 .$$

Higher orders in k should be included to obtain a complete determination of all the variables β,γ, but, at $k=0$, the wave functions are entirely known from the α's.

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