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ELECTRONIC STRUCTURE AND CHARGE DENSITY OF ZIRCONIUM DIBORIDE

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ABSTRACT

Self-consistent calculations of the electronic band structure of zirconium diboride, ZrB_2 , have been performed. The total and individual band charge densities are analysed in terms of their site(zirconium or boron) symmetry and plotted. The total charge density shows very little charge asymmetry about either site.

INTRODUCTION

Zirconium diboride, ZrB_2 , is one of many elemental and alloy borides having the AlB_2 structure shown in Fig. 1 with the relevant distances given in Table I. The Zr-Zr distances (neighbors) are

○ Zr ● B

Fig. 1. Structure of zirconium diboride.

Table I
Distances (neighbors) for
 ZrB_2 , Zr and B

	ZrB ₂ (Å/n)	Zr (Å/n)	B (Å/n)
a	5.99	3.23	4.92
c	6.71	5.15	12.56
c/a	1.11	1.59	2.55
Zr-Zr	3.17(6)	3.18-3.23(12)	
B-B	1.83(3)	1.67-1.80(6)	
Zr-B	2.54(12)		

smaller(fewer) and the B-B distances (neighbors) are larger(fewer) than the elemental materials. Previous calculations for ZrB_2 were performed by Ihara¹ and Johnson² and their coworkers. My results do not differ substantively from these results which agreed with Fermi surface measurements³ and photo-emission spectra¹. The Fermi level falls in a region of low density of states caused by a 1eV overlap of bands five and six. Are these boron bands leading to Zr^{+4} or are these zirconium bands implying B^{-2} , or are the bands of mixed hybrid nature? The distribution of the charge between the zirconium and boron sites gives an answer to this question. This charge can be further decomposed into planar and axial types about each type of

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atom. Plots of individual band and total electron densities and total and component densities of states show these various types and the nature of the bonding between the atoms in real and energy space, respectively. The emphasis in this paper is on the charge distribution and in gaining a physical picture of the interactions.

RESULTS

The results were obtained using the self consistent LAPW method⁴. Table II gives the charge decomposition of the valence bands at Γ . Band 1 is largely s-like on the borons with s-admixture on the zirconium. Band two is largely $3z^2-r^2$ on the zirconiums with some admixture of s-character. Charge density plots for these two bands are combined in Fig. 2 for the xz-plane shown in Fig. 1. The two charge densities are almost nonoverlapping. Band 1 is localized near the central boron plane. There is a buildup of charge between boron atoms. The deviation from s-like spherical symmetry on the borons is due to the admixture of d-like character. Band 2 is confined to the corner zirconiums and to the edges between (the $3z^2-r^2$ nature is evident). There is a minimum between the boron and zirconium atoms. Note that although the potential has a muffin tin form, the band charge densities do not bear this restriction. Bands three and four are doubly degenerate containing the partners xy , x^2-y^2 on the zirconiums and x , y on the borons. The functions are localized in the xy planes at $z=0.0$ and 0.5 . The zirconium plane at $z=0.0$ (not shown) has spherically symmetric ion cores embedded in a background, typical of metallic bonding. The charge density in the boron plane at $z=0.5$ in Fig. 3 shows sp^2 -like covalent bonding one might expect of a graphite-like hexagonal ring of boron atoms.

Table II Charge decomposition of bands at Γ

	band 1	band 2	band 3	band 4	band 5
ϵ (Ryd)	-0.0086	0.6790	0.7125	0.7125	0.7456
Character (%)					
Zr					
s	0.1109	0.0537	0.0000	0.0000	0.0000
x	0.0000	0.0000	0.0000	0.0000	0.0000
y	0.0000	0.0000	0.0000	0.0000	0.0000
z	0.0000	0.0000	0.0000	0.0000	0.0753
xy	0.0000	0.0000	0.2088	0.0713	0.0000
yz	0.0000	0.0000	0.0000	0.0000	0.0000
xz	0.0000	0.0000	0.0000	0.0000	0.0000
x^2-y^2	0.0000	0.0000	0.0713	0.2088	0.0000
$3z^2-r^2$	0.0064	0.4882	0.0000	0.0000	0.0000
2B					
s	0.3953	0.0068	0.0000	0.0000	0.0000
x	0.0000	0.0000	0.0908	0.2661	0.0000
y	0.0000	0.0000	0.2661	0.0908	0.0000
z	0.0000	0.0000	0.0000	0.0000	0.4300

Fig. 2 Charge density for Γ , bands 1 and 2 in an xz -plane ($y=0.0$) with zirconium atoms at corners and boron atoms at $z=0.5$. Contour interval 0.005 electron/(a.u.)³. The muffin-tin spheres are shown to scale. The contour order is dot, dash, chain and solid.

Fig. 3. Charge density for Γ , bands 3 and 4 in an xy -plane ($z=0.5$) showing the boron hexagon. Contours as in Fig. 2

However as Table II shows, s-like character on the borons is in fact symmetry forbidden for these states. The deviation from spherical symmetry ($x^2+y^2=r^2$) is again due to the admixture d-character on the borons (less than 1%). This result was confirmed by explicitly leaving out the d-character.

Band 5 is shown in Fig. 4 in an xz-plane. It has nodes in both the $z=0$ and $z=1/2$ planes. As expected from Table II, its character is z-like, $p\pi$, on the zirconiums (corners) and more so on the borons (in the center) and is typical of a π -bond between the borons.

Fig. 4. Charge density for Γ , band 5. Same plane and contours as in Fig. 2.

Figure 5 shows the total charge density derived from the equivalent of 30 k-points in the Brillouin zone. At the top, the xy-section through the boron hexagon shows a covalent buildup of charge between the borons. The central xz-section shows the localization of this charge around the boron plane with fairly symmetric zirconium cores. There is a minimum in the charge density between the zirconiums and the borons. There is a fairly uniform charge density on the order of 0.02-0.04 electron/(au)³ in the empty space "between" the atoms. This uniform charge density persists in the lower section showing the plane of the zirconiums. There is a minimal tendency to directional bonding and little distortion of the zirconium ion-cores. The LAPW value of the muffin tin charge density outside the spheres is 0.051e/(au)³. The difference is due to the charge associated with the central boron plane, but outside the boron spheres.

Fig. 5. The total valence charge density for ZrB_2 . The top panel shows the xy -plane ($z=0.5$) containing the boron atoms. The middle panel shows the xz -half plane with boron atoms at the top and zirconium atoms at the corners. The bottom panel shows the basal xy -plane ($z=0.0$) of zirconium atoms. Contour interval of 0.01 electron/(au)³. the contour order is again dot, dash, chain, solid.

Figure 6 shows the total and component densities of states for zirconium diboride. The calculated occupied width is about 12.5 eV. There are two major structures below the Fermi energy. There is a 4eV wide low lying peak centered 10-11 eV below the Fermi energy primarily associated with boron s- character. The second structure is seven eV wide and consists of four peaks. The experimental results¹ show an overall width of 13eV, with a 4-5eV broad peak 10eV below the the Fermi level and two other broad peaks centered at 5eV and 3eV below corresponding to two unresolved pairs in our plot. There is a low density of states at the Fermi energy corresponding to a 1.1 eV overlap of bands five and six. Since there are an even number of valence electrons, ZrB_2 is a compensated metal with equal number of fifth band holes and sixth band electrons. We calculate this number to be 0.03 ± 0.02 in reasonable agreement with the Fermi surface measurement² of 0.040 ± 0.003 .

The component densities of states are partitioned into their planar (x,y, xy, x^2-y^2), interplanar (xz, yz) and c- axis ($p\pi$, $3z^2-r^2$) components. There is considerable overlap and mixing of the zirconium and boron states. The zirconium and boron c-axis states are higher in energy and near the Fermi energy. Of the states at the Fermi energy well less than half are due to the planar character of the charge density. This number would be 100% for complete planar character and >60% for a spherical distribution. Thus the carriers largely involve out of plane character. The total number of electrons can similarly be apportioned between planar and perpendicular. This is shown in Table 3.

Table III Valence charge components within the LAPW spheres for ZrB_2

	<u>Zr</u>	<u>2xB</u>
planar	0.99	1.52
interplanar	0.63	0.01
c-axis	0.48	1.13
s	0.19	1.15
sum	2.29	3.81
LAPW	2.19	3.54
"atoms"	2.67	3.16

"Sum" is the sum of the integral of the component densities states and may have a 10% error due to the smaller k-space sample used. The LAPW value is the actual integral of the charge in the LAPW spheres. The "atoms" entry is the value derived from superposition of the atomic charges in the solid environment. If the s-like

Fig. 6. Total and component densities of states for ZrB_2 . See text for further description.

charge is neither planar nor perpendicular, then less than half the total charge in both spheres is of planar character. Silver and Bray⁵ have measured the nuclear quadrupolar splitting at the boron site. They find a small value of 0.12 Mhz to be compared with a value of 5.4 MHz for either a total planar or a total c-axis charge distribution. Using an analysis similar to that of references 2 and 5 we calculate a value of 0.50 ± 0.50 MHz, far from either extreme and in reasonable agreement with 0.12 Mhz value.

CONCLUSIONS

Component densities of states plots show a strong hybridization of zirconium and boron states with less than 0.5 electron transfer from zirconium to the borons. There is a low density of states at the Fermi energy formed by overlap of bands five and six. The five filled bands may be considered to be derived from: 1) boron s; 2) zirconium z^2 ; 3) and 4) boron x, y, zirconium x, y and x^2-y^2 , $3z^2-r^2$; 5) boron z and zirconium z states. These bands mix and broaden with an emptying of band five around the point A in the Brillouin zone, and a filling of the sixth band along the T' line. There are covalent bonds formed between the boron atoms, while the zirconium atoms form spherical ion cores in a fairly uniform background. There is no evidence of a covalent bond between zirconium and boron; this bond is metallic and must partially be responsible for the extreme hardness of this material. The total charge density and charge density at the Fermi energy contain sizeable c-axis components consistent with fairly isotropic properties^{5,6}. It is envisaged that this work will lead to an analytic representation of the energy bands in terms of a linear combination of atomic orbitals, LCAO's, in which both the eigenvalues and the charge character of the eigenvectors have physical meaning. This will allow a realistic treatment of the transport properties.

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