A Study of the Iron Borides. 1. Electron Spectroscopy

David J. Joyner, Oliver Johnson, and David M. Hercules*

Contribution from the Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15260. *Received February 5, 1979*

Abstract: ESCA, X-ray excited Auger (XAES), and electron excited Auger (EAES) studies were performed on Fe, FeB, and Fe_2B. Relative peak areas of the ESCA core levels were used to show that the compositions of the borides' analyzed surfaces were the same as the bulk, i.e., stoichiometric. The absence of binding energy shifts between the iron and boron ESCA core levels compared with the pure elements (iron and β-rhombohedral boron) indicated that no major charge transfer occurred between iron and boron in the borides. This was supported by the XAES, EAES, and plasmon loss spectra. Evidence is given for localized boron bonding in FeB (with covalent bonds between the boron atoms) and isolated boron atoms in Fe_2B. The boron-iron bonding in these compounds is metallic. The iron boride valence bands are consistent with the metallic properties, and their increased width over Fe and different fine structure is due to changes in the d-band substructure.

Introduction

X-ray photoelectron spectroscopy (ESCA) is extremely useful for the study of metallic alloys[1-6] and related materials, giving direct information about electronic structures both from the valence band densities of states (VBDOS) and the positions of core levels. We are concerned in this work with FeB and Fe_2B, which are similar in properties to metal alloys, and not with higher borides such as MB_2 or MB_6 in which the properties are more dominated by the boron structures.

The iron borides are interstitial compounds, the boron atoms occupying interstitial positions in the distorted iron lattice. These materials are metallic in nature and exhibit ferromagnetism; they are extremely hard and brittle, although their melting points are close to that of iron metal. These properties lead to a number of practical uses as well as providing considerable interest for fundamental study.

Despite a number of early and recent studies[7-18] there is no clear understanding of the bonding nature of these compounds. Also, there are no band structure calculations for these borides or even for CoB or MnB, which are isostructural with FeB, only for CrB,[19,20] which has a structure closely related to that of FeB. Further investigation was clearly required to understand the iron borides, FeB and Fe_2B, and we have applied ESCA and Auger electron spectroscopy to this problem. Pure iron and β-rhombohedral boron were also studied for comparative purposes. The latter is of particular interest in itself since no careful photoemission study has been performed to date.[21]

We observed very small binding energy (BE) shifts between the corresponding core levels of Fe, Fe_2B, FeB, and β-rhombohedral boron and conclude that there is little charge transfer between iron and boron. The absence of charge transfer, the nature of the B KLL transitions, and the shapes of the B 1s lines in both borides give evidence that the boron electrons are largely localized around boron, providing bonding in linear chains in FeB but isolated boron atoms in Fe_2B. Bonding is found to be metallic in these compounds, and the ESCA valence bands are consistent with their metallic properties.

In this paper these and other conclusions are elucidated while their application to the electronic structure of the borides is dealt with in part 2,[139] where it is shown that our conclusions are consistent with neutron diffraction data and with the physical properties of the iron borides.

Experimental Section

1. Sample Preparation. The iron metal used was electron beam zone refined with several passes from 99.99% purity starting material (Spex Industries). The boron sample was cut from a β-rhombohedral single crystal of high purity.[22]

The iron monoboride (FeB) and subboride (Fe_2B) samples were prepared by arc melting under argon stoichiometric amounts of 99.8% purity boron (Alfa Ventron) and iron previously zone refined from 99.99% starting material. The action of the arc caused some of the light boron particles to be blown away, and the boron charge had to be replenished several times. The resulting compounds were drop cast to form cylindrical rods which were electron beam zone refined at 2.5×10^{-5} Pa (1 Pa = 7.5×10^{-3} Torr). At least four passes were made.

Excellent X-ray powder diffraction patterns were obtained from the FeB and Fe_2B samples, indicating that they were largely single phase and highly crystalline. Lattice parameters (Å) of a = 4.057, b = 5.502, c = 2.948 (±0.002 Å) were obtained for FeB (orthorhombic) and a = 5.110, c = 4.249 (±0.002 Å) for Fe_2B (tetragonal). These are an improvement on previous patterns[23] and have been submitted for publication.[24]

The FeB samples showed traces of Fe_2B, and the Fe_2B sample traces of an unidentified phase. Brown and Cox[7] similarly observed an impurity in Fe_2B which they identified as an Fe_2B–Fe eutectic, although our optical microscopic analysis indicated that the second phase (in a low volume %) was a solid-state precipitate rather than a eutectic. The FeB sample could not be adequately analyzed by optical microscopy because of many small cracks which had formed during cooling, evidently due to its extremely brittle nature.[25]

Slices of the high-purity end of the zone-refined materials were cut and mounted in a low vapor pressure epoxy resin (Varian Torr-Seal). Both sides were then polished to a mirror finish.

2. Sample Analysis. Before analysis, the samples were ground inside the ESCA spectrometer with a diamond bit at 6.5×10^{-5} Pa.[26] This has been shown to be one of the best methods of preparing an alloy surface in vacuo,[6,27] although, according to a recent study,[28] during grinding of carbon-free iron and ferrous materials a diamond bit may become graphitized and carbon may diffuse into the iron lattice to a depth of 100 Å. With the long periods of grinding necessary to prepare the boride surfaces, this is a possible minor source of contamination in our experiment.

Previous experiments by ourselves and by Mavel et al.[29] showed that air-exposed surfaces of powdered iron borides were seriously contaminated. Sputter cleaning is not practical without subsequent annealing because of composition changes.

ESCA analysis indicated that the iron, boron, and iron boride surfaces were very clean after in situ grinding. The only impurities present were carbon and oxygen (C 1s less than 10% and O 1s less than 5% of the Fe $2p_{3/2}$ peak area). Some samples analyzed by electron excited Auger (EAES) were contaminated with more carbon and oxygen, as the only way of cleaning their surfaces was by the reducing effect of the electron beam. After ESCA and X-ray excited Auger (XAES) studies of the above samples, argon was implanted into them by ion sputtering.

The ESCA and XAES studies were performed on a Hewlett-Packard 5950A ESCA spectrometer with monochromatized Al Kα radiation (1486.6 eV), giving a 0.8-eV fwhm for Au $4f_{7/2}$. The binding energies reported are referenced to Au $4f_{7/2}$ at 83.8 eV, from vapor-deposited gold. A PHI Model 545 scanning Auger microprobe was used for the EAES studies.

3. Surface Stoichiometry. It was important to check the surface stoichiometry of the borides and to look for segregation of one com-

0002-7863/80/1502-1910$01.00/0

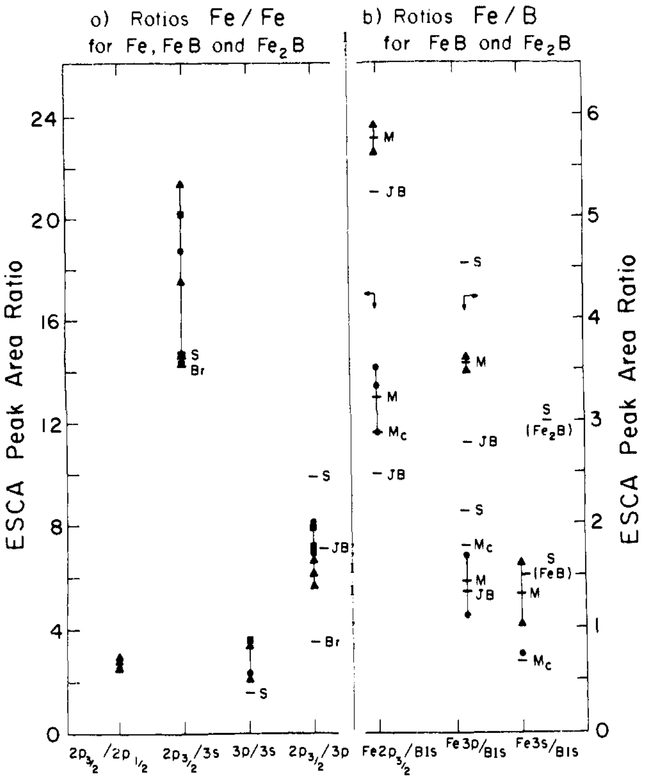

Figure 1. ESCA peak area ratios: (a) ratios of Fe to Fe core levels; (b) ratios of Fe to B 1s. FeB (●), Fe_2B (▲), Fe (■) (each symbol represents one determination). M, mean; M_c, calculated mean = $(M_{Fe_2B}/2)$; S, Scofield;[30] JB, Jørgensen-Berthou;[31] Br, Briggs.[32]

ponent which would make the surface unrepresentative of the bulk. To do this, we measured the peak areas of the iron and boron ESCA core levels (normalized to X-ray power 600 W; 100 scans). Their ratios are plotted in Figure 1. They are compared with ratios predicted by Scofield's calculated cross sections[30] and with experimental sensitivities obtained by Jørgensen and Berthou[31] and Briggs.[32]

To judge the significance of any area ratio changes, the escape depths of the contributing electrons must be considered. The theoretical results of Penn[33] are interpolated to obtain the following escape depths (Å): Fe 3p, 15.8;[34] Fe 3s, 15.5; Fe 2p, 10.0; B 1s, 26.7; B 2s, 29.8. These elemental values are of the order expected from Lindau and Spicer's "universal curve".[35]

The iron/iron intensity ratios of Figure 1a are consistent for iron metal and the borides. All the ratios except $2p_{3/2}/2p_{1/2}$ exhibit similar relative spreads; there are no systematic differences between the ratios for the different samples, even for the ratios 2p/3s and 2p/3p, which are highly surface sensitive. The iron/iron ratios do not therefore indicate significant segregation in the borides or differences in sample oxidation.

The iron/boron ratios of Figure 1b are consistent for FeB and Fe_2B. The means of the FeB ratios (M) are close to those calculated (M_c) as $^1/_2M(Fe_2B)$. The compounds thus have stoichiometric surface compositions unaffected by segregation. This is corroborated by general agreement with literature experimental[31,32] and theoretical[30] ratios. Notable exceptions are the Fe 2p/B 1s and Fe 3s/B 1s ratios, for which the Scofield[30] values are approximately a factor of 2 higher. Similar discrepancies between theory and experiment have been reported by Scofield.

The surface compositions were also monitored after sputtering (in the argon implantation experiment) to observe possible stoichiometry changes. The ratio of Fe 3p/B 1s for the two borides before sputtering was used to obtain a rough measure of ESCA signal intensity as a function of atomic composition. This linear correlation passed through the origin. The Fe 3p/B 1s ratio measured after sputtering was used to determine final atomic compositions. After sputtering for equal times FeB and Fe_2B reached similar compositions (for FeB, Fe 3p/B 1s was 6.4; for Fe_2B the ratio was 7.4) equivalent to approximately Fe_5B. The clear conclusion is that the compounds reached the same equilibrium composition and that boron sputters preferentially.

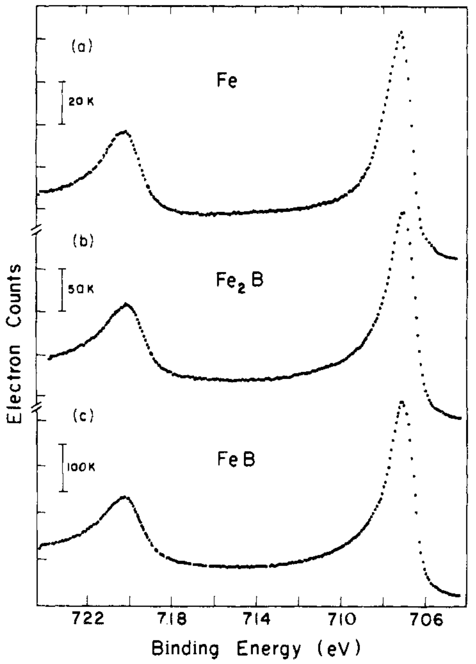

Figure 2. Fe 2p $(^1/_2, ^3/_2)$ ESCA core levels of iron, Fe_2B and FeB. Data is unsmoothed and uncorrected.

Results

1. Core Levels. All ESCA core levels available to Al Kα were measured for the borides and the pure elements. They are listed in Table I as the average of several determinations. Binding energy shifts for the corresponding iron core levels are very small ($\leq$0.4 eV) and the B 1s level BEs agree within 0.1 eV in the two borides and the element. The same BE of Ar 2p (implanted argon) was found in iron and the borides, but that in β-B was 4 eV lower.

The Fe 2p core levels are shown in Figure 2. The iron metal $2p_{3/2}$ peak at 707.2 eV is in agreement with literature values varying between 707.1 and 707.4 eV[21,36-38] (values corrected to Au $4f_{7/2}$ calibration at 83.8 eV). The Fe $2p_{3/2}$ full widths at half maximum (fwhm) for Fe, Fe_2B, and FeB were 1.6, 1.7, and 1.5 eV (±0.1 eV), respectively; the asymmetry parameters[39] at half-peak-maximum were 2.1, 1.8, and 1.6 eV (±0.2 eV), respectively. Differences in the latter largely reflect the width of the high-BE part of fwhm as all the low-BE parts were 0.6 eV wide. The asymmetry of iron at three-quarters-maximum was ~1.5, which compares favorably with the 1.37 value quoted by Pessa.[40]

The narrowness of the iron core levels and the absence of high BE peaks or shoulders indicate the absence of serious iron oxide[41-48] or carbide[36] contamination. The Fe 2p asymmetries should result from electron-hole coupling[49-54] and be correlated with electronic specific heats,[55] although, owing to the possible interference of small amounts of contamination,[56,57] this has not been investigated further.

It was observed that the Fe 3s level was split in the two borides and iron metal. These data will be reported in detail elsewhere.[58] From this multiplet splitting,[59-63] we obtain the following localized moments (μ_B) on iron: Fe, 2.2 (compared with the accepted value of 2.22[64]); FeB, 2.05; Fe_2B, 2.55.

The boron 1s levels (Figure 3) also indicated that the boron component of the samples was pure: there was no low-BE shoulder due to B_4C at 0.8 eV from elemental boron[65] or B_2O_3 peak at ~4 eV higher BE than the element.[66] The large separation between any boron oxide peak and that of the element and the absence of high BE tailing of B 1s ensure that surface oxidation does not affect the peak shapes.

In order to fit the experimental B 1s line shapes to analytical

Table I. ESCA Binding Energies and XAES Kinetic Energies of Iron Borides and Element Core Levels (eV ± 0.1 eV)

	ESCA peaks				Auger peaks[b]									implanted Ar $2p_{3/2}$ × [Δ(Ar 2p)][e,f]
			Fe 2p											
	Fe 3p	Fe 3s[a]	½	3/2	$FeL_3M_{45}M_{45}$	$FeL_{23}M_{23}M_{45}$		Fe 2s	$FeL_{23}M_{23}M_{23}$[c]			B 1s	$BKL_{23}L_{23}$[d]	
Fe	53.1	91.2	720.0	706.9	703.1	651.6	647.1	641.5	610.6	598.3	591.6			241.5 [2.2][g]
β-B												188.0	185.1 180.8	237.0 [2.4]
FeB	53.4	91.6	720.3	707.2	703.1	651.9	647.0	641.5	610.2	597.6	590.9	188.1	181.6	241.5 [2.4]
Fe_2B	53.1	91.6	720.2	707.1	703.1	651.4	646.6	641.1	609.1	598.1	591.6	188.1	182.6	241.3 [2.0]

[a] Parent peaks only—multiplet splitting satellites not listed. [b] The $FeL_{23}M_1M_{23}$ peaks at 563.5 and 550.5 eV, not listed, were also consistent for all samples. [c] The ~598-eV peak does not belong to the $L_{23}M_{23}M_{23}$ doublet and its origin is not understood. [d] Reproducibility ±0.5 eV because of width and low intensity of the B KLL peak. [e] Implantation conditions 6.5×10^{-2} Pa Ar, 1 kV, 25 μA. [f] [Δ] is the 3/2–½ splitting: compare with theoretical splitting of 2.23 eV.[137] [g] Agrees with Wagner, ref 138.

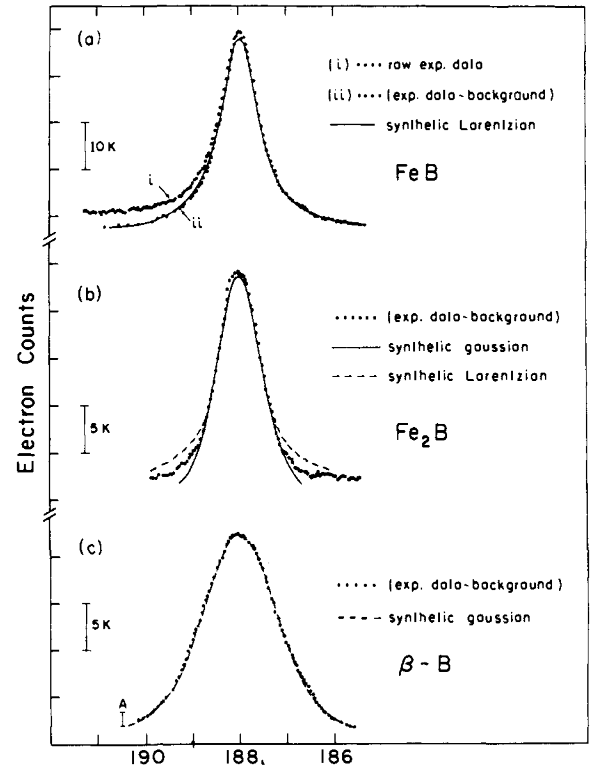

Figure 3. B 1s ESCA core levels of β-boron and the borides. (a) FeB: . . . , experimental data before (i) and after (ii) inelastic-background subtraction; —, synthetic symmetrical (SS) Lorentzian. (b) Fe_2B: . . . , experimental data after inelastic background subtraction; - - -, SS Lorentzian; —, SS Gaussian. (c) β-B: . . . , experimental data after inelastic background subtraction; - - -, SS Gaussian. (A) indicates the background level subtracted at this energy.

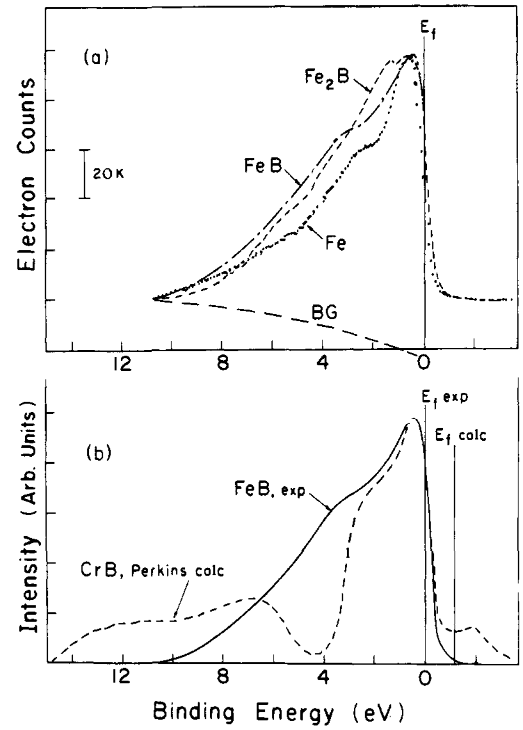

Figure 4. ESCA valence bands. (a) Fe, FeB, and Fe_2B after subtraction of inelastic electron background. BG is inelastic background subtracted from the iron spectrum. (b) Comparison of calculated DOS for CrB by Perkins[20] with the ESCA valence band of FeB from Figure 4a. The structure at high binding energies in the theoretical DOS represents boron states which are not seen in the ESCA EDC because of low photoionization cross sections.

curves, the contribution from inelastically scattered electrons was first removed using the method of Antonides et al.[67] (Similar methods are widely used.[6,56,68,69]) The results are shown in Figure 3. The background-corrected B 1s of FeB is well fitted by a symmetrical Lorentzian with 0.95-eV fwhm; that of Fe_2B is between Lorentzian and Gaussian with fwhm also of 0.95 eV; the B 1s of β-boron is a symmetrical Gaussian of 1.75-eV fwhm.

The β-boron and iron boride B 1s binding energies were close to those observed for LaB_6 (187.9[70] and 190.6 eV[71]) and SmB_6[72] (188.1 eV). For β-rhombohedral boron this is a reasonable comparison, since its structure is based on icosahedra and the hexaborides are composed of B_6 molecular cages similar to the icosahedra.[73] However, the comparison of the iron borides with β-B is more tenuous owing to the considerable differences in their boron lattices.

2. Valence Bands. The valence bands of Fe, FeB, and Fe_2B are compared in Figure 4a. A theoretical calculation of the densities of states (DOS) of CrB[19,20] is shown in Figure 4b. The Fermi level of FeB has been placed on the CrB curve by addition of two electrons to the DOS of the latter.[20] The inelastically scattered electron background has been subtracted from the experimental spectra by the method of Antonides et al.[67] The spectra have also been scaled to the same intensity from the peak maximum to the base line above the Fermi level (E_F).

The FeB and Fe_2B valence bands have high densities at E_F and are broader than the iron valence band. The widths at half-maximum are 3.3 eV for Fe, 4.1 eV for Fe_2B, and 4.4 eV for FeB. The FeB band maximum is at the same position as that of iron, viz., 0.6 eV. Figure 4a shows that the FeB valence band has a shoulder at 3.3 eV below E_F and Fe_2B has two DOS maxima split by 0.6 eV, the one nearest E_F appearing at 0.8 eV, close to the Fe and FeB main-peak position. The 1.4-eV BE peak in Fe_2B is thus an extra feature not appearing in the monoboride.

3. Auger Spectra. The XAES iron LMM peak positions in all compounds agreed with literature values for iron.[75-80] Fine structure was also like that reported in the literature.[76-78,81-83]

Table II. Energy Loss Features from ESCA Core Levels (eV ± 0.2 eV)

sample[a]	Fe 3p			Fe 3s		Fe 2p		B 1s		
						1/2	3/2			
Fe 1	24.12	[9][b]			25.5	25.7	25.7 [10]			
2						25.6	24.6 [10]			
3	24.0	[11]			22.9 [10]	23.8	24.7 [9]			
FeB 1				11.2	23.9 [9]	26.3	25.7 [9]	12.4	19.2	25.5 [9]
2	24.5	28.6			26.3 [12]	25.5 [12]	28.4			27.5 [10]
3										24.8
Fe_2B 1	22.8	27.3	31.2		26.5 [14]	24.1 [9]	26.0 [9]			24.5 [6]
2										24.1 [10]
3	14.9	24.1	[10]		26.3 [14]	22.4 [9]	26.1 [9]			24.3 [10]
β-B 1									50.2	24.3 [6]
2										25.4 [9]
3										25.3 [9]

[a] Indicates each experiment performed. [b] Values in brackets are plasmon fwhms (eV).

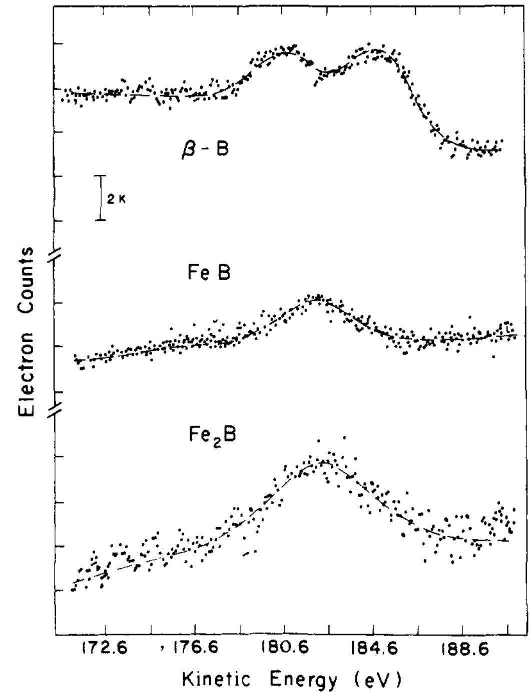

Figure 5. XAES boron KLL spectra of FeB, Fe_2B, and β-rhombohedral boron.

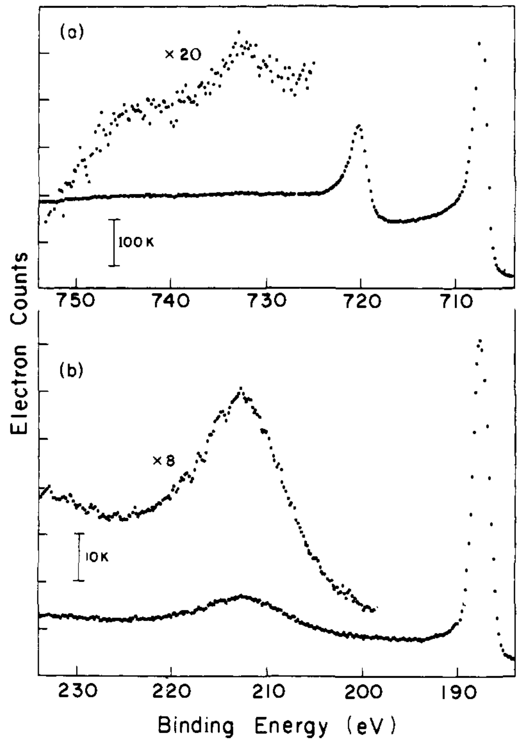

Figure 6. (a) Plasmon loss from Fe 2p (1/2, 3/2) of iron metal. (b) Plasmon loss from B 1s of β-rhombohedral boron.

The Fe $L_3M_{45}M_{45}$ (L_3VV) peak in iron and the borides, which probes the Fe 3d valence band, will be treated in detail elsewhere.[58] The EAES Fe LMM peaks were identical in all compounds, and were like those of iron.[75,79,82] Careful peak intensity analysis indicated identical relative intensities of the LMM features in all samples, although the relative intensities of $L_3M_{23}M_{45}$ and $L_3M_{45}M_{45}$ did reverse upon oxidation, suggesting the importance of valence-band effects.

Because of the low intensities of the XAES boron Auger peaks, only the most intense feature ($KL_{23}L_{23}$ or KVV)[84] was measured, as shown in Figure 5. A single peak with fwhm of ~4 eV was observed for FeB and Fe_2B at 181.6 and 182.6 eV KE, respectively. For β-boron two peaks were seen at 185.1 and 180.8 eV KE.

The EAES B KLL spectra of FeB, Fe_2B, and β-B were also measured. The single main peak at 182 ± 1 eV was close to our XAES values and those in the literature.[75,85] The boride spectra had a shoulder at 172 eV not present in the boron spectrum. These spectra are similar to those of Dagoury and Vigner[86] except that their energies are 13 eV lower than ours and other reports; also their major peaks have satellites at 10 eV higher KE, which we only observed in oxidized boron or bulk boron oxide.

4. Energy Loss Features. The discrete electron energy loss features for all core levels available to Al Kα (except Fe 2s) are listed in Table II with the corresponding fwhm's in parentheses. The results of each determination are reported because of a rather large spread in the values. The energy loss spectra from Fe 2p of iron metal and B 1s of β-boron are shown in Figure 6.

In each compound there is generally a single major loss feature for each core level occurring at approximately the same energy difference and having similar fwhm's. This indicates that they are due to bulk plasmon excitation. Extra loss features occurring with some peaks are extremely weak and not understood. The average plasmon fwhm of about 9 eV is close to a previous report for iron (8 eV) obtained for electron excited plasmons on a Varian Auger spectrometer.[87] The generally higher fwhm's of the Fe 3s and 3p losses is due to overlapping of plasmons from each half of these core levels doublets.

Most determinations of the B 1s plasmons gave values of 24–25 eV. That of the β-B boron is at about the same energy and its 50.2-eV peak is apparently the first harmonic of the B 1s plasmon; its area is ~20% of that of the primary plasmon. The most reproducible Fe plasmons, at 26.0 ± 0.5 eV, were obtained from the 2p and 3s levels (the former is the most intense peak and the latter is in a region of very low and flat background).

It will be noted that even plasmons giving the closest agreement exhibit reproducibilities of only about ±0.5 eV, owing to inherently weak intensities.

Discussion

1. Interpretation of Core Level Binding Energies and Shapes. From Table I the BEs of the Fe core levels in the mono- and subborides are within 0.4 eV of those in iron metal. The B 1s level in the borides is within 0.1 eV of the β-rhombohedral boron level. If these shifts represented actual transfer of electrons, they would correspond to an electron transfer of ~0.01 electron for iron or boron.[88,89]

However, such binding-energy shifts cannot be simply interpreted in terms of electron transfer because of various complications. First, complex charge distribution often occurs in alloys and related materials; for example, Fuggle et al.[90] found that in aluminum-noble metal alloys increases in core level BEs of both elements upon alloying precluded a simple charge-transfer interpretation. Second, atomic volume changes[91] and final state effects[92] (extra- and intraatomic relaxation) have to be considered. Thus, in many studies, with the exception of those involving gold,[4,90] only very small BE shifts were observed upon alloying.[93] This has been explained[94] by the cancellation of such opposing effects as atomic volumes and relaxation.

Argon implantation should provide information about relaxation energy (E_R) since the only effects on the argon core binding energies are nonchemical due to its closed-shell nature. Such relaxation and crystal potential effects in argon implantation experiments have been extensively studied by Citrin and Hamann.[95,96] However, FeB and Fe_2B reach the same composition after argon sputtering: Fe_5B. We cannot therefore directly obtain relaxation information about either FeB or Fe_2B, only about the nominal compound Fe_5B. The fact that the BE of Ar implanted in Fe_5B is exactly the same as in Fe permits the reasonable assumption that the same would be observed for FeB and Fe_2B.

It should be noted, however, that there may be a difference in the relaxation process for argon and metal atoms. For transition metals, E_R involves relaxation of conduction electrons into the outer d orbitals of the metal atom having the core hold; for the closed shell argon atom, E_R involves relaxation of the conduction electrons of the metal matrix into "excited" 4s orbitals or the argon core hole state. Thus, implanted argon BEs may not be a direct indicator of metallic relaxation.

Atomic volumes are discussed in detail in part 2, where it is concluded that there are no appreciable volume changes that would modify the electron density around iron in FeB and Fe_2B. However, reduction in the volume of boron in these compounds is found, leading to increased electron density around boron in the borides and a decrease in BE.

Argon implanted in β-boron gave a 4-eV lower BE than when implanted in Fe, FeB, or Fe_2B. This unexpected change indicates a greater E_R in β-boron than in the borides. A positive E_R correction applied to the boron BE would be opposite to the BE changes expected from the volume difference between β-boron and the borides. Thus, it appears that the absence of a chemical shift for B in the iron borides is due to cancellation of opposing effects of atomic volume and relaxation energies.

It may be concluded from the above considerations that the absence of a chemical shift in the iron borides is the result of a negligible change in electron density around iron and cancellation of opposing effects for boron.[97] A similar conclusion about charge transfer in FeB was reached in a recent K-absorption edge study.[98] In the absence of electronic charge transfer between iron and boron, there is indication that the boron valence electrons are largely localized in the borides (see part 2), and that the boron atoms in FeB are covalently bonded in linear chains.

Bonding information can also be obtained from the shape of the B 1s photoemission lines (Figure 3). The B 1s line of FeB is a symmetrical Lorentzian, indicative that lifetime broadening dominates photoemission. This is typical of the solid state when complicating factors do not interfere, and suggests a simple-metal nature of boron in FeB. The observation of a boron 1s line shape between Gaussian and Lorentzian in Fe_2B means that the normal lifetime-caused width is partly overshadowed by an effect causing Gaussian broadening. Thus, the B 1s natural line width in Fe_2B is narrower than in FeB. The origin of the Gaussian contribution is not clear since the most likely effect, phonon broadening,[99,100] is generally very small, even in the free electron metals.[101] The phonon energy of boron has unfortunately not been determined.

This narrowing of B 1s in Fe_2B compared to FeB indicates that the Fe_2B core hole is the longer lived. Since the primary mechanism for decay of this photohole is the Auger process,[102] this points to a slower Auger recombination rate in Fe_2B than in FeB. Recent studies have suggested[103,104] that when the Auger transition involves valence electrons on the hole state atom (as in the B KLL) the transition rate depends on the electron density around the core hole, i.e., on the chemical environment. It is shown later that the B KLL Auger transitions do not probe the boron valence bands, being highly localized, and they should therefore be very sensitive to local chemical differences. Since we believe that boron is covalently bonded in FeB but not in Fe_2B, chemical effects should dominate and would explain the different Auger transition rates and B 1s widths in the two compounds. This is also consistent with the above conclusion that there is a difference in the electron density around boron in the two borides.

The symmetrical Gaussian line shape of the β-boron B 1s also indicates the presence of a nonlifetime effect. Because of the width of this peak (1.75 eV), instrumental broadening can be ruled out. Also, the phonon broadening effect is not likely to be important, because phonon energies[101] are generally ≤0.3 eV for compounds other than ionic solids. Another possible cause of the Gaussian line shape is charge broadening, but this is unlikely for two reasons. First, charging of β-B was slight; the BE of B 1s increased only 1.2 eV when the optimized electron flood gun was turned off. (This is in agreement with the low emissivity[85] of β-B and its small band gap of ~1.5 eV.[105-108]) Second, the B 1s fwhm did not change significantly from 1.8 eV when the surface charged more positively (in the above test) or when it became more conductive by deposition of a heavy gold layer.

We also considered whether the increased width of the B 1s peak in β-B might indicate the presence of several unresolved peaks caused by chemically inequivalent lattice sites. In the unit cell of the β-rhombohedral lattice there are 105 atoms with three distinguishable sites, of coordination numbers 6, 8, and 9. However, the relative numbers of these sites are 91, 12, and 2, respectively, so they could not produce a symmetrical ESCA B 1s envelope. Therefore, the reason for the shape and width of this peak is not understood at present.

2. Interpretation of ESCA Valence Bands. The shape of the iron valence band agrees well with literature results,[69,109-111] consisting of two main peaks and a long tail. States near the Fermi level (E_F) are largely 3d, while the high BE tail represents the flat 4s band. The peak maxima at 0.6 and 2.3 eV (corrected) also agree with most recent ESCA and UV PES determinations.[69,109-111] The shoulder at 2.3 eV in Figure 4a seems to be wider than previous workers have shown. Our density of states of iron at E_F is higher than previous reports as a result of the calibration difference; the steep slope around the Fermi level confirms the surface cleanliness since iron oxide contamination would reduce this slope significantly.[112-115]

The observation of a continuity of occupied states up to E_F in the Fe_2B and FeB ESCA valence bands (Figure 4a) explains the metallic nature of the compounds. Most experiments on Fe, Fe_2B, and FeB gave densities of states at E_F of 50-70% (relative to the peak maximum intensity) with no obvious systematic differences. These densities would be expected to follow the order $Fe_2B \gg FeB > Fe$ since the electronic specific heats (mJ/K^2·g-atom) are 10.35, 5.32, and 4.74, respectively. Because of the steep slope around E_F the apparent DOS(E_F) is seriously altered by small calibration errors. However, the data do indicate that the DOS(E_F) for the borides (determined in ESCA) are at least as large as that of iron, as predicted by the specific-heat data.

The theoretical total DOS of FeB[20] is compared in Figure 4b with the ESCA VBDOS. There is a reasonable qualitative agreement with experiment considering that certain factors[69] (matrix modulation effects, resolution, etc.) have not been folded into the calculated curve, and that this also shows the boron states. The curves have been positioned so that the major feature lines up even though the Fermi levels do not coincide. This may be due to the use of a different lattice structure in the calculation (CrB). According to Perkins' calculation[19,20] at least some of the monoboride's B 2p density appears between 0 and 2 eV BE, so that the boron states overlap the conduction band at the Fermi level. It may therefore be meaningful to consider the boron chains of FeB as metallic conductors, and, if the boron atoms are strongly bonded to one another (as concluded above), these infinite chains may constitute pseudounidimensional conductors.[116]

Recent synchrotron photoemission studies in the photon energy range 25-180 eV[117] have shown well-resolved boron states in FeB between binding energies of 5 and 15 eV. Similar positions were previously reported in ZrB_2.[74] The ESCA valence bands of FeB and Fe_2B show no evidence of boron features in this energy region, even at the high BE side where the B 2s states should appear. From the theoretical Al Kα cross sections,[30] a B 2s/Fe 3d area ratio of 0.2 is expected.

The ESCA valence band in the region 0-5 eV BE clearly contains largely Fe 3d/4s states, and the observed differences between Fe, Fe_2B, and FeB are therefore due to differences in the iron d-band substructure or energy distribution. The differences in the valence band 3d density of states of the iron borides will be discussed further in part 2 and in a later publication.[117]

One interesting aspect of ESCA valence band studies is whether an alloy valence band can be approximated as the sum of appropriately weighted pure element bands. This has been used, for example, as a test of the rigid band theory.[118,119] Although the boron states are not seen in the ESCA valence bands, our synchrotron studies indicate that the boron and iron contributions to FeB are well resolved, suggesting that the rigid band model does not apply to this compound. However, in the absence of a calculated DOS for boron as pseudoisolated atoms or bonded in one-dimensional chains, it is impossible to make detailed conclusions about valence band addition in these iron borides.

3. Interpretation of Auger Spectra. Auger spectra were measured to provide additional information on chemical bonding in the iron borides. The Fe LMM peaks involve iron core level (2p) transitions and should exhibit larger binding energy shifts caused by electronic structural changes than X-ray photoemission peaks.[120] The fact that the corresponding Fe LMM transitions (from XAES and EAES) appear at the same energies in Fe, Fe_2B, and FeB (see Table I) further substantiates the conclusions from the ESCA core-level positions.

The boron $KL_{23}L_{23}$ (KVV) transition probes the boron valence band and might provide information about the 2p states[84] unavailable from the ESCA VBDOS. Comparison of the B KVV spectra (Figure 5) shows that the FeB shape and fwhm (~4 eV in XAES) are similar to Fe_2B. Synchrotron photoemission studies[117] have shown that the boron valence band of FeB is about 6 eV wide so that the B KVV spectra with fwhm's of about 4 eV are too narrow to represent 2 × (boron valence bandwidth); the valence band is therefore not being probed. It has recently been shown that Auger transitions involving valence electrons do not necessarily provide DOS information. Thus, some transition and noble metals do have "band-like" CVV spectra,[14,121,122] while others are "atomic-like".[123-125] On the other hand, quasi-free-electron metals and semiconductors generally give band-like spectra,[123,126,127] and DOS structure has been determined from them.

An atomic-like spectrum would be expected for Fe_2B, in which the boron atoms are too far apart to bond to one another and do not strongly bond to iron atoms, and are therefore practically isolated.[128] The close similarity of the FeB KLL spectrum to that of Fe_2B is extra evidence that the FeB is also atomic-like. From the above considerations, paralleling the case of the light-metal boron in FeB with simple metals, this might be expected if the Auger process sampled the portion of B 2p electrons which are localized. Such localization of the B 2p states is reasonable if boron binding is confined within boron chains as indicated above.

It was assumed above that the boron Auger transitions are actually $KL_{23}L_{23}$.[84] This would strictly require interatomic transitions with one p electron participating from each of two adjacent boron atoms. While this is reasonable in FeB, where the boron nearest neighbor is another boron at 1.78 Å, it seems less likely in Fe_2B, which has its nearest Fe and B atoms at nearly equal distances. In this case it would be interesting to investigate whether interatomic Fe-B transitions contribute or whether the intraatomic process becomes important. The latter might result in KL_1L_1 spectra, or $KL_{23}L_{23}$ spectra with the boron atom having more apparent p-like electronic states than normally assigned to it.[129] We cannot make any conclusions on these points from the present study, but they are clearly of considerable interest. The 1-eV difference in boron KVV KE for FeB and Fe_2B arises from the different chemical environments of boron in the two compounds. Because of the greater relaxation in the Auger process there is no longer the cancellation of relaxation and volume effects which was seen in the boron 1s levels.

The B KVV spectrum of β-rhombohedral boron would be expected to be band-like by comparison with other semiconductors,[123] and it should therefore exhibit the self-fold of the 2p DOS. It is indeed wider than the boride spectra, and the observation of a doublet in this KVV spectrum may provide important DOS information, although discussion of that aspect is left for another publication.[58]

4. Interpretation of Energy Loss Features. The 26-eV plasmon loss for iron core levels of the borides and iron metal is higher than previous reports of 23[130,131] and 22 eV,[87] while the 24.5-eV plasmon loss of B 1s is in excellent agreement with an electron-excited study (24 eV) by Dagoury and Vigner.[86] The similar plasmon energy and fwhm's for all Fe core levels indicate that the borides and iron metal behave alike under plasmon excitation, and, as the plasmon energy is directly related[132] to the number of oscillating electrons, no significant shift of electron density has taken place in agreement with the conclusions obtained from the ESCA core level studies.

The reason for the observed higher plasmon energy for Fe core levels over B 1s is not obvious. Since the plasmon represents a collective electron oscillation the same energy would be expected for losses from both elements in the borides, although Sun et al.[133] reported different plasmon energies for the various components of ternary alloys and Spalding and Metherell[134] found losses in a binary alloy to be intermediate between those of the parent elements. Again, the similar B 1s plasmon energies of β-B and the two borides must be coincidental because there cannot be the same numbers of electrons oscillating in β-B as in the borides. The β-B loss energy is quite close to that calculated from the free-electron equation (viz., 23 eV) for three electrons per atom. Thus, the effective electron mass[135] in β-B must have nearly the free-electron value.

Computation of the ratios of plasmon/parent peak areas is also interesting as it shows the proportion of photoemitted electrons which are undergoing energy loss. All samples showed the same area ratios for corresponding plasmons: for Fe $2p_{1/2}$, 3s and 3p, 10–20%; for Fe $2p_{3/2}$, 2–5%; for B 1s, 50 ± 5%.

The samples are again behaving in a like manner as expected from the above data. The similar numbers of electrons suffering loss from Fe 3s and 3p is predicted by the plasmon intensity being a function of $1/\sqrt{E}$[136] since these two core levels are quite close in energy. But on this basis the Fe 2p ratios should be higher than those of Fe 3s and 3p, which they are not. This discrepancy is probably caused by separating the two adjacent 2p plasmons; consideration of their total area should give better agreement.

It is interesting that the 50% plasmon/parent ratio of B 1s is higher than warranted by its binding energy (from the above equation), suggesting some dependence of this phenomenon on the nature of the photoemitting atom.

Conclusions

Binding-energy shifts of 0.2–0.4 eV between the iron core levels of the borides and iron metal are not considered significant. After considering atomic volumes and extraatomic relaxation effects it was concluded that this result indicates similar electron densities around iron in the borides and iron itself, and thus the absence of significant charge transfer between iron and boron. This is supported by the similarity between the Fe LMM Auger spectra of the borides and iron, and by identical plasmon energies from corresponding core levels of all samples.

The same binding energies for B 1s were observed in the borides and β-rhombohedral boron. This was concluded to result from the cancellation of opposed relaxation and atomic volume effects. The B 1s of β-boron was broader than those of the borides by ~1 eV. The origin of this broadening and of the Gaussian line shape of the β-boron line was not understood. Bonding between Fe and B is found to be metallic. From ESCA and crystallographic considerations, boron is bonded in linear chains in FeB, but the boron atoms are isolated in Fe_2B. A difference in the chemical environments of boron in the two borides was also deduced from the B 1s line shapes—for FeB, a typical lifetime Lorentzian, whereas for Fe_2B appearance of a Gaussian contribution possibly indicates reduction of solid-state broadening because the boron atoms are more isolated. These conclusions were supported by the atomic-like nature of the B KLL transition of both borides.

High densities of states at the Fermi level in the ESCA valence bands of the borides are consistent with their metallic properties. The borides' valence bands are broader than that of iron owing to changes in the d-electron bands substructure. The ESCA valence bands did not show any evidence of boron states, but information on these has been obtained from a Synchrotron photoemission study.[117]

Finally, despite the well-known difficulty of accurately quantifying ESCA, we have shown that computation of relative peak areas can give a useful check of surface stoichiometry and hence of the surface phase in comparison to the bulk.

Acknowledgments. We are grateful to Professor H. D. Brody for useful discussions and for providing electron beam zone refining and metallurgical facilities. The β-rhombohedral single crystal was kindly supplied by Wacker-Chemie of München, West Germany, the theoretical DOS of CrB was communicated by Professor P. G. Perkins. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

References and Notes

(1) R. M. Friedman, J. Hudis, M. L. Perlman, and R. E. Watson, *Phys. Rev. B*, **8**, 2433 (1973).
(2) N. J. Shevchik and C. M. Penchina, *J. Phys. F*, **5**, 2008 (1975).
(3) P. T. Andrews and L. A. Hisscott, *J. Phys. F*, **5**, 1568 (1975).
(4) T. S. Chou, M. L. Perlman, and R. E. Watson, *Phys. Rev. B*, **14**, 3248 (1976).
(5) T. Collins and P. T. Andrews, *J. Phys. F*, **7**, L43 (1977).
(6) S. P. Kowalczyk, F. Apal, G. Kaindl, F. R. McFeely, L. Ley, and D. A. Shirley, *Solid State Commun.*, **25**, 847 (1978).
(7) P. J. Brown and J. L. Cox, *Philos. Mag.*, **23**, 705 (1971).
(8) J. D. Cooper, T. C. Gibb, N. N. Greenwood, and R. V. Parish, *Trans. Faraday Soc.*, **60**, 2097 (1964).
(9) R. B. Creel and R. G. Barnes, *J. Chem. Phys.*, **56**, 1549 (1972).
(10) G. V. Samsonov, Yu M. Goryachev, and B. A. Kovenskaya, *J. Less-Common Met.*, **47**, 147 (1976).
(11) M.-C. Cadeville and E. Daniel, *J. Phys.* (*Paris*), **27**, 449 (1966).
(12) R. Kuentzler, *J. Phys.* (*Paris*), **32**, C1-634 (1971).
(13) G. Fischer and A. J. P. Meyer, *C. R. Hebd. Seances Acad. Sci., Ser. B*, **265**, 521 (1967).
(14) N. Lundquist, H. P. Meyers, and R. Westin, *Philos. Mag.*, **7**, 1187 (1962).
(15) T. Shinobara and H. Watanabe, *Sci. Rep. Tohoku Univ.*, **A185**, 385 (1966).
(16) I. D. Weisman, L. J. Swartzendruber, and L. H. Bennett, *Phys. Rev.*, **177**, 465 (1969).
(17) H. Bernas and I. A. Campbell, *Phys. Lett. A*, **24**, 74 (1967).
(18) R. S. Perkins and P. J. Brown, *J. Phys. F*, **4**, 906 (1974).
(19) P. G. Perkins and A. V. J. Sweeney, *J. Less-Common Met.*, **47**, 165 (1976).
(20) P. G. Perkins, private communication.
(21) D. A. Shirley, R. L. Martin, S. P. Kowalczyk, F. R. McFreely, and L. Ley, *Phys. Rev. B*, **15**, 544 (1977).
(22) M. Prudenziata, "Boron and Refractory Borides", V. L. Matkovich, Ed., Springer-Verlag, West Berlin, 1977, p 241.
(23) The Powder Diffraction File, JCPDS, Swarthmore, Pa., cards 3-957 and 3-1053.
(24) D. J. Joyner and P. E. D. Morgan, Powder Diffraction File, JCPDS, Swarthmore, Pa., in press.
(25) T. Lundström in ref 19, p 351.
(26) R. J. Colton and J. W. Rabalais, *J. Electron Spectrosc. Relat. Phenom.*, **7**, 359 (1975).
(27) B. O. Elfström and I. Olefjord, *Phys. Scr.*, **16**, 436 (1977).
(28) R. Komanduri and M. C. Shaw, *Philos. Mag.*, **34**, 195 (1976).
(29) G. Mavel, J. Escard, P. Costa, and J. Castaing, *Surf. Sci.*, **35**, 109 (1973).
(30) J. H. Scofield, *J. Electron Spectrosc. Relat. Phenom.*, **8**, 129 (1976).
(31) C. K. Jørgensen and H. Berthou, *Faraday Discuss. Chem. Soc.*, **53**, 26 (1972).
(32) D. Briggs, "Handbook of X ray and Ultra Violet Photoelectron Spectroscopy," Heyden, London, 1977.
(33) D. R. Penn, *J. Electron Spectrosc. Relat. Phenom.*, **9**, 29 (1976).
(34) This result by Penn has been corroborated experimentally. See: S. Evans, R. G. Pritchard, and J. M. Thomas, *J. Phys. C*, **10**, 2483 (1977).
(35) I. Lindau and W. E. Spicer, *J. Electron Spectrosc. Relat. Phenom.*, **3**, 409 (1974).
(36) I. N. Shabanova and V. A. Trapeznikov, *J. Electron Spectrosc. Relat. Phenom.*, **6**, 297 (1975).
(37) K. Kishi and M. W. Roberts, *Surf. Sci.*, **62**, 252 (1977).
(38) A. I. Eacharov, *Izv. Akad. Nauk SSR, Ser. Fiz.*, **40**, 362 (1976).
(39) S. Doniach and M. Šunjić, *J. Phys. C*, **3**, 285 (1970).
(40) V. M. Pessa, *Phys. Rev. B*, **15**, 1223 (1977).
(41) G. Ertl and K. Wandelt, *Surf. Sci.*, **50**, 479 (1975).
(42) C. R. Brundle, T. J. Chuang, and K. Wandelt, *Surf. Sci.*, **68**, 459 (1977).
(43) M. Oku and K. Hirokawa, *J. Electron Spectrosc. Relat. Phenom.*, **8**, 475 (1976).
(44) L. I. Yin, S. Ghose, and I. Adler, *Appl. Spectrosc.*, **26**, 355 (1972).
(45) G. C. Allen, M. C. Curtis, A. J. Hooper, and P. M. Tucker, *J. Chem. Soc., Dalton Trans.*, 1525 (1974).
(46) K. Kishi and S. Ikeda, *Bull. Chem. Soc. Jpn.*, **16**, 341 (1973).
(47) R. Holm and S. Storp, *Appl. Phys.*, **9**, 217 (1976).
(48) K. Asami and K. Hashimoto, *Corros. Sci.*, **21**, 201 (1977).
(49) S. Hüfner and G. K. Wertheim, *Phys. Rev. B*, **11**, 678 (1975).

(50) S. Hüfner and G. K. Wertheim, *Phys. Rev. B*, **11**, 5197 (1975).

(51) S. Hüfner, G. K. Wertheim, D. N. E. Buchanan, and K. W. West, *Phys. Lett. A*, *46*, 420 (1974).

(52) V. M. Pessa, *Phys. Scr.*, **15**, 352 (1977).

(53) H. Kaga, A. Kotani, and Y. Toyogawa, *Physica* (*Utrecht*), **86–88B**, 1191 (1977).

(54) E. Antonangeli, A. Balzarotti, A. Bianconi, P. Perfetti, P. Ascarelli, and N. Nisticò, *Solid State Commun.*, **21**, 201 (1977).

(55) K. Siegbahn, *Pure Appl. Chem.*, **48**, 77 (1976).

(56) R. S. Williams, P. S. Wehner, G. Apal, J. Stöhr, D. A. Shirley, and S. P. Kowalczyk, *J. Electron Spectrosc. Relat. Phenom.*, **12**, 477 (1977).

(57) C. R. Brundle and A. F. Carley, *Chem. Phys. Lett.*, **33**, 41 (1975).

(58) D. J. Joyner, O. Johnson, and D. M. Hercules, *J. Phys. F.*, **10**, 169 (1980).

(59) G. K. Wertheim, "Electronic States of Inorganic Compounds", P. Day, Ed., Reidel, Dordrecht, 1975, pp 393–408.

(60) J. C. Carver, G. K. Schweitzer, and T. A. Carlson, *J. Chem. Phys.*, **57**, 973 (1972).

(61) C. S. Fadley and D. A. Shirley, *Phys. Rev. A*, **2**, 1109 (1970).

(62) S. P. Kowalczyk, L. Ley, R. A. Pollak, F. R. McFeely, and D. A. Shirley, *Phys. Rev. B*, **7**, 4009 (1973).

(63) F. R. McFeely, S. P. Kowalczyk, L. Ley, and D. A. Shirley, *Solid State Commun.*, **15**, 1051 (1974).

(64) C. Kittel, "Elementary Solid State Physics", Wiley, New York, 1962, Table 8.4, p 276.

(65) D. N. Hendrickson, J. M. Hollander, and W. L. Jolly, *Inorg. Chem.*, **9**, 612 (1970).

(66) (a) This position of oxidized boron in the iron borides has been determined in samples whose surfaces were seriously contaminated before grinding. The B^{3+}–B^0 binding energy difference (B 1s) thus determined was ~4 eV (previous workers quoted 5 and 6 eV—ref 50 and 66a, respectively). We determined the chemical shift for B 1s in bulk B_2O_3 to be ~5 eV. (b) M. Aono, S. Kawai, S. Kono, M. Okusawa, T. Sagawa, and Y. Takehara, *J. Phys. Chem. Solids*, **37**, 215 (1976).

(67) E. Antonides, E. C. Janse, and G. A. Sawatzky, *Phys. Rev. B*, **15**, 1669 (1977).

(68) F. J. Szalkowski and C. A. Megerle, *Phys. Lett. A*, **48**, 117 (1974).

(69) H. Höchst, A. Goldmann, and S. Hüfner, *Z. Phys.*, **B24**, 245 (1976).

(70) T. M. Duc, G. Hollinger, Y. Jugnet, J. P. Mercurio, A. Berrada, J. Etourneau, and P. Hagenmuller, *Conf. Ser. Inst. Phys.* (*Rare Earth Actinides*), **No. 37**, 134 (1978).

(71) M. Aono, C. Oshima, T. Tanaka, E. Bannai, and S. Kawai, *J. Appl. Phys.*, **49**, 2761 (1978).

(72) J.-N. Chazalviel, M. Campagna, G. K. Wertheim, and P. H. Schmidt, *Phys. Rev. B*, **14**, 4586 (1976).

(73) P. G. Perkins in ref 19, p 31.

(74) H. Ihara, M. Hirabayashi, and H. Nakagawa, *Phys. Rev. B*, **16**, 726 (1977).

(75) L. E. Davis, N. C. Macdonald, P. W. Palmberg, G. E. Riach, and R. E. Weber, "Handbook of Auger Electron Spectroscopy", 2nd ed., Physical Electronics Inc., 1976.

(76) S. Aksela, M. Pessa, and M. Karras, *Z. Phys.*, **237**, 381 (1970).

(77) L. I. Yin, E. Yellin, and I. Adler, *J. Appl. Phys.*, **42**, 3595 (1971).

(78) J. P. Coad, *Phys. Lett. A*, **37**, 437 (1971).

(79) J. P. Coad and J. C. Rivière, *Z. Phys.* **244**, 19 (1971).

(80) W. A. Coughlan and R. E. Clausing, *At. Data*, **5**, 317 (1973).

(81) S. P. Kowalczyk, Ph.D. Thesis, Lawrence Berkeley Laboratory, University of California, Berkeley, 1976, LBL Report No. 4319.

(82) G. C. Allen, P. M. Tucker, and R. K. Wild, *Surf. Sci.*, **68**, 469 (1977).

(83) Physical Electronics, Inc., to be published; preprint in *Phi Interface*, **1**, 5 (1978).

(84) Y. Strausser and J. J. Uebbing, "Varian Chart of Auger Electron Energies", Varian Corp., Palo Alto, Calif., 1970.

(85) W. Klein, *J. Less-Common Met.*, **47**, 101 (1976).

(86) G. Dagoury and D. Vigner, *Vide*, **187**, 51 (1977).

(87) A. G. Moldovan, Ph.D. Thesis, University of Pittsburgh, 1978.

(88) From T. A. Carlson, "Photoelectron and Auger Spectroscopy", Plenum Press, New York, 1975, p 188; Fe 3d sensitivity is 35.0 eV per electron.

(89) A boron 1s value is not given by Carlson (see ref 88), but we assume that it is the same as for B 2s, i.e., 20.7 eV/electron.

(90) J. C. Fuggle, E. Källne, L. M. Watson, and D. J. Fabian, *Phys. Rev. B*, **16**, 750 (1977).

(91) R. E. Watson, M. L. Perlman, and J. F. Herbst, *Phys. Rev. B*, **13**, 2358 (1976).

(92) R. Hoogewijs, L. Fiermans, and J. Vennik, *Surf. Sci.*, **69**, 273 (1977).

(93) For examples of such ESCA studies of alloys see ref 6 and 34; E. Z. Kurmaev, F. Werfel, O. Brümmer, and R. Flükiger, *Solid State Commun.*, **21**, 239 (1977); J. Hedman, M. Klasson, R. Nilsson, C. Nordling, M. F. Sorokina, O. I. Kljushnikov, S. A. Nemnonov, V. A. Trapeznikov, and V. G. Zyryanov, *Phys. Scr.*, **4**, 195 (1971).

(94) S. P. Kowalczyk, L. Ley, F. R. McFeely, R. A. Pollak, and D. A. Shirley, *Phys. Rev. B*, **9**, 381 (1974).

(95) P. H. Citrin and D. R. Hamann, *Chem. Phys. Lett.*, **22**, 301 (1973).

(96) P. H. Citrin and D. R. Hamann, *Phys. Rev. B*, **10**, 4948 (1974).

(97) Another possibility needs to be mentioned. Change in multiplet splitting between the compounds could result in alteration of the spectral weighting with consequent iron peak shift. But this can be ruled out because all the core levels remain in the same positions.

(98) S. I. Salem, C. N. Chang, P. L. Lee, and V. Severson, *J. Phys. C*, **11**, 4085 (1978).

(99) P. H, Citrin, P. Eisenberger, and D. R. Hamann, *Phys. Rev. Lett.*, **33**, 965 (1974).

(100) P. H. Citrin and D. R. Hamann, *Phys. Rev. B*, **15**, 2923 (1977).

(101) C. P. Flynn, *Phys. Rev. Lett.*, **37**, 1445 (1976).

(102) K. Siegbahn et al., "ESCA Applied to Free Molecules", North-Holland Publishing Co., Amsterdam, 1969.

(103) R. W. Shaw, Jr., and T. D. Thomas, *Phys. Rev. Lett.*, **29**, 689 (1972).

(104) R. M. Friedman, J. Hudis, and M. L. Perlman, *Phys. Rev. Lett.*, **29**, 692 (1972).

(105) A. N. Arsen'eva-Geil', A. A. Berezin, and E. V. Mel'nikova, *Sov. Phys.-Solid State* (*Engl. Transl.*), **17**, 1624 (1976).

(106) W. H. Strehlow and E. L. Cook, *J. Phys. Chem. Ref. Data*, **2**, 163 (1973).

(107) W. Dietz and H. Herrmann, "Boron: Preparation, Properties and Applications", Vol. 2, G. K. Gaulé, Ed., Plenum Press, New York, 1965, p 107.

(108) W. C. Shaw, D. E. Hudson, and C. G. Darrelson, *Phys. Rev.*, **107**, 419 (1957).

(109) L. Ley, O. B. Dabbousi, S. P. Kowalczyk, F. R. McFeely, and D. A. Shirley, *Phys. Rev. B*, **16**, 5372 (1977).

(110) S. Hüfner and G. K. Wertheim, *Phys. Lett. A*, **47**, 349 (1974).

(111) M. Pessa, P. Heimann, and M. Neddermeyer, *Phys. Rev. B*, **14**, 3488 (1976).

(112) N. S. McIntyre and D. G. Zetaruk, *Anal. Chem.*, **49**, 1521 (1977).

(113) D. E. Eastman and J. L. Freeouf, *Phys. Rev. Lett.*, **34**, 395 (1975).

(114) S. F. Alvarado, M. Erbudak, and P. Munz, *Physica* (*Utrecht*), **86–88B**, 1188 (1977).

(115) P. S. Bagus, C. R. Brundle, T. J. Chuang, and K. Wandelt, *Phys. Rev. Lett.*, **39**, 1229 (1977).

(116) The same conclusion was made in an X-ray iron K-edge study of the two borides. See: E. A. Zhurakovsky, *Dokl. Akad. Nauk Ukr. SSR*, **7**, 12 (1969).

(117) D. J. Joyner, J. H. Weaver, O. Johnson, and D. M. Hercules, to be published.

(118) R. E. Watson and M. L. Perlman, *Struct. Bonding* (*Berlin*), **24**, 83 (1975).

(119) G. K. Wertheim, *NATO Adv. Study Inst., Ser. B*, 32 (1978).

(120) T. E. Gallon, *NATO Adv. Study Inst., Ser. B*, 230 (1978).

(121) C. J. Powell, *Solid State Commun.*, **26**, 557 (1978).

(122) E. Antonides and G. A. Sawatzky, *Inst. Phys., Conf. Ser.*, **No. 39**, 134 (1978).

(123) J. M. Rojo and A. M. Baró, *J. Phys. C*, **9**, L543 (1976).

(124) G. A. Sawatzky, *Phys. Rev. Lett.*, **39**, 504 (1977).

(125) C. J. Powell, *Phys. Rev. Lett.*, **30**, 1179 (1973).

(126) A. J. Jackson, C. Tate, T. E. Gallon, P. J. Bassett, and J. A. D. Matthew, *J. Phys.*, **5**, 363 (1975).

(127) G. F. Amelio, *Surf. Sci.*, **22**, 301 (1970).

(128) Compare with the chemisorbed atom case: M. Salmerón, A. M. Baró, and J. M. Rojo, *Surf. Sci.*, **53**, 689 (1975).

(129) Compare with the case of Be where 2p electrons have been detected. See R. G. Musket and R. J. Fortner, *Phys. Rev. Lett.*, **26**, 80 (1971).

(130) E. A. Bakulin, M. M. Bredov, and V. V. Shcherbinino, *Sov. Phys.-Solid State* (*Engl. Transl.*), **17**, 1763 (1976).

(131) J. L. Robins and J. B. Swan, *Proc. Phys. Soc., London*, **76**, 857 (1960).

(132) H. Raether, *Springer Tracts Mod. Phys.*, **38**, 84 (1965).

(133) T. S. Sun, J. M. Chen, R. K. Viswanadham, and J. A. S. Green, *Appl. Phys. Lett.*, **31**, 580 (1977).

(134) D. R. Spalding and A. J. F. Metherell, *Philos. Mag.*, **18**, 41 (1968).

(135) R. A. Pollak, L. Ley, F. R. McFeely, S. P. Kowalczyk, and D. A. Shirley, *J. Electron Spectrosc. Relat. Phenom.*, **3**, 381 (1974).

(136) Reference 88, p 256.

(137) Theoretical splitting from ref 88, Appendix 2. The present differences in experimental splitting are due to very low signal/noise ratios, making position assignment difficult.

(138) C. D. Wagner, *Faraday Discuss. Chem. Soc.*, **60**, 293 (1975).

(139) O. Johnson, D. J. Joyner, and D. M. Hercules, *J. Phys. Chem.*, in press.