

EXAFS and XANES Study of Vanadium in β -Rhombohedral Boron

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The local structure and bonding of vanadium doped β -rhombohedral boron at a composition VB_{-165} has been investigated using a combined EXAFS/XANES technique utilizing synchrotron radiation as a light source. In this alloy, the V atoms are found to be 12-fold coordinated by B atoms at a distance of $2.17 \pm 0.02 \text{ \AA}$. This result agrees well with the assignment of the A_1 site for V in the alloy from single crystal diffractometry. In addition, the V K -edge XANES spectrum exhibits a number of outstanding absorption features when compared with pure vanadium and VB_2 , the latter is used to model the B environment of V in β -boron: (a) with respect to pure vanadium, there is a positive shift of the photoionization threshold of 1.5 eV in VB_{-165} ; (b) two well-defined bound states at 7.7 and 11.6 eV appear; and (c) a shift of the white line position ($4p$ final state) from 19 eV in pure vanadium and VB_2 to 24.8 eV in VB_{-165} . The XANES spectral features are qualitatively interpreted in terms of a matrix-isolation effect of individual V atoms in the β -boron lattice and a subsequent loss of metallic-like character. © 1986 Academic Press, Inc.

Introduction

The formation of solid solutions with addition of a few atomic percent of various metals to β -rhombohedral boron has been reported in a number of studies (1-9). The ability of β -boron to form such solid solutions may easily be rationalized qualitatively in terms of the openness and hole structure in the boron lattice (1). Assuming a boron radius of 0.88 \AA , the degree of space filling by the boron atoms in undoped β -boron was estimated to be only 36%. Crystallographically, these metal-doped boron materials retain the basic rhombohedral structure in which the metal goes into various interstitial holes causing a slight volume expansion of the host lattice. The volume expansion is correlated monotonically with increased hardness (solution

hardening) in a series of solid solutions with $3d$ transition metals (10).

The structure and site distribution of metals in a number of $\text{B}_{100-x}\text{M}_x$ solid solutions ($M = \text{Sc, Cr, Mn, Fe, Cu, and Zr}$) have been investigated in detail using X-ray diffractometry (1-8). The findings are summarized in Table I. Metals such as Cr, Mn, Fe, and Cu having atomic radii $\sim 1.30 \text{ \AA}$ tend to reside in the A_1 and D holes, whereas Sc and Zr with larger radii $\sim 1.60 \text{ \AA}$ prefer the larger E hole (1). However, the type of sites and their occupancy are not unique. In MnB_{23} and CuB_{28} (2), the metal atoms enter three sets of holes: A_1 , D , and E , while in CrB_{41} (1) and FeB_{49} (6) only the A_1 and D holes are occupied. This, as well as the differences in occupation of the holes by the four metals, cannot be explained as size-factor effects since their Goldschmidt

radii are almost equal. Similarly, Sc (7) which is almost the same size as Zr (8), occupies an additional third site substituting for two B(4) atoms in the β -boron lattice. The explanation must be sought in the electronic interaction of the metal atoms with the β -boron network. Such electronic structure and bonding information on these metal-doped boron systems are not presently available.

In this paper we report an X-ray spectroscopic investigation using synchrotron radiation as a light source to elucidate the local atomic structure and bonding of vanadium-doped β -boron from analysis of the EXAFS (extended X-ray absorption fine structure) and XANES (X-ray absorption near-edge structure) spectra about the K -edge of vanadium in the solid solution. The bond distance and coordination about the vanadium site are found to be in good agreement with a recent crystallographic determination of the same system (11), while the XANES data sheds new light on the bonding on such metal-doped boron systems.

Experimental

The preparation of polycrystalline boules of vanadium doped β -boron, VB₋₁₆₅, by rf-induction melting of a mixture of 99.99% β -boron and 99.95% vanadium metal has been given elsewhere (11). Powdered specimens were obtained by pulverizing cut pieces of the grown boules in a tungsten carbide shatterbox (12). Spectral specimens were then prepared by packing the powder into 6- μ m X-ray polypropylene envelopes sufficiently large that the X-ray beam impinged only on the sample.

Room-temperature vanadium K -edge spectra were obtained on a beam line VII-3 wiggler side station at the Stanford Synchrotron Radiation Laboratory (SSRL) during a dedicated run of Stanford Positron Electron Accelerator Ring (SPEAR) at an electron energy of 3.0 GeV and an injection current at 75 mA. The beam was monochromatized

TABLE I
SITES AND OCCUPANCIES OF VARIOUS METAL
ATOMS IN β -BORON

System	Goldschmidt radius of metal (Å)	Type of site ^a	Occupancy (%)	Ref.
ScB ₂₈	1.62	D	31	(7)
		E	73	
		S ^b		
CrB ₄₁	1.30	A ₁	72	(1)
		D	18	
MnB ₂₃	1.35	A ₁	26	(2)
		D	43	
		E	66	
FeB ₄₉	1.26	A ₁	51	(6)
		D	19	
CuB ₂₈	1.28	A ₁	6	(2-5)
		D	43	
		E	50	
ZrB ₅₁	1.60	D	28	(8)
		E	—	

^a Ref. (1).

^b Two B(4) atoms are substituted by Sc at this site.

with double Si(220) crystals and a 1-mm entrance slit, which yielded a resolution of approximately 0.3 eV at the V K -edge of 5465 eV (13). The spectra of vanadium in VB₋₁₆₅ were measured using the fluorescence EXAFS technique (14). This technique monitors the V K_{α} fluorescence intensity, which is proportional to the degree of absorption of the incident beam, and hence monitors the X-ray absorption spectrum. Calibrations of the spectrometer were made before and after scanning the vanadium-doped boron specimen using a 5- μ m vanadium metal foil. A Stern-Heald-type fluorescence detector was used (15). Helium and nitrogen were used as detector gases in the incident ion chamber and fluorescence detector, respectively. The incident beam was detuned 50% to minimize harmonic contents. An all-helium path from the Be window to the sample was used to minimize absorption and scattering by air. Further details of the measurement procedure have been described elsewhere (16). To model the structural environment of vanadium in VB₋₁₆₅ in the EXAFS analysis the V K -edge spectrum of crystalline VB₂ was also

measured using a standard transmission technique (17).

Results and Discussion

Data Reduction and Simulation

In Fig. 1a the experimental V K -edge EXAFS spectrum at room temperature for VB₋₁₆₅ is plotted as I_F/I_0 versus energy, where I_F is the V $K\alpha$ fluorescence intensity and I_0 is the incident intensity. The zero of energy is taken with respect to the first inflection point in the derivative spectrum of pure vanadium metal at 5465.0 eV (see Fig. 5b). Data reduction followed a standard

procedure (18) of correcting for spectrometer shift, deglitching, pre-edge and post-edge background removal, edge normalization, extraction of the EXAFS signal $\chi(k)$, Fourier transform of $\chi(k)$, and inverse transform to isolate the EXAFS contribution from a selected region in real space. The pre-edge background is obtained by a linear regression analysis in the range -100 to -20 eV. The post-edge background above 30 eV in the EXAFS region was generated analytically using a series of cubic splines (19) of equal segments. The ends of each segment are so connected that the derivatives are continuous across the ends.

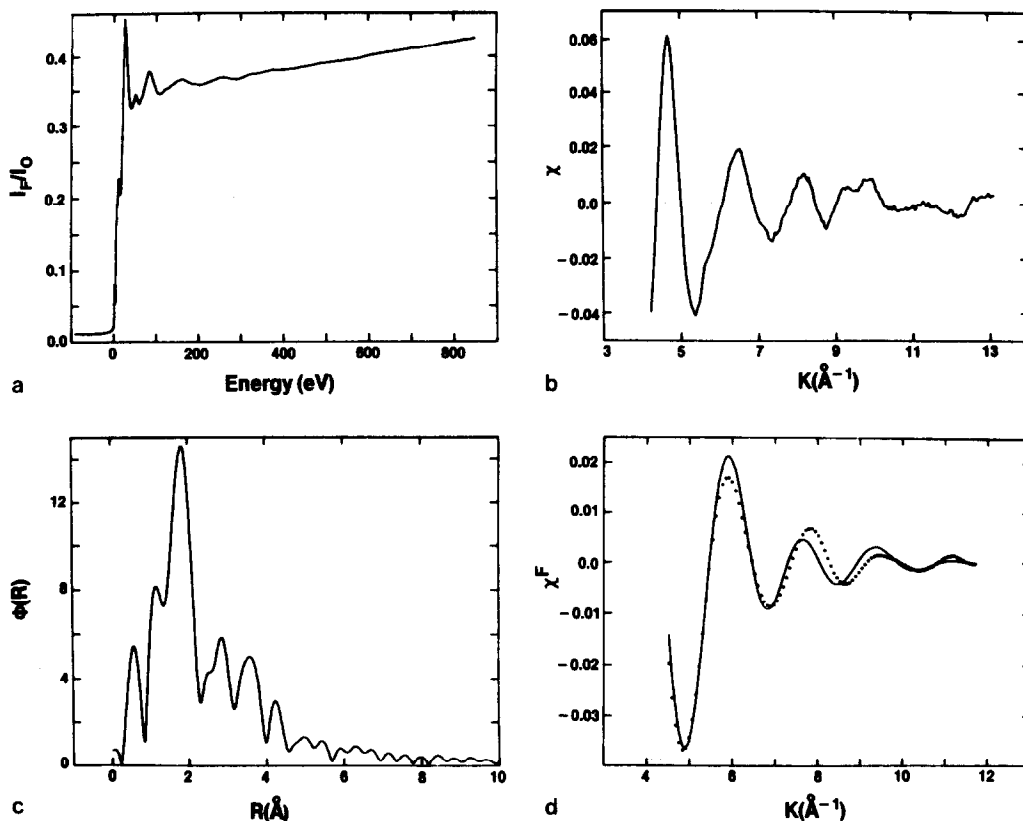


FIG. 1. (a) Room-temperature experimental scan of V K -edge XANES and EXAFS in VB₋₁₆₅, the energy scale is with respect to the V K -edge first inflection of V metal at 5465 eV (see Fig. 5b) as zero. (b) Normalized EXAFS plotted as χ vs k , (c) Fourier transform of $k\chi$, and (d) experimental inverse transform χ^F (line) and simulated (points) EXAFS in the region 0.8 to 2.2 Å about the central absorbing V atom in VB₋₁₆₅.

Two such splines were found adequate. The energy scale was then converted to k scale using $k = 1/\hbar\sqrt{2m(E - E_0)} = \sqrt{0.263(E - E_0)}$ where E_0 is the energy threshold of the absorption edge (13). The normalized EXAFS $\chi(k)$ at energies above ~ 30 eV was obtained by subtracting the smooth post-edge background $\mu_0(k)$ from the measured absorption $\mu(k)$ and dividing by the step jump S at the absorption edge with the McMaster correction (20) $M(k)$ as a function of energy:

$$\chi(k) = \frac{\mu(k) - \mu_0(k)}{S \cdot M(k)}. \quad (1)$$

The Fourier transform of $\chi(k)$ yields a radial structure function $\Phi(R)$ in real space:

$$\Phi(R) = (2\pi)^{-1/2} \int_{k_{\min}}^{k_{\max}} W(k) k^n \chi(k) \exp(2ikR) dk, \quad (2)$$

where $W(k)$ is a Hanning function defined as

$$W(k) = \frac{1}{2} \left\{ 1 - \cos 2\pi \left[\frac{k - k_{\min}}{k_{\max} - k_{\min}} \right] \right\} \quad (3)$$

as was applied to the first and last 1% of the usable EXAFS data defined by k_{\min} and k_{\max} and $n = 1, 2,$ or 3 to weigh the data in k space (21). In Fig. 1b, the normalized V EXAFS for VB₋₁₆₅ is plotted as $\chi(k)$ vs k . The Fourier transform of this k^1 -weighted signal yields a radial peak at just below 2 Å shown in Fig. 1c. Inverse transform on this radial structure peak in the region of 0.8 to 2.2 Å yields a filtered χ^F signal in k space (solid line in Fig. 1d) which was used to simulate the local structure of the vanadium sites in the β -rhombohedral boron lattice.

In the single-scattering approximation (21, 22), the observed EXAFS $\chi(k)$ may be described by

$$\chi(k) = \frac{-1}{k} \sum_j A_j \sin[2r_j k + \phi_j(k)] \quad (4)$$

having oscillatory terms with frequencies $[2r_j k + \phi_j(k)]$, and amplitude terms A_j given

by

$$A_j = \frac{N_j}{r_j^2} f_j(\pi, k) \exp\left(\frac{-2r_j}{\lambda}\right) \exp(-2\sigma_j^2 k^2). \quad (5)$$

The parameters on the right side of Eqs. (4) and (5) may be classified as (a) scattering parameters: phase shift $\phi_j(k)$, backscattering amplitude $f_j(\pi, k)$, and mean free path λ , and (b) structural parameters: coordination number N_j , bond distance r_j , and Debye-Waller factor σ_j . The summation is over all coordination shells j participating in the EXAFS event. In a model system such as VB₂, for which N_j and r_j are known, EXAFS may be used to generate a set of self-consistent scattering parameters for the V-B pair; this information can then be transferred to the vanadium-doped β -boron to determine structural parameters. A least-squares procedure (23) is set up to minimize the variance S , where

$$S = \sum_i^n (\chi_i^F - \chi_i)^2. \quad (6)$$

Here χ_i^F are the Fourier-filtered experimental data and χ_i is the analytical expression given in Eq. (4) which describes χ_i^F for n data points. Since $\chi(k)$ is not a linear function of the various parameters, a Taylor series expansion is used which expresses $\chi(k)$ in terms of approximate parameter values, P_j and parameter adjustments, $\Delta P_j = P_j - P_j^i$. When the least-squares condition is applied, a set of simultaneous equations is obtained in terms of ΔP_j rather than P_j . The equations are solved for the adjustment, ΔP_j , and the parameters were adjusted by ΔP_j to give a new set of estimates. The procedure was then reiterated with the new estimates P_j^i and so until the new solution differed from the last by less than a desired value, which is usually 1%.

Determination of V-B Phase Shift and B Envelope Function

VB₂ belongs to the AlB₂ (C32)-type struc-

ture (24): hexagonal, space group $D_{6h}^1(C6/mmm)$ and $z = 1$ VB_2 unit per primitive cell. The structure consists of alternate layers of metal and boron stacked along the c axis. Each V atom has six equidistant closest metal neighbors in its plane, and 12 equidistant B neighbors at 2.31 Å, six in the layer above and six in the layer below the metal atom. Correspondingly each B atom has three B neighbors in its plane and forms six B–V bonds.

The experimental V K -edge EXAFS scan for VB_2 , the normalized EXAFS χ and the corresponding Fourier transform $\Phi(R)$ of χ are shown in Figs. 2a–c. From the structure of VB_2 it is evident that the first two radial structure peaks at ~ 2 and ~ 2.5 Å in Fig. 2c correspond, respectively, to the shell of 12

B atoms and six V atoms about the X-ray absorbing V atom in the VB_2 crystal structure. The inverse transform of the first peak (solid curve in Fig. 2d) indeed shows an experimental envelope characteristic of a low- Z backscattering atom, i.e., boron. This inverse transform is used to obtain a self-consistent phase shift for the V–B pair in a simulation in which parameterized values of Lee *et al.* (25) in the form

$$\phi(k) = A_0 + A_1k + A_2k^2 + A_3/k^3 \quad (7)$$

are used as initial input. The envelope function $f_B(\pi, k)\exp(-2r/\lambda)$ for B obtained empirically from the filtered EXAFS itself (Fig. 2d) was fixed in the simulation. Structural parameters $N = 12$, $r = 2.31$ Å, and $\sigma = 0$ were used as fixed inputs, while $\Delta E_0 (=$

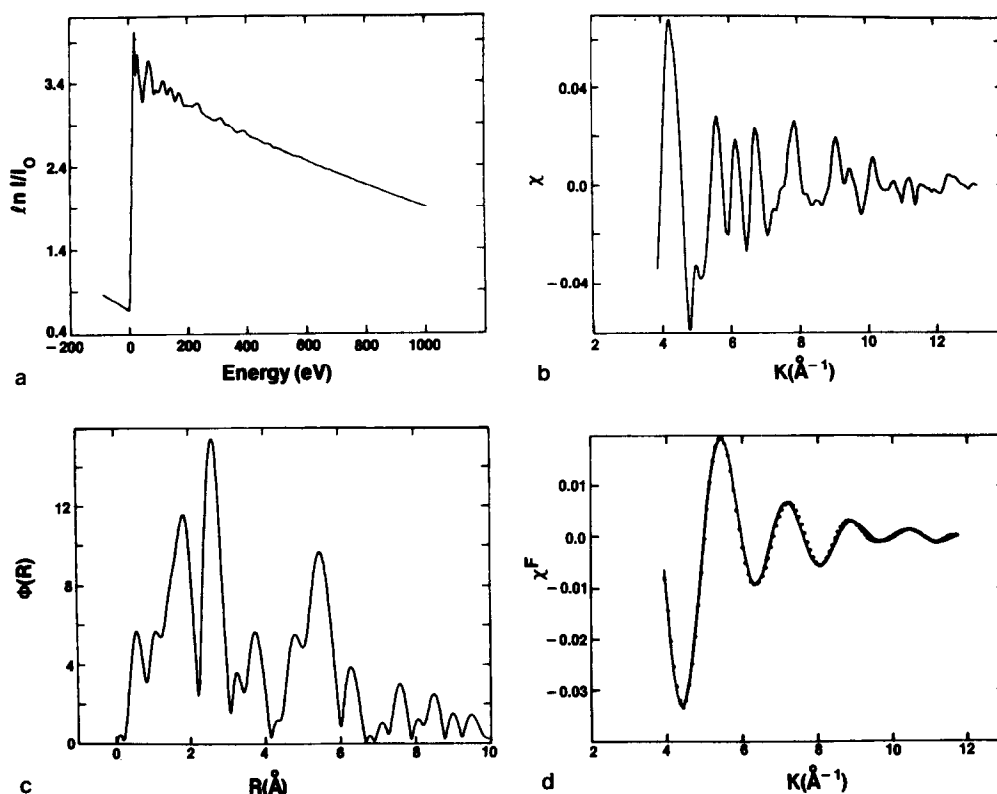


FIG. 2. (a) Experimental scan of V K -edge XANES and EXAFS in VB_2 . (b) Normalized EXAFS plotted as χ vs k , (c) Fourier transform of $k\chi$, and (d) inverse transform χ^F (line) and simulated (points) EXAFS in the region 0.8 to 2.2 Å about the V atom in VB_2 , and $\Delta E_0 = 23.8$ eV was used.

$E_0(\text{theoretical} - E_0(\text{experimental}))$ was allowed to vary. The simulation was performed in k^0 space to emphasize the backscattering contribution of B at low k . The results are shown in Fig. 2d where the solid curve denotes the Fourier-filtered spectrum and the points denote the simulated spectrum. The empirical V-B phase shift shown in Fig. 3 compares well with those of Lee *et al.* (25) when a ΔE_0 value of 23.8 eV was used. The simulation was fitted with a standard deviation 2.2% of the maximum amplitude of the experimental χ^F function.

V Environment in VB₋₁₆₅

The phase-shift function empirically determined for the V-B pair and B backscattering envelop extracted from the inverse transform of first shell of crystalline VB₂ as described above were then transferred and used to determine N , r , and σ for the V site(s) in VB₋₁₆₅. The σ^2 values of the vanadium in β -boron lattice was calculated relative to the value for the V-B pair in VB₂ crystal (taken as zero as stated above). Curve fitting was performed systematically using various combinations of V-B subshells and V sites associated with the A_1 and D holes in the β -boron structure (1). It

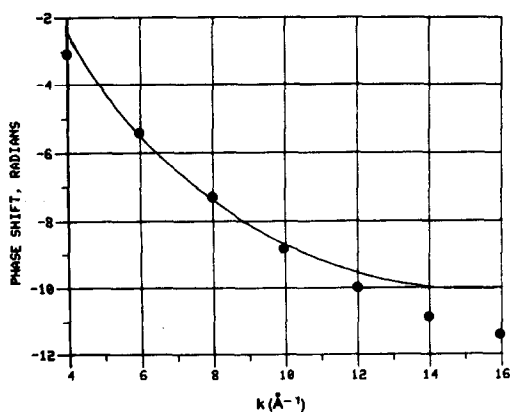


Fig. 3. Comparison of phase-shift function for V-B: points—parameterized values of Lee *et al.*; line—empirically derived using VB₂ as a model and $\Delta E_0 = 23.8$ eV.

was found that a one-shell fit yielded the best fit with physically meaningful parameters for the VB₋₁₆₅ alloy: $N = 12.2$, $r = 2.17$ Å, and $\sigma = -.00347$ Å². The simulated spectrum is shown in Fig. 1d as the dotted curve and has a standard deviation of 5.4% of the maximum amplitude of the experimental χ^F spectrum denoted by the solid curve in Fig. 1d.

Recent single-crystal diffractometric study (11) from our laboratory shows that in VB₋₁₆₅, the V atoms are found only at the 12-fold coordinated A_1 sites having 6B at 2.167 Å, 3B at 2.133 Å, and 3B at 2.145 Å. Within the accuracy of the EXAFS technique (± 0.02 Å for r and $\pm 10\%$ for N) the EXAFS results are in good agreement with those obtained by X-ray diffraction. In a higher V-containing VB₋₁₆₅ alloy, X-ray diffraction reveals that V is found to occupy both A_1 and D sites in the β -boron lattice. For the A_1 site, the coordination is again 12, but the average B separation increases to 2.168 Å. For the D site, the coordination is 15 and the average B separation is 2.382 Å (11).

XANES and Bonding of V in β -Boron

As the region near an X-ray absorption edge is scanned in energy, the ejected photoelectron sequentially probes the empty electronic levels of the material. The resulting XANES within 30 eV of threshold has long been known to be rich in chemical and structural information (26, 27). A recent systematic study (17) of a series of vanadium compounds of known chemical structure shows that the observed V XANES spectra contain information such as valence, site symmetry, ligand type and bond distance and coordination geometry about the X-ray absorbing atom.

In Fig. 4, the normalized V K -edge XANES spectrum in the region ± 60 eV of VB₋₁₆₅ is shown together with those of pure vanadium metal and VB₂. The corresponding derivative spectra are shown in Fig. 5

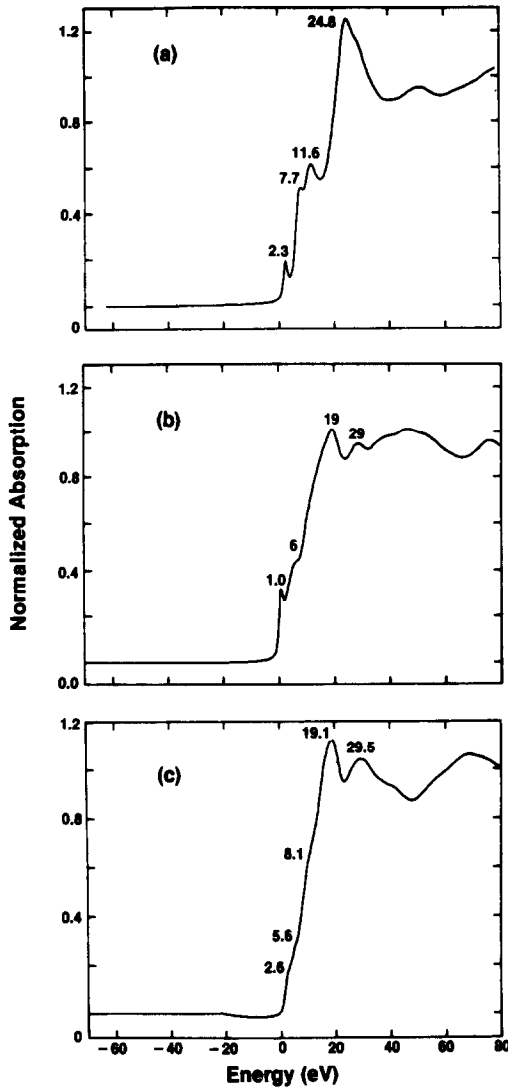


FIG. 4. Normalized V K -edge XANES spectra of (a) VB_{-165} ; (b) V metal, and (c) VB_2 .

and were obtained each by drawing a curve through points given by

$$\frac{dA}{dE} = \frac{A(E + \Delta) - A(E)}{\Delta}, \quad (8)$$

where Δ is the energy step of the absorption spectrum. As mentioned in the experimental section, the energy scale is set with respect to the first inflection point of pure vanadium at 5465.0 eV (Fig. 5b). This

inflection point marks the onset of photoejection of the K electron in vanadium metal. Details of the normalization procedure have been given elsewhere (17). In VB_{-165} , this threshold energy is shifted positively by 1.5 eV (Fig. 5a), similar to that in VB_2 . This positive chemical shift is indicative of a positive oxidation state (17) of V in

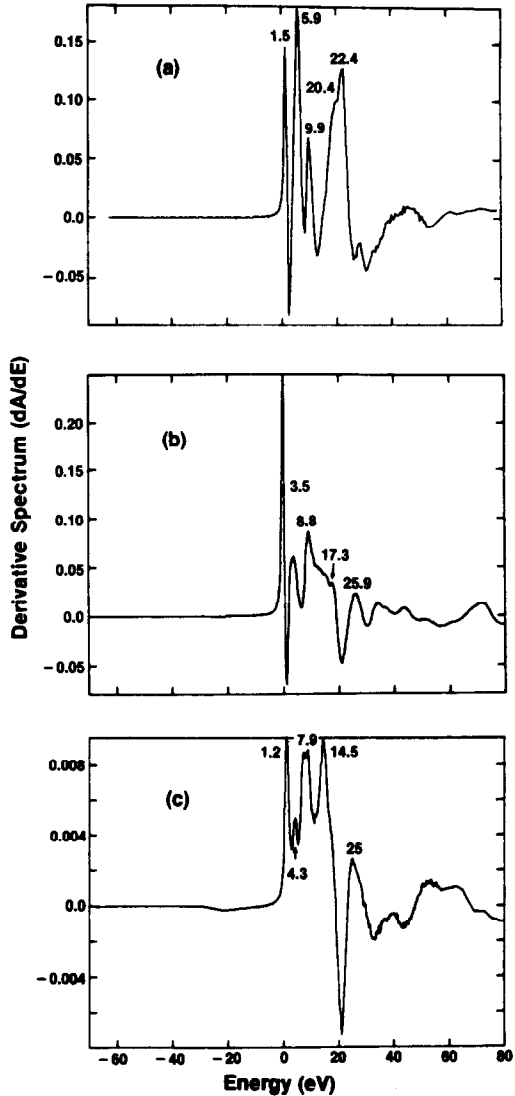


FIG. 5. Derivative V K -edge spectra of (a) VB_{-165} , (b) V metal, and (c) VB_2 . Peaks in these spectra correspond to inflection points in the corresponding spectra shown in Fig. 4.

VB₋₁₆₅. Electrical conductivity studies suggest that the V may occur as V⁵⁺ ions. At higher energy, two well defined bound states at 7.7 and 11.6 eV in the XANES spectrum of VB₋₁₆₅, which are present in neither the spectrum of pure vanadium nor of VB₂. These bound states may be characteristic of this class of metal-doped β -boron materials, in which V, as in the present case, is matrix isolated from other V atoms in the structure. The V-V distance, i.e., the separation between adjacent A₁ sites in rhombohedral boron, is about 6.5 Å. In VB₂, each V atom has six contact V neighbors in a plane. Hence the metallic character of VB₂ is reflected in the similarity of its XANES with the metal spectrum in the region of the white line at ~19 eV as well as the absorption at 29 eV (cf. Figs. 4b and c). However, in the case of VB₋₁₆₅, the white line is shifted to 24.8 eV and the intensity is higher. It is thus evident from these XANES features that there is quite dramatic rearrangement of the electronic configurations in isolating a V atom in the A₁ site of the β -boron lattice. Assignments and detailed interpretation of the various transitions observed in the XANES spectra shown in Fig. 4 await quantum mechanical molecular orbital calculations.

Concluding Remarks

In this report we demonstrate the usefulness of a combined application of EXAFS and XANES using synchrotron radiation as a light source to probe the local atomic structure and bonding of metal sites in β -boron. Our structural results for the case of VB₋₁₆₅ agree well with X-ray diffraction data in terms of the V-B bond distance and coordination of the X-ray absorbing V center. In addition, bonding information and electronic interaction of the metal dopant with the β -boron lattice, not previously available, may now be deduced by analysis of the near-edge spectrum with aid of ap-

propriate model compounds. With intense synchrotron radiation sources emitted from wiggler devices (28), one can extend the X-ray technique to much lower concentration of metal dopant (say 500 ppm) and study the preferential site occupancy systematically as a function of concentration. Tunability of the synchrotron radiation also permit investigation of a host of metal dopants, say the 3d transition metals, and their effect on the semiconducting and thermoelectric properties (29) of this class of novel materials. Further experiments are underway in the laboratory and results will be reported in future publications.

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