

## K-edge absorption spectra of selected vanadium compounds

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High-resolution vanadium *K*-edge absorption spectra have been recorded for a number of selected vanadium compounds of known chemical structure with use of the synchrotron radiation available at the Stanford Synchrotron Radiation Laboratory (SSRL). The compounds studied include the oxides VO, V<sub>2</sub>O<sub>3</sub>, V<sub>4</sub>O<sub>7</sub>, V<sub>2</sub>O<sub>4</sub>, and V<sub>2</sub>O<sub>5</sub>; the vanadates NH<sub>4</sub>VO<sub>3</sub>, CrVO<sub>4</sub>, and Pb<sub>5</sub>(VO<sub>4</sub>)<sub>3</sub>Cl; the vanadyl compounds VOSO<sub>4</sub>·3H<sub>2</sub>O, vanadyl bis(1-phenyl-1,3-butane) dionate, vanadyl phthalocyanine, and vanadyl tetraphenylporphyrin; the intermetallics VH, VB<sub>2</sub>, VC, VN, VP, and VSi<sub>2</sub>; and V<sub>2</sub>S<sub>3</sub> and a vanadium-bearing mineral, roscelite. Vanadium in these compounds exhibits a wide range of formal oxidation states (0 to +5) and coordination geometries (octahedral, tetrahedral, square pyramid, etc.) with various ligands. The object of this systematic investigation is to gain further understanding of the details of various absorption features in the vicinity of the *K* absorption edge of a constituent element in terms of its valence, site symmetry, coordination geometry, ligand type, and bond distances. In particular, the intensity and position of a well-defined pre-edge absorption in some of these compounds have been analyzed semiquantitatively within a molecular-orbital framework and a simple coordination-charge concept.

### I. INTRODUCTION

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 x-ray-absorption near-edge structure (XANES) within 30 eV of threshold has long been known to be rich in chemical and structural information.<sup>1,2</sup> Attempts to correlate a large number of XANES spectra for transition-metal and post-transition-metal oxides, including those of vanadium, were made by White and McKinstry,<sup>3(a)</sup> and Rao *et al.*<sup>3(b),3(c)</sup> Reconciliations of molecular-orbital theory with XANES spectra were made by Best<sup>4</sup> for tetrahedrally coordinated oxy complexes of transition metals, by Seka and Hanson<sup>5</sup> for octahedral complexes, and by Fischer<sup>6</sup> and Tsutsumi *et al.*<sup>7</sup> for Ti and V compounds. In addition, Fischer and Baun<sup>8</sup> have taken an alternate approach using calculated band structures<sup>9,10</sup> for Ti, its oxides, nitride, carbide, and boride to correlate the Ti *L*<sub>3,2</sub> spectra from these materials.

All of the earlier efforts suffered from the (varying) poor resolution of their experiments. With the availability of intense and well-collimated synchrotron x-radiation sources, these spectra can now be measured more quickly, simply, and with greater resolution than ever before. A number of interesting papers have recently been published on *K*-edge<sup>11-19</sup> and *L*-edge<sup>20-22</sup> spectra measured with synchrotron sources. For *K*-edge spectra of transition-metal compounds there are generally weak but distinct ab-

sorption features just before the onset of the main absorption edge. These features have been attributed by Shulman *et al.*<sup>11(a)</sup> to electronic transitions from *1s* to *nd*, *ns* (nondipole), and *np* (dipole-allowed) empty states. For *L*-edge absorption, the transitions are from *2s* and *2p* to some higher, empty *p* and *s* or *d* states, respectively.<sup>23</sup> Recently, the linearly polarized characteristic of synchrotron radiation has been used to determine the orientation dependence of the *K*-edge spectra in single crystals,<sup>24,25</sup> and has enabled certain types of geometric information about the x-ray-absorbing species to be deduced.

Vanadium exhibits a wide range of oxidation states (-1, 0, . . . , +5) and coordination geometries (octahedral, tetrahedral, square pyramid, and trigonal bipyramidal as well as dodecahedral) with various ligands in its compounds.<sup>26</sup> This richness in chemical structures gives rise to a number of outstanding absorption features in the vicinity of the V *K* edge<sup>3,27,28</sup> and *L* edge<sup>29</sup> that are useful in the systematic study and understanding of the effect of bonding and coordination symmetry on the observed XANES (Ref. 30) spectra. In this study we utilize synchrotron radiation from the Stanford Positron Electron Accelerator Ring (SPEAR) available at the Stanford Synchrotron Radiation Laboratory (SSRL) to obtain high-resolution *K*-edge XANES spectra of vanadium in a series of selected compounds of well-defined coordination geometry and known bond distances. The intensity and position of the near-edge spectral features are analyzed within a quantum molecular-orbital framework and a simple coordination-charge concept. The XANES spectra

of these compounds have also been used to model and elucidate the V sites in tunicate blood cells,<sup>31</sup> in coal,<sup>32</sup> and in crude oil.<sup>33</sup>

## II. EXPERIMENTAL DETAILS

The compounds studied in the present investigation include the vanadium oxides VO, V<sub>2</sub>O<sub>3</sub>, V<sub>4</sub>O<sub>7</sub>, V<sub>2</sub>O<sub>4</sub>, and V<sub>2</sub>O<sub>5</sub>; the vanadates NH<sub>4</sub>VO<sub>3</sub>, CrVO<sub>4</sub>, and Pb<sub>5</sub>(VO<sub>4</sub>)<sub>3</sub>Cl (the mineral vanadinite); the vanadyl compounds VOSO<sub>4</sub>·3H<sub>2</sub>O, vanadyl bis(1-phenyl-1,3-butane) dionate (VOPBD), vanadyl phthalocyanine (VPc), and vanadyl tetraphenylporphyrin (VTPP); the intermetallics VH, VB<sub>2</sub>, VC, VN, VP, and VSi<sub>2</sub>; and V<sub>2</sub>S<sub>3</sub> and another vanadium-containing mineral, namely roscelite, KAlV<sub>2</sub>Si<sub>3</sub>O<sub>10</sub>(OH)<sub>2</sub>. The compounds VO, VB<sub>2</sub>, and V<sub>2</sub>S<sub>3</sub> were purchased from Cerac Inc., the vanadyl compounds from Eastman Kodak, NH<sub>4</sub>VO<sub>3</sub> from Fischer Scientific, the two minerals from Ward's Natural Science Establishment, Rochester, New York, and the remaining materials from Alfa Inorganic Chemicals. Phase purity of all the inorganic compounds and the two minerals was checked by in-house powder diffraction to be better than 98%. The organic vanadyl compounds were Kodak certified.

Spectral samples for transmission study were prepared by mulling -400-mesh powders of vanadium compounds with Duco cement,<sup>34</sup> squeezing the mull between two 2 in. × 3 in. microscope slides to obtain a uniform thickness and subsequently gliding the slides apart to allow the films to cure in air. Details of the casting procedure will be described elsewhere.<sup>35</sup> The case films were allowed to cure for about 30 min and were then removed from the microscope slides with a sharp razor blade. The concentration of the powder in the mull and thickness of the film were manipulated so as to provide 1 to 2 absorption lengths of the material at an energy just above the vanadium K edge with the use of a single or a duplex film.

Room-temperature vanadium K-edge absorption spectra were measured with the EXAFS I-5 spectrometer at SSRL during a dedicated run of SPEAR at an electron energy of 3 GeV and a storage-ring current of ~100 mA. The synchrotron x-ray beam from SPEAR was monochromatized with a channel-cut Si(220) crystal (not detuned) and a 1-mm entrance slit, which yielded a resolution of approximately 0.3 eV at 5 keV. Spectra were recorded in four energy regions about the V K edge at ~5465.0 eV: -100 to -50 eV in 10-eV steps, -50 to +50 eV in 0.5-eV steps, 50 to 500 eV in 3-eV steps, and 500 to 1000 eV in 7-eV steps. This scanning procedure yielded quality data of both pre-edge and post-edge (EXAFS) backgrounds for subsequent normalization of the XANES spectra. Calibrations of the spectrometer were made before, between, and after scanning various vanadium compounds using a 5-μm-thick (2.5 absorption lengths) vanadium-metal foil.<sup>36</sup> The concentration of vanadium in VPc, VTPP, and roscelite was only a few percent by weight. Spectral specimens of these materials were made by simply packing the powder in 6-μm-thick polypropylene bags and then taking their spectra with a fluorescence technique<sup>37</sup> using a Ti-filter ion-chamber assembly described elsewhere.<sup>32,38</sup> To minimize air scatter-

ing during fluorescence measurements, the sample chamber was purged with helium.

## III. RESULTS AND DISCUSSION

### A. Normalized XANES and derivative spectrum

In order to compare quantitatively the intensity of absorption features in various vanadium compounds, the experimental K-edge spectra were normalized. The procedure is illustrated graphically in Fig. 1 for the case of vanadium metal. The solid curve is the raw experimental data plotted as  $A = \ln(I_0/I)$  versus energy. The pre-edge region AB (-100 to -10 eV) is linearly fitted and extrapolated above the edge energy to C. The post-edge (EXAFS) background XY from 50 to 1000 eV was determined by using a cubic-spline-fit procedure with three equal segments and extrapolating below the edge energy to Z. The absorption jump is given by PQ at  $E = 0$  eV. The zero of energy is taken with respect to the first inflection point of the vanadium metal in the derivative spectrum at 5465.0 eV, which marks the threshold or onset of photoejection of the 1s electron in vanadium metal.<sup>36</sup> The derivative spectrum within ±70 eV of the K absorption edge is shown in Fig. 2(a) and was obtained by drawing a curve through points given by

$$\frac{dA}{dE} = \frac{A(E + \Delta) - A(E)}{\Delta}, \quad (1)$$

with  $\Delta$  the energy step size of the absorption spectrum. This derivative spectrum and those spectra shown later in Figs. 4, 7, 9, 11, and 13 are characterized by a well-defined and intense peak at the onset of photoejection in the region 0–5 eV. This feature is followed by a number of strong and narrow peaks to about 30 eV, defining the XANES region. At higher energies, structures in the derivative spectrum are much broader and lower in intensity, characteristic of the EXAFS oscillations. Thus, the

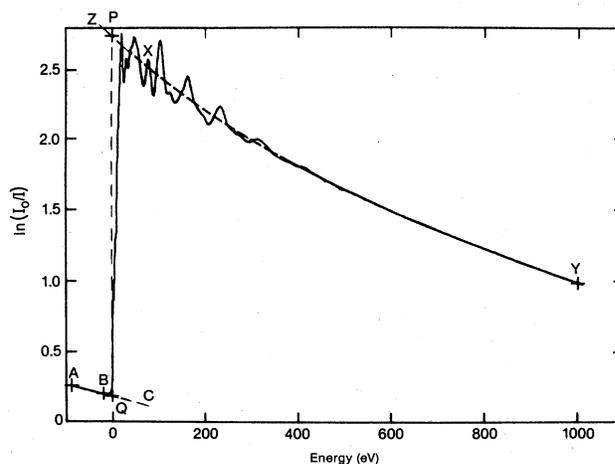


FIG. 1. Room-temperature V K-edge absorption spectrum of vanadium metal showing schematically the edge-normalization procedure (see text). The zero of energy is taken with respect to the first peak in the derivative spectrum shown in Fig. 2(a) at 5465 eV.

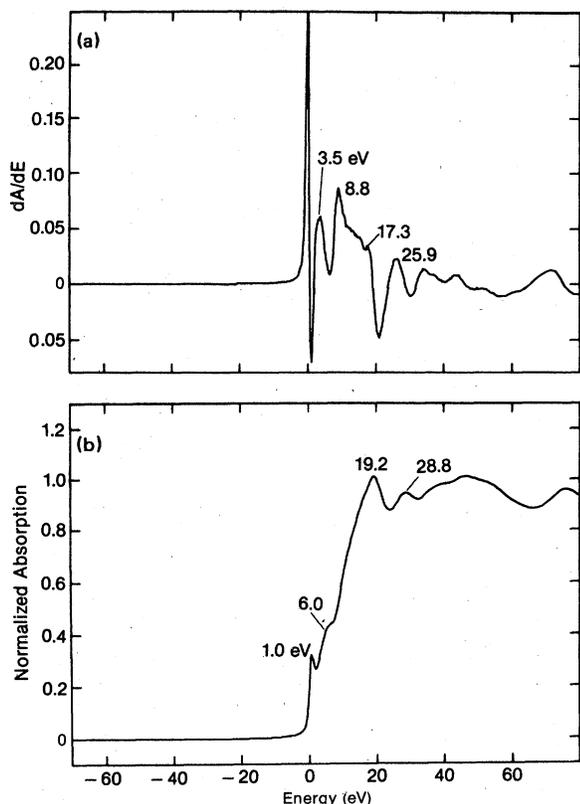


FIG. 2. (a) Derivative and (b) normalized absorption spectra of vanadium metal in the range  $\pm 70$  eV.

derivative spectrum may be used operationally to separate the XANES and EXAFS regions of the experimental x-ray-absorption spectrum.<sup>38(b)</sup>

The normalized XANES spectrum was obtained by subtracting the smooth pre-edge absorption  $AC$  from every point in the experimental spectrum in Fig. 1 in the range  $\pm 70$  eV and dividing by the step height  $PQ$  at  $E = 0$  eV. As seen in Fig. 2(b), the normalized  $K$ -edge XANES spectrum of bcc vanadium metal is characterized by a sharp absorption peak at 1 eV, a shoulder at 6 eV, and following these, a steeply rising edge (the main absorption edge at  $\sim 10$  eV) that leads to various well-defined peaks at 19.2 and 28.8 eV, and to others at higher energy in the EXAFS region. The inflection point associated with each of these absorption features shows up more clearly as a peak in the derivative spectrum which facilitates the enumeration as well as location of the absorption features, particularly those on the rising edge of the XANES spectrum.

In the following sections the  $K$ -edge XANES spectra of vanadium in the oxides, in octahedral, square pyramidal, and tetrahedral coordination, will be presented and discussed in some detail. Spectra of some vanadium intermetallic compounds will also be presented and discussed.

### B. Vanadium oxides

Vanadium forms a series of oxides over a range of formal oxidation states (valence).<sup>39</sup> The crystal structures of

VO,  $V_2O_3$ ,  $V_4O_7$ ,  $V_2O_4$ , and  $V_2O_5$  are known. These oxides provide a useful series of materials for the systematic study of the effects of valence and coordination geometry on the XANES spectrum of the central metal atom coordinated by the same ligand. VO has a NaCl structure with regular octahedral  $VO_6$  units.<sup>40</sup>  $V_2O_3$  has a corundum structure in which  $V^{3+}$  ions are sixfold-coordinated by oxygen ions at two distinct distances, 1.96 and 2.06 Å.<sup>41</sup>  $V_4O_7$  is a mixed valence oxide consisting of both  $V^{3+}$  and  $V^{4+}$  ions. The structure consists of a distorted hexagonal-close-packed oxygen array with vanadium atoms occupying the octahedral sites (distorted) so as to form rutile blocks which extend indefinitely in the triclinic  $a$ - $b$  plane. The rutile blocks are four-octahedra thick along the perpendicular to this plane. There are four crystallographic, nonequivalent vanadium sites with V-O distances ranging from 1.883 to 2.101 Å.<sup>42</sup> The crystal structure of  $V_2O_4$  is monoclinic and is a distorted form of rutile.<sup>43</sup> The V atoms are again sixfold-coordinated by oxygens, but are much displaced from the center of the octahedron, resulting in a short V-O bond of length 1.76 Å. In  $V_2O_5$ , the V is fivefold coordinated in a distorted tetragonal pyramid of oxygen.<sup>44</sup> The apex-oxygen distance is only 1.585 Å, whereas the basal V-O distances vary from 1.78 to 2.02 Å. The site symmetry of the V atom decreases from  $O_h$  in VO to  $C_3$  in  $V_2O_3$ ,  $C_1$  in both  $V_2O_7$  and  $V_2O_4$ , and  $C_s$  in  $V_2O_5$ . The relevant structural parameters of these oxides and other compounds studied here are summarized in Table I.

The spectra of Fig. 3 show that the V  $K$ -edge XANES in these oxides exhibit a pre-edge absorption feature which grows in intensity upon going from  $V_2O_3$  to  $V_2O_5$ , followed by a weak shoulder on a rising absorption curve

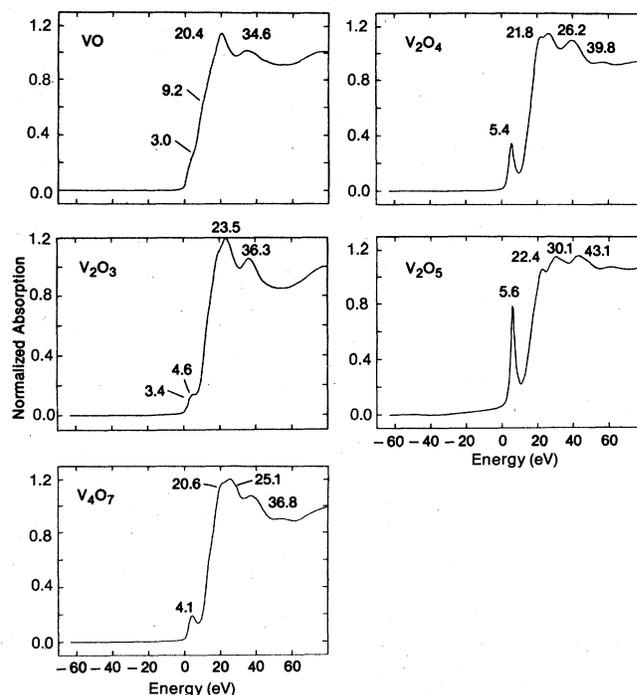


FIG. 3. Normalized  $K$ -edge XANES spectra of vanadium oxides, the zero of energy taken at 5465 eV.

TABLE I. Relevant structural parameters of vanadium compounds. Note: roscelite is  $\text{KAlV}_2\text{Si}_3\text{O}_{10}(\text{OH})_2$ , VOPBD is vanadyl bis(1-phenyl-1,3-butane) diolate, VPc is vanadyl phthalocyanine, and VTPP is vanadyl tetraphenylporphyrin. (av denotes average.)

Compound	Formal valence	Bond type	No. of bonds ( <i>N</i> )	Bond distance (Å)	Reference
V metal	0	V-V	8	2.622	26
VO	2	V-O	6	2.05	40
V <sub>2</sub> O <sub>3</sub>	3	V-O	3	1.96	41
			3	2.06	
V <sub>4</sub> O <sub>7</sub>	3,4	V-O	6	1.883, 1.897, 1.937, 2.032, 2.042, 2.101	42
V <sub>2</sub> O <sub>4</sub>	4	V-O	6	1.76, 1.86, 1.87, 2.01, 2.03, 2.05	43
V <sub>2</sub> O <sub>5</sub>	5	V-O	5	1.585, 1.780, 1.878, 1.878, 2.021	44
V <sub>2</sub> S <sub>3</sub>	3	V-S	6	2.08 (av), <i>N,R</i> by EXAFS	54
roscelite	3	V-O	6	~2.0	53
VOPBD	4	V-O	5	1.612, 1.946, 1.952, 1.986, 1.982	56
VOSO <sub>4</sub> ·3H <sub>2</sub> O	4	V-O	1	1.56	60
		V-OSO <sub>3</sub>	2	2.02	
		V-OH <sub>2</sub>	2	2.05, 2.08	
VPc	4	V-O	1	1.58	59
		V-N	4	2.008, 2.024, 2.034, 2.038	
VTPP	4	V-O	1	1.62	57,58
		V-N	4	2.097, 2.099, 2.102, 2.110	
NH <sub>4</sub> VO <sub>3</sub>	5	V-O	4	1.66, 1.66, 1.81, 1.81	61
CrVO <sub>4</sub>	5	V-O	4	1.72, 1.72, 1.80, 1.80	62,63
Pb <sub>5</sub> (VO <sub>4</sub> ) <sub>3</sub> Cl	5	V-O	4	~1.75	65, 66
VH	1	V-H	6		68
VB <sub>2</sub>	4	V-B	12	2.31	69
VC	4	V-C	6	2.091	70
VN	3	V-N	6	2.07	71
VP	3	V-P	6	2.41	72
VS <sub>2</sub>	4	V-Si	6	2.50	74
			6	2.64	

(the absorption edge) which culminates in a strong peak in the vicinity of ~20 eV. This strong peak has been assigned as the dipole-allowed transition  $1s \rightarrow 4p$ ,<sup>11(a),14</sup> the lower-energy shoulder as the  $1s \rightarrow 4p$  shakedown transition,<sup>11(b)</sup> and the pre-edge feature at threshold as the forbidden transition  $1s \rightarrow 3d$ .<sup>11(a),14</sup> At energies equal to and above the  $1s \rightarrow 4p$  transition, absorption features may arise from a transition to higher  $np$  states, shape resonances,<sup>45-47</sup> and/or multiple scattering.<sup>48,49</sup> The latter two effects are much more complicated to analyze.

Since the initial  $1s$  state is a gerade state, the  $1s \rightarrow 3d$  transition is strictly dipole forbidden, as it is in the case with VO, which contains regular octahedral VO<sub>6</sub> units having a center of inversion. When the symmetry of the ligands is lowered from  $O_h$ , the inversion center is broken, as in the case of V<sub>2</sub>O<sub>3</sub>, V<sub>4</sub>O<sub>7</sub>, and V<sub>2</sub>O<sub>4</sub> with distorted octahedral VO<sub>6</sub> groups, and as in V<sub>2</sub>O<sub>5</sub> with distorted square-pyramidal VO<sub>5</sub> groups. The pre-edge absorption becomes dipole allowed due to a combination of stronger  $3d-4p$  mixing and overlap of the metal  $3d$  orbitals with the  $2p$  orbitals of the ligand.<sup>11</sup>

The intensity variation of the pre-edge peak across the oxide series is noteworthy. As seen in Fig. 3 the oscillator strength increases with progressive relaxation from perfect octahedral symmetry (as in VO) to distorted octahedral VO<sub>6</sub> groups, as in V<sub>2</sub>O<sub>3</sub>, V<sub>4</sub>O<sub>7</sub>, and V<sub>2</sub>O<sub>4</sub>, and to a lower coordination with a short V-O bond (see Table I) in square-pyramidal symmetry (as in V<sub>2</sub>O<sub>5</sub>). The "molecular-cage"-size effect on the oscillator strength of this transition to the  $3d$  orbitals in  $K$ -edge spectra, as noted by Kutzler *et al.*,<sup>50(a)</sup> appears to be operative here. We shall discuss the cage size effect in more detail in Sec. III G in conjunction with other vanadium compounds which also exhibit a strong  $1s \rightarrow 3d$  pre-edge transition.

Closer examination of the spectrum of V<sub>2</sub>O<sub>3</sub> shows that there is a multiplet structure in the pre-edge peak region. The multiplet structure which has previously been observed in V<sub>2</sub>O<sub>3</sub> [Ref. 50(a)] shows splittings of ~1.3 and ~2.0 eV, and can be seen more clearly in the corresponding derivative spectrum in Fig. 4. The splittings in the  $1s \rightarrow 3d$  transition is caused by crystal-field splitting of the ground state,<sup>11</sup> and in the case of V<sub>2</sub>O<sub>3</sub> the  $d$  levels of

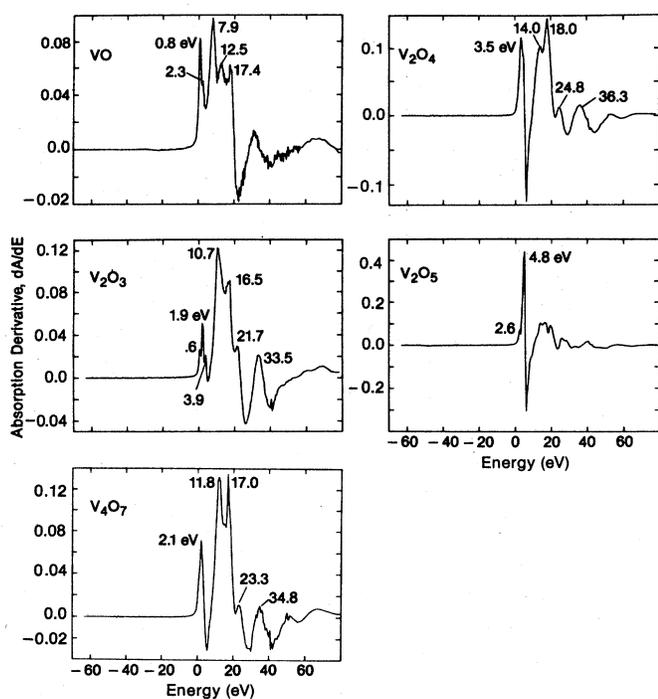


FIG. 4. Derivative plots of the  $K$ -edge spectra of vanadium oxides shown in Fig. 3.

$V^{3+}$  ions in a  $C_3$  site are split into  $A + 2E$  symmetries. A similar triplet pre-edge structure is also observed in roscelite and  $V_2S_3$ , as well as in other transition-metal compounds with crystal symmetry similar to  $TiO_2$  (Ref. 18) (see following section). A doublet splitting is also evident in the case of  $V_2O_5$  shown in Fig. 4.

The energy positions of various absorption features are found to be correlated with the oxidation state (formal valency) of V in the oxides. The experimental data are summarized in Table II. With an increase in oxidation state, (a) the absorption threshold as defined by the position of the first peak in the derivative spectrum, (b) the absorption edge as defined by the second peak in the derivative curve, (c) the energy of the pre-edge peak, and (d) the  $1s \rightarrow 4p$  transition above the absorption edge all shift to higher energies. The energy shifts, so-called chemical shifts, are found to follow Kunzl's law<sup>51,52</sup> and to vary linearly with the valence of the absorbing vanadium atom, as shown in Fig. 5. The positive shift in the threshold energy with valence increase can be understood conceptually to be due to an increase in the attractive potential of the nucleus on the  $1s$  core electron and a reduction in the repulsive core Coulomb interaction with all the other electrons in the compound. The lines in Fig. 5 are least-squares-fitted lines with slopes of 1.4, 1.1, 2.5, and 3.2 eV per valence increase for the threshold, pre-edge peak, absorption edge, and  $1s \rightarrow 4p$  transition, respectively. The increase in slope merely reflects tighter binding of the inner  $3d$  and  $4s$  levels with respect to the outermost

TABLE II. Energy positions of various spectral features in the V  $K$ -edge XANES spectra of vanadium compounds,  $\pm 0.2$  eV.

Compound	Threshold	Pre-edge peak	Main edge	$1s \rightarrow 4p$ transition
V metal	0	10	8.8	19.3
VO	0.8		8	20.4
$V_2O_3$	1.9	3.4	10.7	23.5
$V_4O_7$	2.1	4.1	11.8	25.1
$V_2O_4$	3.5	4.5	14	26.2
$V_2O_5$	4.8	5.6	15.1	30.1
$NH_4VO_3$	4.1	4.8	17.2	26.6
$CrVO_4$	4.1	4.8	17.6	24.2
vanadinite	3.9	4.5	$\sim 18$	25.1
$V_2S_3$	0.6		10.5	23.5
roscelite	1.9	2.6	10.6	21.5
VOPBD	3.5	4.1	14.9	19.8
VPc	3.0	3.9	13.4	27.3
VTPP	3.5	4.1	13.4	25.7
$VOSO_4 \cdot 3H_2O$	4.1	4.8	15.6	21.0
VH	0.61		6	18.7
$VB_2$	1.2		7.9	19.1
VC	1.5	5.4	9.9	20.4
VN	1.5	4.8	8.7	19.8
VP	1.5	4.8 (shoulder)	7	20.0
$VSi_2$	0.5		7.9	27.7

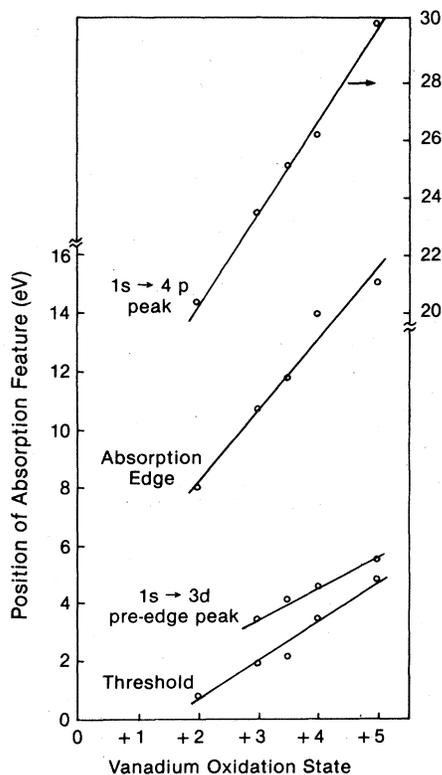


FIG. 5. Oxidation state vs energy positions of various absorption features in the V *K*-edge XANES spectra of various vanadium oxides.

4*p* levels, which are more easily perturbed by valence change.

Finally, a comparison with earlier data on these oxides is in order. A number of *K*-edge absorption studies have been reported using x-ray-tube sources.<sup>3,27,28</sup> All of these earlier studies failed to measure many of the narrow spectral features in both the pre-edge and edge regions because of the poor resolution of their experiments. For example, the pre-edge peaks for  $V_4O_7$  and  $V_2O_4$  shown in Fig. 3 were not resolved and that for  $V_2O_5$  was severely suppressed in intensity.<sup>3,27,28</sup> Sample overthickness and phase purity contributed to the sources of differences. The structureless absorption feature above the *K* edge in  $V_2O_5$  was attributed to a lack of octahedral symmetry of the V center,<sup>28</sup> which is not so, as shown in Fig. 3. This was an artifact due to sample overthickness in a transmission experiment. In the same study<sup>28</sup> a pre-edge peak not expected of V in perfect octahedral symmetry was recorded for VO. The sample in all likelihood was contaminated with  $V_2O_5$ .

### C. V in octahedral coordinates

Roscoelite is a one-layer monoclinic mica in which the  $Al^{3+}$  ions in the octahedral  $AlO_6$  sheet are partially substituted ( $\sim 17\%$ ) by  $V^{3+}$  ions which occupy distorted octahedral sites.<sup>53</sup> The V *K*-edge spectrum of roscoelite is shown in Fig. 6 and is qualitatively similar to that in pure  $V_2O_3$ . The pre-edge absorption in roscoelite again exhibits a triplet feature, but is more intense and much better resolved than that in  $V_2O_3$ . The normalized peak intensi-

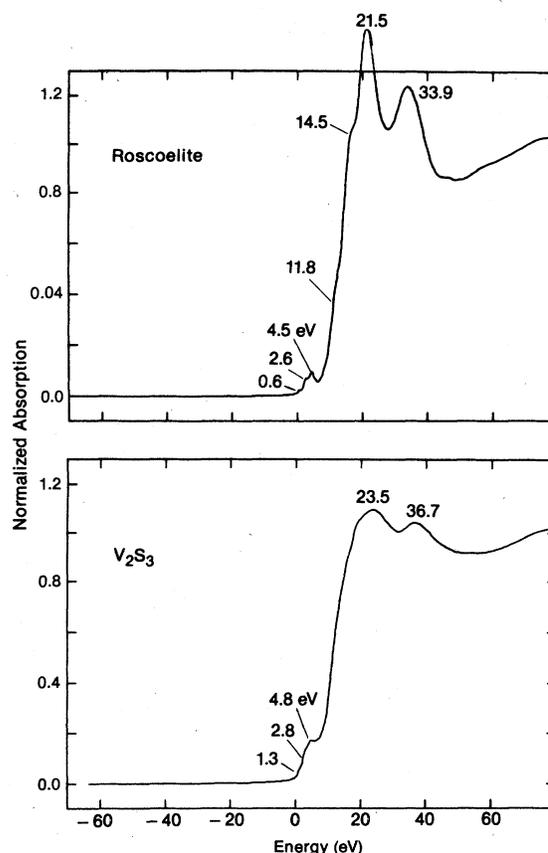


FIG. 6. Normalized V *K*-edge XANES spectra of roscoelite and  $V_2S_3$ .

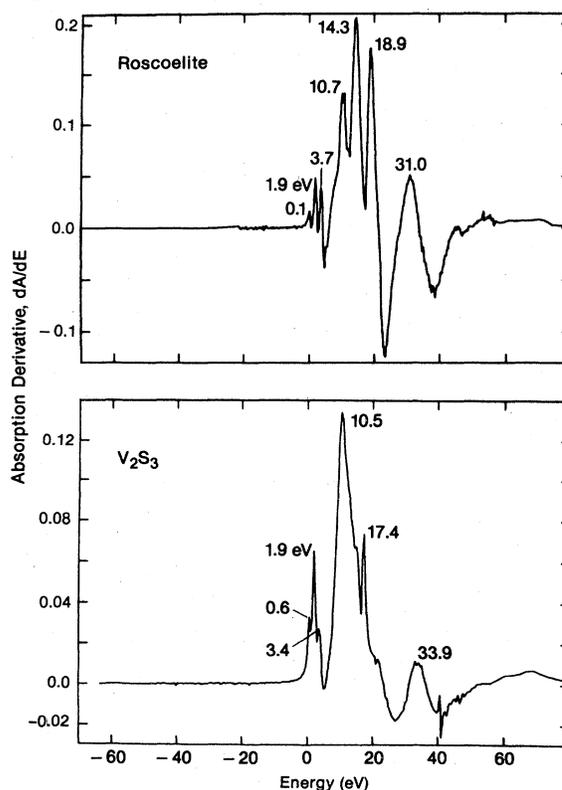


FIG. 7. Derivative plots of the *K*-edge spectra of roscoelite and  $V_2O_3$  shown in Fig. 6.

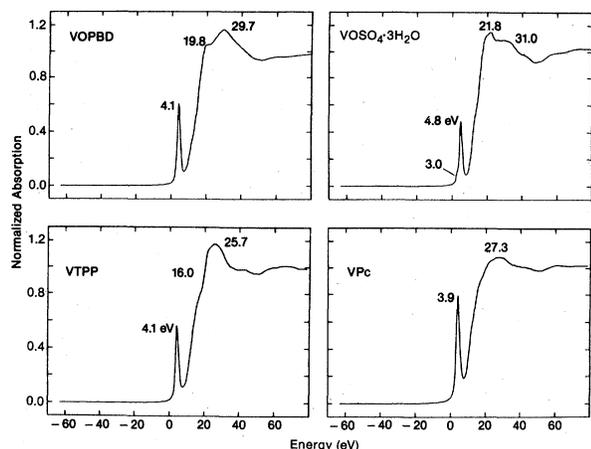


FIG. 8. Normalized V *K*-edge XANES spectra of a series of vanadyl compounds. VOPBD is vanadyl bis(1-phenyl-1.3-butane) dionate, VTTP is vanadyl tetraphenylporphyrin, and VPc is vanadyl phthalocyanine.

ty of the  $1s \rightarrow 4p$  transition above the edge at 21.5 eV is also higher ( $> 1.4$ ), indicating a larger emptiness of the final *p* state in roscoelite induced by the smaller and more polarizing next-nearest  $Al^{3+}$  neighbor as compared with pure  $V_2O_3$ .

$V_2S_3$  is also monoclinic,<sup>54,55</sup> but the crystal structure has not been determined. Its V *K*-edge XANES is also plotted in Fig. 6 and bears general resemblance to those of  $V_2O_3$  and roscoelite, suggesting that the  $V^{3+}$  ions are six-fold coordinated by  $S^{2-}$  in a distorted octahedral environment. The positions of the threshold, pre-edge peak, edge, and  $1s \rightarrow 4p$  transition are quite similar to those of  $V_2O_3$  and roscoelite (see Table II). The triplet pre-edge feature is better seen in the derivative spectrum shown in Fig. 7.

Compared with  $V_2O_3$  and roscoelite, the  $1s \rightarrow 4p$  transition in  $V_2S_3$  is broader and lower in peak intensity. This may be due largely to a ligand (electronegativity) effect to be discussed in Sec. III H.

#### D. V in tetragonal square-pyramidal coordination

Fivefold coordination is typical of a number of vanadyl compounds containing a short V—O bond of length  $\sim 1.6$  Å. Vanadium in these compounds is generally tetravalent, although pentavalent vanadium compounds such as  $V_2O_5$  and the oxyhalides of vanadium ( $VOX_3$ , *X* denoting F, Cl, or Br) are also known to have a short V—O bond.<sup>26</sup> In Fig. 8 the *K*-edge spectra of a series of vanadyl compounds are shown. The respective formal valence, bond type, and nearest-neighbor bond distances are given in Table I. Like  $V_2O_5$ , the XANES spectra of these compounds are typified by a strong  $1s \rightarrow 3d$  pre-edge absorption. The energy position of this pre-edge peak, as well as those of the absorption threshold, absorption edge, and the  $1s \rightarrow 4p$  transition, are summarized in Table II. In VOPBD,<sup>56</sup> vanadium is tetravalent and is coordinated by oxygens at distances of 1.61, 1.95, and 1.98 Å. In VTTP (Refs. 57 and 58) and VPc (Ref. 59), vanadium is also tetravalent. The basal plane of the square pyramids is now replaced by nitrogen ligands. As seen from the bond distances given in Table I, the tetragonal pyramid unit in both the porphyrin and phthalocyanine compounds is more regular than that in VOPBD, and consists primarily of a single distance to the basal ligands. However, there is a discernible difference between these two compounds: both the V—O and V—N distances in the phthalocyanine are shorter than those in the porphyrin compound. This difference in bond distance appears to correlate with the intensity of the pre-edge  $1s \rightarrow 3d$  absorption, again indicative of a “molecular-cage-size” effect. The smaller the

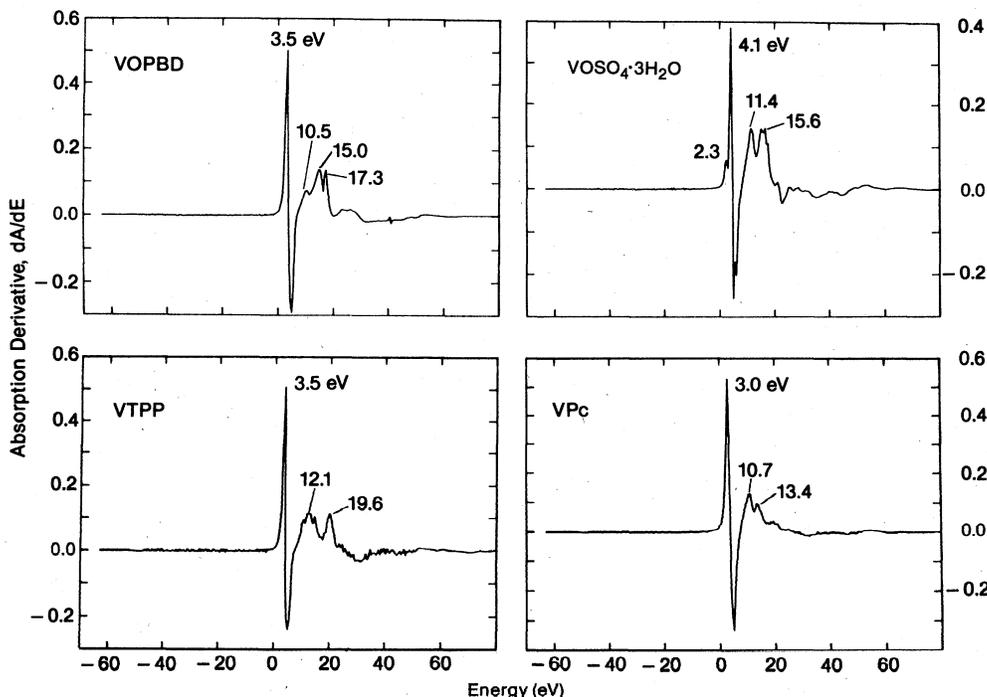


FIG. 9. Derivative plots of the *K*-edge spectra of vanadyl compounds shown in Fig. 8.

case, the higher the intensity of this transition, as in the case of VPc.

In  $\text{VOSO}_4 \cdot 3\text{H}_2\text{O}$  the tetravalent vanadium center is essentially fivefold coordinated by a short vanadyl oxygen at 1.56 Å, two oxygens from two  $\text{SO}_4^{2-}$  groups at 2.02 Å, and two more oxygens from two water molecules of hydration at 2.06 Å. However, there is a sixth oxygen from a third water molecule at a further distance of 2.28 Å.<sup>60</sup> This situation is similar to  $\text{V}_2\text{O}_5$ , in which the sixth oxygen is yet at a further distance, 2.78 Å, from a  $\text{VO}_5$  unit below the vanadium, and is too far to be considered in the primary coordination sphere.<sup>44</sup> It is interesting to note that, like  $\text{V}_2\text{O}_5$ ,  $\text{VOSO}_4 \cdot 3\text{H}_2\text{O}$  also exhibits a weak shoulder on the low-energy side of the pre-edge peak. The shoulder feature is easily discernible in the derivative spectra of  $\text{VOSO}_4 \cdot 3\text{H}_2\text{O}$  shown in Fig. 9, and in Fig. 4 for  $\text{V}_2\text{O}_5$ .

#### E. V in tetrahedral coordination

The intense dipole-allowed absorption occurring in the pre-edge region of the *K*-edge spectra of transition metals in  $\text{CrO}_4^{2-}$ ,<sup>4</sup>  $\text{MnO}_4^-$ ,<sup>17</sup>  $\text{MoO}_4^{2-}$ ,<sup>52</sup>  $\text{MoS}_4^{2-}$ ,<sup>52</sup> and, more recently,  $\text{TiO}_4$  units,<sup>18(a)</sup> is well known. The presence of this absorption is indicative of a tetrahedral environment of the x-ray-absorbing transition metal. This characteristic pre-edge absorption is also found in *K*-edge spectra of vanadium in fourfold coordination. In Fig. 10, a series of V *K*-edge XANES spectra are shown for the cases of

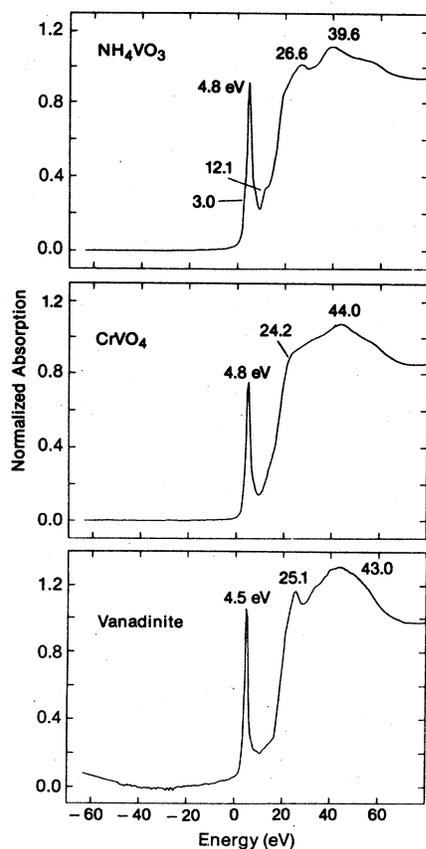


FIG. 10. Normalized V *K*-edge XANES spectra of  $\text{NH}_4\text{VO}_3$ ,  $\text{CrVO}_4$ , and vanadinite.

$\text{NH}_4\text{VO}_3$ ,  $\text{CrVO}_4$ , and  $\text{Pb}_5(\text{VO}_4)_3\text{Cl}$ , the vanadinite mineral. Curvature in the pre-edge background of the vanadinite spectrum was due to scattering by air that was not completely purged out of the sample chamber. Vanadium is pentavalent in these compounds. The energy positions associated with various absorption features in the XANES are similar to those of  $\text{V}_2\text{O}_5$  (see Table II).

$\text{NH}_4\text{VO}_3$  is a metavanadate isostructural with  $\text{KVO}_3$ , space group  $Pbam$  ( $D_{2h}^9$ ) with  $Z=4$  per unit cell.<sup>61</sup> The structure consists of tetrahedral  $\text{VO}_4$  chains similar to those in diopside  $\text{CaMg}(\text{SiO}_3)_2$ . However, there are two types of V—O bonds in the tetrahedral chain. Within the  $\text{VO}_4$  tetrahedron two bonds are formed with oxygen atoms which link the tetrahedra together and have a V—O distance of 1.81 Å. The other two bonds are formed with terminal (unlinked) oxygens in the mirror plane and have a shorter V—O distance of 1.66 Å. The asymmetry of the vanadium tetrahedron has been ascribed to the tendency of V to form multiple bonds with oxygens.<sup>61</sup>

$\text{CrVO}_4$  is also orthorhombic, space group  $Cmcm$  with  $Z=4$  per unit cell.<sup>62,63</sup> Since V and Cr have very similar atomic scattering factors, x-ray-diffraction measurements have not been able to correctly locate the V and Cr atoms in the structure. By using the characteristic pre-edge absorption, Lytle<sup>64</sup> showed that the Cr *K* edge in  $\text{CrVO}_4$  did not exhibit a pre-edge line, whereas the V edge did, and concluded that V is in the fourfold-coordinated  $C_{2v}$  sites and Cr is in the sixfold-coordinated  $C_{2h}$  sites of the structure. Like  $\text{NH}_4\text{VO}_3$ , there exists two V—O distances in  $\text{CrVO}_4$ , 1.72 and 1.80 Å, the difference of which is smaller than that in  $\text{NH}_4\text{VO}_3$ .

Vanadinite,  $\text{Pb}_5(\text{VO}_4)_3\text{Cl}$ , is a mineral isostructural with fluorapatite.<sup>65</sup> In this compound the pentavalent V center is fourfold coordinated with oxygens and takes the place of phosphorus in the apatite structure. No crystal-structure determination has been made of this mineral. The V—O bond distance was estimated to be  $\sim 1.75$  Å.<sup>66</sup> The width of the pre-edge peak is narrowest for the mineral, 2.2 eV compared with 3.0 and 3.5 eV for  $\text{CrVO}_4$  and  $\text{NH}_4\text{VO}_3$ , respectively. The width may be correlated with the spread of V—O distances in the various  $\text{VO}_4$  tetrahedra: 0.15 Å in  $\text{NH}_4\text{VO}_3$  and 0.08 Å in  $\text{CrVO}_4$ . Extrapolating, it is likely that the V—O bond distance in  $\text{Pb}(\text{VO}_4)_3\text{Cl}$  is single valued. The sharpness of the pre-edge peak is also reflected in the derivative spectra shown in Fig. 11. In fact, the weak shoulder on the low-energy side of the pre-edge absorption for  $\text{NH}_4\text{VO}_3$  is clearly brought out in Fig. 11.

#### F. V intermetallic compounds

Vanadium forms alloys and intermetallic compounds with a large number of elements.<sup>67</sup> We have measured several intermetallic compounds of V with the light elements: VH,  $\text{VB}_2$ , VC, VN, VP, and  $\text{VSi}_2$ . The normalized XANES spectra are shown in Fig. 12 and the corresponding derivative curves are shown in Fig. 13.

VH has a body-centered-tetragonal structure,<sup>68</sup> but details of the atomic arrangement within the unit cell have not been determined. The V *K*-edge spectrum of this hydride is rather structureless, consisting essentially of an

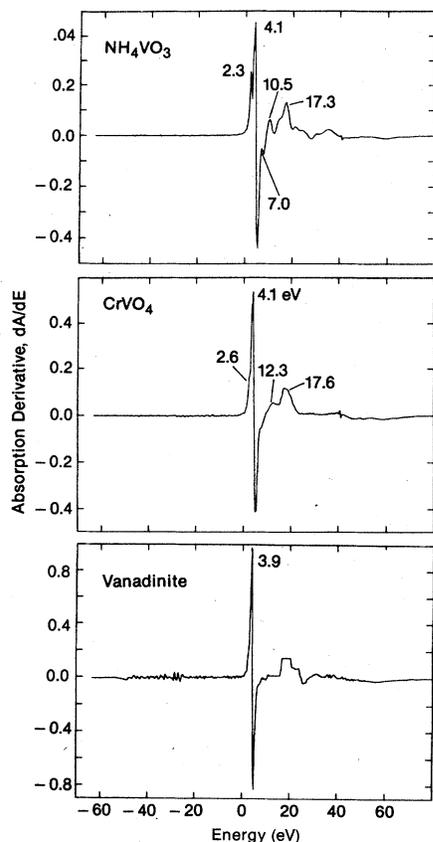


FIG. 11. Derivative plots of the  $K$ -edge spectra of  $\text{NH}_4\text{VO}_3$ ,  $\text{CrVO}_4$ , and vanadinite shown in Fig. 10.

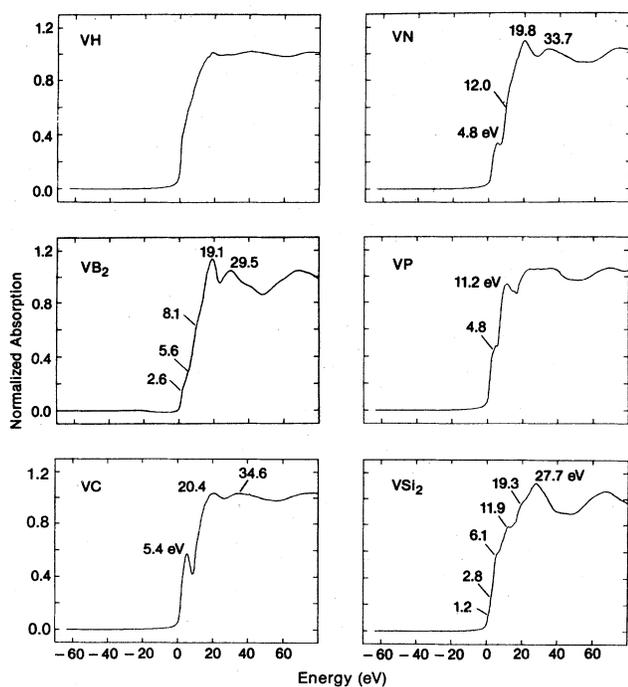


FIG. 12. Normalized V  $K$ -edge XANES spectra of a series of intermetallic compounds.

absorption edge. Weak absorptions on the rising part of the edge are discernible only in the derivative spectrum.

$\text{VB}_2$  belongs to the space group  $D_{6h}^1$  with  $Z=1$  per unit cell.<sup>69</sup> The V and B atoms occupy  $D_{6h}$  and  $D_{3h}$  sites, and lie in alternate planar layers in the hexagonal structure. Each V atom has six equidistant, closest metal neighbors in its plane, and 12 equidistant B neighbors, six in the layer above and six in the layer below the metal atom. The existence of a center of inversion symmetry precludes a  $1s \rightarrow 3d$ -type transition in the pre-edge region.

VC (Ref. 70) and VN (Ref. 71) have the same NaCl structure as VO. The near-edge spectrum of the latter has been plotted in Fig. 3. VP has a NiAs structure with V atoms in  $D_{3d}$  sites.<sup>72</sup> The spectra of the intermetallics VC, VN, and VP exhibit a pre-edge absorption, and in the case of VC, a pre-edge peak at 5.4 eV is well resolved. Since there exists a center of inversion in both  $O_h$  and  $D_{3d}$  symmetries, the  $1s \rightarrow 3d$  transition is dipole forbidden and is only quadrupole allowed (but with low intensity). The experimental intensities of the pre-edge absorption in both VN and VC are quite high when compared with those of  $\text{V}_2\text{O}_3$ ,  $\text{V}_2\text{S}_3$ , and roscelite, which are shown in Fig. 6. It is further noted that the intensity of the pre-edge peak increases upon going through the series VO, VP, VN, and VC, and may be correlated with the character of the unoccupied states above the Fermi level which become less metal-like and more ligand-like.<sup>73</sup>

$\text{VSi}_2$  belongs to space group  $D_6^2$  with  $Z=3$  per unit cell.<sup>74</sup> V atoms are situated in  $C_2$  sites in the structure. In the region 5–25 eV, the V  $K$ -edge spectrum exhibits a multitude of unresolved absorptions which can be enumerated more easily in the corresponding derivative

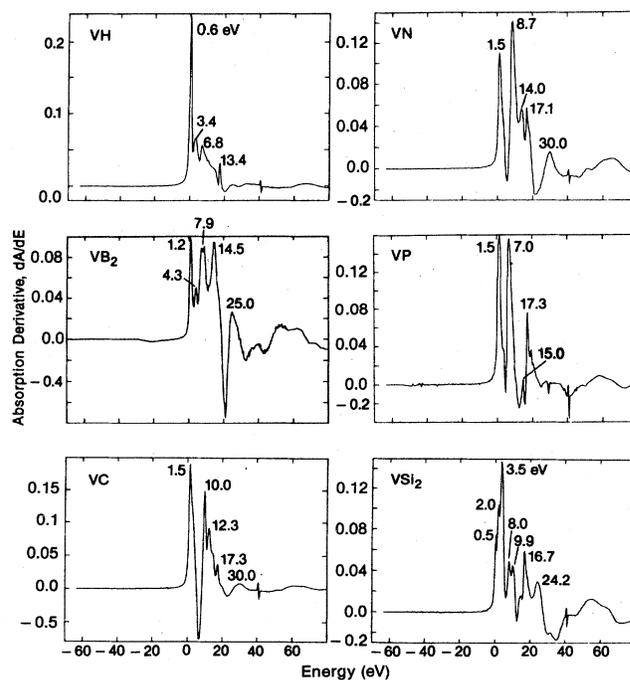


FIG. 13. Derivative plots of the  $K$ -edge spectra of the series of intermetallic compounds shown in Fig. 12. The spike above 40 eV is a glitch.

spectrum of Fig. 13.

The energy positions of the absorption threshold, the edge, and  $1s \rightarrow 4p$  transition for these intermetallic compounds are given in Table II. In general, these energies are lower than those of the oxides and other compounds discussed in the preceding sections. The XANES spectra of these intermetallics vary from being rather featureless, such as that of VH, to being rather complex, such as that of VSi<sub>2</sub>.

### G. Intensity of the pre-edge absorption

As seen in the preceding sections, the pre-edge absorption is an outstanding feature in the *K*-edge XANES spectra of vanadium in a number of the compounds selected for this study (see Table III). Empirically, the strength of this pre-edge transition is found to be dependent on the size of the "molecular cage" defined by the nearest-neighbor ligands coordinating to the x-ray-absorbing vanadium center. This correlation is illustrated in a series of plots of the observed intensity versus a cage-size parameter. In Fig. 14 the intensity was obtained as the product of the normalized peak height and width at half height,  $\nu_{1/2}$ . The cage-size parameter was defined as an average bond distance,  $\bar{R} = (1/n) \sum_i^n R_i$ , where  $n$  is the number of nearest-neighbor bonds given in Table I. In Fig. 14 for each geometry type it is clear that the smaller the "molecular cage," the higher the intensity of the pre-edge absorption. This has been noted qualitatively in the preceding sections. Here an attempt is made to obtain theoretical foundation, within a quantum-mechanical framework, for this intensity variation with cage size. Ideally, the theoretical explanation should be independent of cage geometry and therefore be more general than the correlation empirically given in Fig. 14.

For *K*-edge XANES, the pre-edge absorption is due to a transition from an initial  $1s$  state,  $\phi_{1s}$ , of the central x-ray-absorbing vanadium atom to some final molecular-orbital state,  $\phi_f$ , of the vanadium-ligand cluster.  $\phi_f$  may be given as a linear combination of the appropriate atomic orbitals  $\phi_i$ 's which include the  $2p$  orbitals of the oxygen and/or nitrogen ligands:

TABLE III. Spectral characteristics of pre-edge peak in vanadium compounds.

Compound	Energy position ( $\pm 0.2$ eV)	Peak height ( $\pm 0.02$ )	Half-width $\nu_{1/2}$ ( $\pm 0.2$ eV)	Intensity height $\times \nu_{1/2}$
V <sub>2</sub> O <sub>3</sub>	3.4	0.06	~7	~0.4
V <sub>4</sub> O <sub>7</sub>	4.1	0.19	5.1	0.97
V <sub>2</sub> O <sub>4</sub>	4.5	0.35	4.1	1.43
V <sub>2</sub> O <sub>5</sub>	5.6	0.79	3.15	2.48
VOPBD	4.1	0.61	2.38	1.45
VOSO <sub>4</sub> ·3H <sub>2</sub> O	4.1	0.48	2.04	0.98
VPc	3.9	0.79	2.63	2.09
VTTP	4.1	0.57	2.29	1.31
NH <sub>4</sub> VO <sub>3</sub>	4.8	0.91	2.55	2.32
CrVO <sub>4</sub>	4.8	0.82	2.30	1.89
Pb <sub>5</sub> (VO <sub>4</sub> ) <sub>3</sub> Cl	4.5	1.06	1.96	2.07

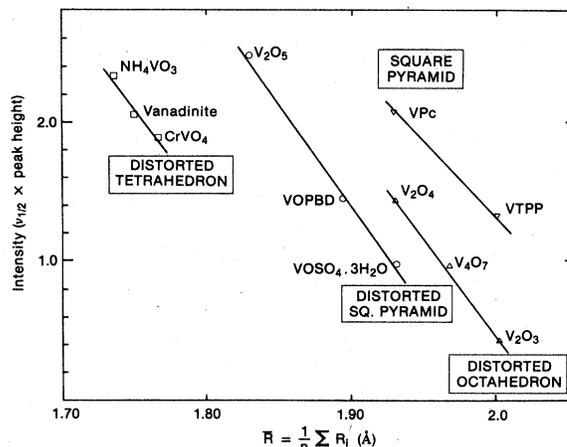


FIG. 14. Intensity of pre-edge absorption vs average bond length  $\bar{R}$  of first shell ligands in various cage geometries.

$$\phi_f = \sum c_i \phi_i \quad (2)$$

In the dipole approximation, the matrix element associated with the transition is

$$\langle \phi_f | M | \phi_{1s} \rangle = \sum c_i \langle \phi_i | M | \phi_{1s} \rangle, \quad (3)$$

where  $M$  is the dipole operator. The intensity  $I$  is proportional to the square of the matrix element,

$$I \propto \left| \sum c_i \langle \phi_i | M | \phi_{1s} \rangle \right|^2. \quad (4)$$

Using the Slater-type-orbital (STO) expression derived by Wahl, Cade, and Roothaan<sup>75</sup> for the one-electron-two-center molecular integrals, Eq. (4) may be approximated by

$$I \propto \left| \sum c_i R_i^2 \exp(-\zeta_i R_i) \right|^2, \quad (5)$$

where the  $c_i$  are the LCAO coefficients such that  $\sum c_i^2 = 1$ ,  $R_i$  is the bond distance of the  $i$ th ligand in Bohr units, and the  $\zeta_i$  are the atomic-orbital exponents. A large value of  $\zeta_i$  implies a fast decay of the orbital away from the nucleus, i.e., a localized orbital.

Rewriting Eq. (5) using a two-term expression on the right-hand side (rhs) which includes only the short vanadyl bond,  $R_1$ , and the average,  $R_2$ , of the remaining longer vanadium-ligand distance for the vanadium compounds studied here, we obtain

$$I \propto [c_1(\gamma R_1)^2 \exp(-\zeta \gamma R_1) + c_2(\gamma R_2)^2 \exp(-\zeta \gamma R_2)]^2, \quad (6)$$

where  $\gamma = 1.89$  Bohr units/ $\text{\AA}$ , and  $R_1$  and  $R_2$  are now in angstroms. Equation (6) is designed to evaluate the effect of the short V—O bond on the observed pre-edge intensity. A plot of  $\ln I$  versus

$$\ln [c_1(\gamma R_1)^2 \exp(-\zeta \gamma R_1) + c_2(\gamma R_2)^2 \exp(-\zeta \gamma R_2)]$$

should yield a theoretical slope of 2 for a proper choice of  $c_1$ ,  $c_2$ , and  $\zeta$ .

A series of systematic iterations were undertaken to calculate the slope of  $\ln I$  versus  $\ln$ [rhs of Eq. (6)] using the

observed pre-edge intensity and the known bond distances (Table I) for the vanadium compounds shown in Fig. 14. The steps in the analysis are given in the following. (a) Fixing  $\xi=2$ , the free-atom value for oxygen, and varying the  $c_1/c_2$  ratio, the slope never attains or exceeds 2.0, but instead maximizes at 1.8 with  $c_1/c_2 \sim 0.3$ . (b) However, when  $\xi$  is varied at fixed  $c_1/c_2$ , the slope is found to be dependent on  $\xi$  and can have values greater or smaller than 2.0. With  $c_1/c_2$  in the range 0.3 to 1.0,  $\xi$  varies from 1.67 to 1.75 in order to have the slope equal to 2.0. This range of  $\xi$  values (which is smaller than the free-atom value) is consistent with a value of 1.7 calculated for the  $O^-$  ion.<sup>76</sup> (c) Finally, by using  $\xi=1.70$  as a fixed value, the slope was found to vary monotonically with  $c_1/c_2$ . A least-squares fit of the slope versus  $c_1/c_2$  yields a slope of 2 at  $c_1/c_2=1.10$ . This  $c_1/c_2$  ratio yields a 55% =  $100[c_1^2/(c_1^2+c_2^2)]$  contribution of the short bond to the observed intensity according to Eq. (6).

In Fig. 15, a self-consistent simulation with  $c_1=c_2$  is plotted for the vanadium compounds which show the pre-edge transition. The solid line having a slope of 2.05 was calculated using  $\xi=1.7$  for all compounds including those of VPc and VTPP, each of which contains four N ligands. When  $\xi=1.6$  is used in the second term in the rhs of Eq. (6) for these two compounds, we obtain the dotted line in Fig. 15, the slope of which is lower (1.97), but within the accuracy of the simulation.

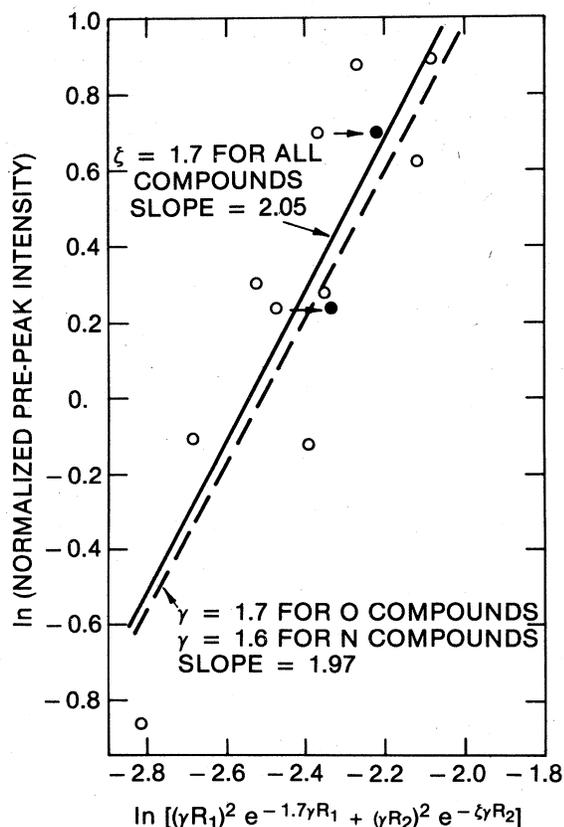


FIG. 15. Plot of  $\ln I$  vs  $\ln[(\gamma R_1)^2 e^{-1.7\gamma R_1} + (\gamma R_2)^2 e^{-\xi\gamma R_2}]$  using the same (solid line) and different (dotted line) values of  $\xi$  for oxygen and nitrogen compounds.

Thus, using a quantum-mechanical expression of the kind given in Eq. (6), one can combine a set of geometry-sensitive curves such as those shown in Fig. 14 into a single curve (Fig. 15) which contains structural information in terms of bond distances as well as bonding information in terms of orbital exponents,  $\xi$ , for the appropriate ligands. Furthermore, the effect of the short V—O bond on the pre-edge intensity can also be evaluated in terms of the  $c_i$  coefficients. However, the intensity is dependent on two (or more) bond lengths in the molecular cage, and thus it is not possible to use the relationship given in Eq. (6) to predict the bond length.

#### H. Energy shifts and coordination charge

In Sec. III B we saw that the energy positions (or chemical shifts<sup>52</sup>) of the threshold, the pre-edge peak, the  $K$  edge, and the  $1s \rightarrow 4p$  transition in the XANES spectra of the oxides of vanadium are related linearly to the formal valence of the central vanadium atom (see Fig. 5). This, of course, is Kunz's law,<sup>52</sup> and has been shown to be useful for systems having the same ligand type,<sup>77-80</sup> e.g., oxygen in the oxide series VO,  $V_2O_3$ ,  $V_4O_7$ ,  $V_2O_4$ , and  $V_2O_5$ . More generally, the chemical shifts in x-ray-edge spectra are due to a combination of valence, electronegativity of the bonding ligands, coordination number, and other structural features. These factors may approximately be accounted for by the concept of coordination charge,  $\eta$ , defined by Batsanov<sup>81</sup> as

$$\eta = Z - CN, \quad (7)$$

where  $Z$  is the formal valence of the central atom,  $C$  is the degree of covalency which equals  $1 - i$ ,  $i$  being ionicity, and  $N$  is the coordination number. For a purely ionic material like NaCl,  $C=0$  and  $\eta=Z$ , i.e., the valence of a constituent atom equals its coordination charge.

Now the multiple-bond ionicity  $i$  is given by

$$i = 1 - \frac{Z}{N} \exp\left[-\frac{1}{4}(X_A - X_B)^2\right], \quad (8)$$

and

$$I = 1 - \exp\left[-\frac{1}{4}(X_A - X_B)^2\right] \quad (9)$$

is the single-bond ionicity.<sup>82</sup> Combining Eqs. (7)–(9), we obtain

$$\eta = ZI, \quad (10)$$

which is the charge appearing at the periphery of the atom as a result of chemical bonding to its ligands. In qualitative terms, the coordination-charge concept simply states that as the valence electrons are pulled away from the metal atom by the electronegativity  $X_B$  of the coordinating ligands, all of the other electrons of the central atom become more tightly bound in order to shield the unchanging nuclear charge. Hence, a  $K$ -shell transition must increase in energy with an increase in the product of valence  $Z$  and ionicity  $I$ . The coordination-charge concept has been used by Cramer *et al.*<sup>12</sup> to identify the chemical state of Mo in nitrogenase from chemical-shift data of a series of Mo model compounds. More recently, Lytle *et al.*<sup>20(b)</sup> have correlated the intensity of the  $L_{III}$

TABLE IV. Calculation of coordination charge.

Element	Pauling electronegativity $X^a$	Vanadium bond ionicity $I$	Bond type	Coordination charge $\eta$
V	1.63	0 (by definition)	V-V	0
O	3.44	0.56	$V^{2+}-O$	1.12
			$V^{3+}-O$	1.68
			$V^{3.5+}-O$	1.95
			$V^{4+}-O$	2.24
			$V^{5+}-O$	2.80
N	3.04	0.39	$V^{3+}-N$	1.17
			$V^{4+}-N$	1.56
			$O-V^{4+}-N_4$	1.70
S	2.58	0.20	$V^{3+}-S$	0.60
C	2.55	0.19	$V^{4+}-C$	0.76
B	2.0	0.034	$V^{4+}-B$	1.36
P	2.19	0.075	$V^{3+}-P$	0.22
Si	1.90	0.018	$V^{4+}-Si$	0.07
H	2.20	0.078	$V^{1+}-H$	0.08

<sup>a</sup>From F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, 2nd ed. (Interscience, New York, 1972), p. 15.

white line in some Au, Pt, and Ir compounds with coordination charge on the metal atoms.

In Table IV the pertinent quantities are listed and the coordination charge calculated for a variety of vanadium formal valences and ligands relevant to this investigation. In cases where the first coordination shell is mixed, a weighted average electronegativity was used. In Fig. 16 the energy positions of the absorption threshold as determined by the first peak in the derivative spectra [Figs. 2(a), 4, 7, 9, 11, and 13] and the main absorption edge (Table II) for all the vanadium compounds studied here are plotted versus coordination charge. Although there is considerable scatter, particularly for the main absorption edge where a variety of spectral features occurring in the edge make identification of the edge rather subjective, the

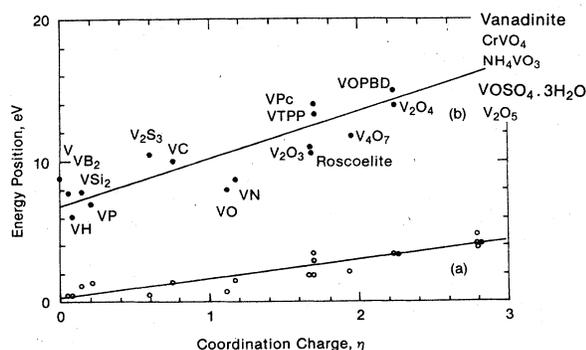


FIG. 16. Coordination charge on the V absorber vs energy positions of (a) the threshold of K photoelectron ejection, and (b) main absorption edge of V in all the vanadium compounds studied here. The lines are least-squares-fitted lines.

simple coordination-charge concept allows a much more systematic and general organization of the data than valence alone. In compounds such as VH, VB<sub>2</sub>, VSi<sub>2</sub>, VP, and VC, the bonding is essentially metallic in nature. The coordination charge of the vanadium center in these intermetallic compounds is low and yields lower threshold and K-edge energies compared with the more strongly chemically bonded oxides and oxy compounds. Ligand electronegativity effects can be seen in the cases of V<sub>2</sub>S<sub>3</sub> versus V<sub>2</sub>O<sub>3</sub>, and the nitrogen-containing VPc and VTPP versus VOPBD and V<sub>2</sub>O<sub>4</sub>. For compounds that exhibit a pre-edge absorption, the energy position of this feature is plotted versus  $\eta$  in Fig. 17. The lines in both Figs. 16 and 17 were drawn using linear regression analysis and have slopes equal to 3.4, 1.4, and 0.9 eV per coordination-charge unit for the K edge, the threshold, and the pre-edge peak, respectively. The differences in slopes are sta-

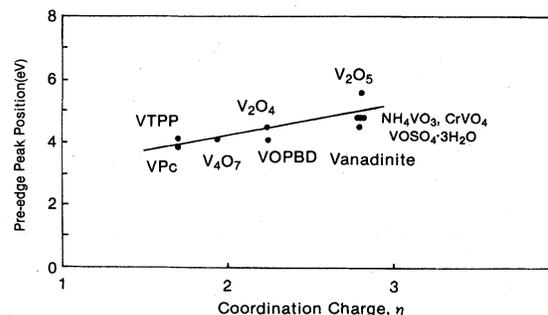


FIG. 17. Coordination charge on the vanadium absorber vs energy position of pre-edge absorption in some vanadium compounds. The line is least-squares-fitted to the experimental points.

tistically significant. They are also chemically reasonable in that the pre-edge peak (with final states primarily of V  $3d$  character) is at lower energy and is expected to be more tightly bound, and, hence, less sensitive to changes in valence and ionicity than the more diffuse, higher-energy  $4s$  and  $4p$  final states. In general terms, the well-defined  $3d$  level is "hard." The  $ns$  and  $np$  continua are "softer."

#### IV. CONCLUDING REMARKS

With intense and well-collimated synchrotron radiation as a light source, high-resolution spectral features in the vicinity of the x-ray-absorption edges not previously recorded with conventional x-ray-tube sources can now be obtained routinely and with good accuracy. The existence of a wide range of chemical structures in vanadium compounds greatly facilitates a systematic study of the effect of valence, site symmetry, coordination geometry, ligand electronegativity, and bond distances on various absorption features in the XANES spectra of a single constituent atom.

Particularly informative is the pre-edge absorption in the V  $K$ -edge spectra of these compounds. Its occurrence, energy position, and intensity can now be understood in terms of site symmetry, coordination charge on the x-ray-absorbing V atom, bond distances, and electronegativity of the coordinating ligands. In perfect octahedral symmetry which has a center of inversion, the  $1s \rightarrow 3d$  transition is only quadrupole allowed and thus is very weak. Progressively lowering the site symmetry to distorted octahedral, square-pyramidal, and tetrahedral geometries promotes the dipole allowedness of the pre-edge absorption and yields an increasing intensity. This is due to the different mixing of metal and ligand character allowed by the change in local symmetry about the metal atom. This trend of intensity change with local site symmetry is seen clearly in the pre-edge peaks of VO,  $V_2O_3$ ,  $V_4O_7$ ,  $V_2O_5$  (Fig. 3), and the vanadates (Fig. 10).

The observed intensity of the pre-edge can be related quantitatively to cage size of the metal-ligand cluster defined by the short V—O bond length and the average of the remaining longer V—ligand bonds according to

$$I \sim [c_1(\gamma R_1)^2 \exp(-\zeta \gamma R_1) + c_2(\gamma R_2)^2 \exp(-\zeta \gamma R_2)]^2,$$

as described in Sec. III G. Systematic simulations lead to

a self-consistent value for the orbital exponent value  $\zeta$  of 1.67–1.75, which agrees with the theoretical value of 1.70 for the  $O^-$  ions. Using a theoretical slope of 2 as a criterion of fit in the plot of  $\ln I$  versus

$$\ln[c_1(\gamma R_1)^2 \exp(-\zeta \gamma R_1) + c_2(\gamma R_2)^2 \exp(-\zeta \gamma R_2)],$$

the contribution of the short bond in determining the intensity of the pre-edge peak is found to be 55%. The value is much higher than the values of 16–20% that correspond to the fractions of short V—O bond to the total number of V—ligand bonds in these compounds.

In this study the XANES spectra of VH, VB<sub>2</sub>, VC, VN, VP, and VSi<sub>2</sub> are also reported. The V  $K$ -edge spectra of these intermetallics may be rather structureless, as in the case of VH, or rather complex, as in the case of VSi<sub>2</sub>. The understanding of the near-edge absorption features of these intermetallics is far from being satisfactory when compared with the nonmetallic oxygen and nitrogen compounds discussed in this study. Band-structure effects are expected to play a role in determining the observed absorption characteristics, but calculations are not available for these vanadium intermetallic compounds at sufficient energy above the Fermi level. In the cases of VO (Ref. 83) and VC (Ref. 84) the band structures were calculated only to a few electron volts above the Fermi level. It is our hope that further theoretical work will be stimulated for this class of materials in the future, and that the calculated density of states and projected density of states will become available for energies 20–30 eV above the Fermi level.

Finally, it may be remarked that the trends observed for various spectral variables in the V  $K$ -edge XANES spectra of these compounds represent a useful data base for an improved understanding of absorption-edge theory and/or for characterizing and identifying the structure and bonding of V in unknown materials

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<sup>1</sup>M. C. Srivastava and H. L. Nigam, *Coord. Chem. Rev.* **9**, 275 (1972).

<sup>2</sup>L. V. Azaroff and D. M. Pease, in *X-ray Spectroscopy*, edited by L. V. Azaroff (McGraw-Hill, New York, 1974), Chap. 6.

<sup>3</sup>(a) E. W. White and H. A. McKinstry, *Adv. X-Ray Anal.* **9**, 376 (1966); (b) P. R. Sarode, S. Ramasesha, W. H. Madhusudan, and C. N. R. Rao, *J. Phys. C* **12**, 2439 (1979); (c) A. Manthiram, P. R. Sarode, W. H. Madhusudan, J. Gopala-Krishnan, and C. N. R. Rao, *J. Phys. Chem.* **84**, 2200 (1980).

<sup>4</sup>P. E. Best, *J. Chem. Phys.* **44**, 3248 (1966).

<sup>5</sup>W. Seka and H. P. Hanson, *J. Chem. Phys.* **50**, 344 (1969).

<sup>6</sup>D. W. Fischer, *J. Appl. Phys.* **41**, 3561 (1970).

<sup>7</sup>K. Tsutsumi, O. Aita, and K. Ichikawa, *Phys. Rev. B* **10**, 4638 (1977).

<sup>8</sup>D. W. Fischer and W. L. Baun, *J. Appl. Phys.* **39**, 4757 (1968).

<sup>9</sup>L. F. Mattheis, *Phys. Rev.* **134**, A970 (1964).

<sup>10</sup>V. Ern and A. C. Switendick, *Phys. Rev.* **137**, A1927 (1965).

<sup>11</sup>(a) R. G. Shulman, Y. Yafet, P. Eisenberger, and W. E. Blumberg, *Proc. Nat. Acad. Sci. U.S.A.* **73**, 1384 (1976); (b) R. A. Bair and W. A. Goddard III, *Phys. Rev. B* **22**, 2767 (1980).

<sup>12</sup>S. P. Cramer, T. K. Eccles, F. W. Kutzler, K. O. Hodgson, and L. E. Mortenson, *J. Am. Chem. Soc.* **98**, 1287 (1976).

- <sup>13</sup>V. O. Kostroun, R. W. Fairchild, C. A. Kukkonen, and J. W. Wilkins, *Phys. Rev. B* **13**, 3268 (1976).
- <sup>14</sup>V. W. Hu, S. I. Chan, and G. S. Brown, *Proc. Nat. Acad. Sci. U.S.A.* **74**, 3821 (1977).
- <sup>15</sup>J. E. Miller, O. Jepsen, O. K. Anderson, and J. W. Wilkins, *Phys. Rev. Lett.* **40**, 720 (1978).
- <sup>16</sup>S. P. Cramer, K. O. Hodgson, E. I. Stiefel, and W. E. Newton, *J. Am. Chem. Soc.* **100**, 2748 (1978).
- <sup>17</sup>M. Belli, A. Scafati, A. Bianconi, S. Mobilio, L. Palladino, A. Reale, and E. Burattini, *Solid State Commun.* **35**, 355 (1980).
- <sup>18</sup>(a) R. B. Greegor, F. W. Lytle, D. R. Sandstrom, J. Wong, and P. Schultz, *J. Non-Cryst. Solids* **55**, 27 (1983); (b) L. A. Grunes, *Phys. Rev. B* **27**, 2111 (1983).
- <sup>19</sup>C. L. Spiro, J. Wong, F. W. Lytle, R. B. Greegor, D. Maylotte, and S. Lamson, *Science* (to be published).
- <sup>20</sup>(a) P. S. P. Wei and F. W. Lytle, *Phys. Rev. B* **19**, 679 (1979); (b) F. W. Lytle, P. S. P. Wei, R. B. Greegor, G. H. Via, and J. H. Sinfelt, *J. Chem. Phys.* **70**, 4849 (1979).
- <sup>21</sup>K. J. Rao, J. Wong, and M. J. Weber, *J. Chem. Phys.* **78**, 6228 (1983).
- <sup>22</sup>K. J. Rao and J. Wong, *J. Chem. Phys.* (to be published).
- <sup>23</sup>M. Brown, R. E. Peierls, and E. A. Stern, *Phys. Rev. B* **15**, 738 (1977).
- <sup>24</sup>D. H. Templeton and L. K. Templeton, *Acta Crystallogr. Sect. A* **36**, 237 (1980).
- <sup>25</sup>F. W. Kutzler, R. A. Scott, J. M. Berg, K. O. Hodgson, S. Doniach, S. P. Cramer, and C. H. Chang, *J. Am. Chem. Soc.* **103**, 6083 (1981).
- <sup>26</sup>R. J. H. Clark, in *Comprehensive Inorganic Chemistry*, edited by J. C. Bailar, H. J. Emeleus, R. Nyholm, and A. F. Trotman-Dickenson (Pergamon, Oxford, 1973), Vol. 3, Chap. 34.
- <sup>27</sup>E. E. Vainshtein, E. A. Zhurakovskii, V. S. Nespor, and G. V. Samsonov, *Sov. Phys. J.* **5**, 996 (1961).
- <sup>28</sup>S. I. Salem, C. N. Chang, and T. J. Nash, *Phys. Rev. B* **18**, 5168 (1978).
- <sup>29</sup>D. W. Fischer, *J. Appl. Phys.* **40**, 4151 (1969).
- <sup>30</sup>This acronym was coined by A. Bianconi, *Appl. Surf. Sci.* **6**, 392 (1980).
- <sup>31</sup>T. D. Tullins, W. O. Gillum, R. M. K. Carlson, and K. O. Hodgson, *J. Am. Chem. Soc.* **102**, 5670 (1980).
- <sup>32</sup>D. H. Maylotte, J. Wong, R. L. St. Peters, F. W. Lytle, and R. B. Greegor, *Science* **214**, 554 (1981).
- <sup>33</sup>J. Wong, F. W. Lytle, D. H. Maylotte, G. H. Via, *Fuel* (to be published).
- <sup>34</sup>A trademark of the DuPont Company.
- <sup>35</sup>J. Wong, *Nucl. Instrum. Methods* (to be published).
- <sup>36</sup>J. A. Bearden and A. F. Burr, *Rev. Mod. Phys.* **39**, 125 (1967).
- <sup>37</sup>J. Jaklevic, J. A. Kirby, M. P. Klein, A. S. Robertson, G. S. Brown, and P. Eisenberger, *Solid State Commun.* **23**, 679 (1977).
- <sup>38</sup>(a) F. W. Lytle, R. B. Greegor, D. R. Sandstrom, E. C. Marques, J. Wong, C. L. Spiro, G. P. Huffman, and F. E. Huggins, *Nucl. Instrum. Methods* (to be published); (b) J. B. Pendry, in *EXAFS and Near-Edge Structure*, Vol. 27 of *Springer Series in Chemical Physics*, edited by A. Bianconi, L. Incoccia, and S. Stipcich (Springer, New York, 1983), pp. 4-10.
- <sup>39</sup>J. Stringer, *J. Less-Common. Met.* **8**, 1 (1965).
- <sup>40</sup>N. Schonberg, *Acta Chem. Scand.* **8**, 221 (1954).
- <sup>41</sup>R. E. Newnham and Y. M. de Haan, *Z. Kristallogr.* **117**, 235 (1962).
- <sup>42</sup>M. Marezio, D. B. McWhan, P. D. Dernier, and J. P. Remeika, *J. Solid State Chem.* **6**, 419 (1973).
- <sup>43</sup>G. Anderson, *Acta Chem. Scand.* **10**, 623 (1956); F. Thesbald, R. Cabala, and J. Bernard, *J. Solid State Chem.* **17**, 431 (1976).
- <sup>44</sup>H. G. Bachmann, F. R. Ahmed, and W. H. Barnes, *Z. Kristallogr. Mineral.* **115**, 110 (1961).
- <sup>45</sup>J. L. Dehmer, *J. Chem. Phys.* **56**, 4496 (1972).
- <sup>46</sup>D. Dill and J. L. Dehmer, *J. Chem. Phys.* **61**, 692 (1974).
- <sup>47</sup>J. L. Dehmer and D. Dill, *J. Chem. Phys.* **65**, 5327 (1976).
- <sup>48</sup>P. J. Durham, J. B. Pandry, and C. H. Hodges, *Solid State Commun.* **38**, 159 (1981).
- <sup>49</sup>G. N. Greaves, P. J. Durham, G. Diakun, and P. Quinn, *Nature* **294**, 139 (1981).
- <sup>50</sup>(a) F. W. Kutzler, C. R. Natoli, D. K. Misemer, S. Doniach, and K. O. Hodgson, *J. Chem. Phys.* **73**, 3274 (1980); (b) A. Bianconi and C. R. Natoli, *Solid State Commun.* **27**, 1177 (1978).
- <sup>51</sup>V. Kunzl, *Collect. Trav. Chim. Techeolovaquie* **4**, 213 (1932), cited in Ref. 51.
- <sup>52</sup>C. Mande and V. B. Sapre, in *Advances in X-ray Spectroscopy*, edited by C. Bonnelle and C. Mande (Pergamon, New York, 1983), Chap. 17, pp. 287-301.
- <sup>53</sup>E. W. Heinrich and A. A. Levinson, *Am. J. Sci.* **253**, 39 (1955).
- <sup>54</sup>F. Hullinger, *Struct. and Bonding (Berlin)* **4**, 83 (1968).
- <sup>55</sup>D. Tudo, *Rev. Chim. Miner.* **2**, 153 (1965).
- <sup>56</sup>P.-K. Hon, R. L. Belford, and C. E. Pfluger, *J. Chem. Phys.* **43**, 1323 (1965).
- <sup>57</sup>R. C. Pettersen, *Acta Crystallogr. Sect. B* **25**, 2527 (1969).
- <sup>58</sup>F. S. Molinaro and J. Albers, *Inorg. Chem.* **15**, 2278 (1976).
- <sup>59</sup>R. F. Ziolo, C. H. Griffiths, and J. M. Troup, *J. Chem. Soc., Dalton Trans.* 2300 (1980).
- <sup>60</sup>P. F. Theobald and J. Galy, *Acta Crystallogr. Sect. B* **29**, 2732 (1973).
- <sup>61</sup>H. T. Evans, Jr., *Z. Kristallogr. Mineral.* **114**, 257 (1960).
- <sup>62</sup>R. W. G. Wychoff, *Crystal Structures*, 2nd ed. (Wiley-Interscience, New York, 1965), Vol. 3, p. 37.
- <sup>63</sup>K. Brandt, *Ark. Kemi, Mineral. Geol.* **17A**, No. 6 (1943).
- <sup>64</sup>F. W. Lytle, *Acta Crystallogr.* **22**, 221 (1967).
- <sup>65</sup>A. F. Wells, *Structural Inorganic Chemistry*, 3rd ed. (Clarendon, Oxford, 1962), p. 183.
- <sup>66</sup>W. E. Baker, *Am. Mineral.* **51**, 1712 (1966).
- <sup>67</sup>W. Rostoker, *The Metallurgy of Vanadium* (Wiley, New York, 1958).
- <sup>68</sup>A. J. Maeland, *J. Phys. Chem.* **68**, 2197 (1964), and references therein.
- <sup>69</sup>B. Post, F. W. Glaser, and D. Moskowitz, *Acta Metall.* **2**, 20 (1954).
- <sup>70</sup>E. Rudy, F. Benesovsky, and L. Toth, *Z. Metallkd.* **54**, 345 (1963).
- <sup>71</sup>R. W. G. Wyckoff, *Crystal Structures*, 2nd ed. (Wiley, New York, 1963), Vol. 1, p. 91.
- <sup>72</sup>N. Schonberg, *Acta Chem. Scand.* **8**, 226 (1954).
- <sup>73</sup>V. A. Gubanov, B. G. Kasimov, and E. Z. Kurmaev, *J. Phys. Chem. Solids* **36**, 861 (1975).
- <sup>74</sup>H. J. Wallbaum, *Z. Metallkd.* **33**, 378 (1941).
- <sup>75</sup>A. C. Wahl, P. E. Cade, and C. C. Roothaan, *J. Chem. Phys.* **41**, 2578 (1964), Eq. (3.12).
- <sup>76</sup>L. C. Cusachs and J. H. Corrington, in *Sigma Molecular Orbital Theory* (Yale University Press, New Haven, Conn., 1970), p. 257.
- <sup>77</sup>W. H. Zinn, *Phys. Rev.* **46**, 659 (1930).
- <sup>78</sup>V. P. Barton, *Phys. Rev.* **71**, 406 (1947).
- <sup>79</sup>I. Manescu, *C. R. Acad. Sci.* **255**, 537 (1947).
- <sup>80</sup>G. L. Glenn and C. G. Dodd, *J. Appl. Phys.* **39**, 5372 (1968).

- <sup>81</sup>S. S. Batsanov, *Electronegativity of Elements and Chemical Bonds*, Novosibirsk, 1962, cited in I. A. Ovsyannikova, S. S. Batsanov, L. I. Nasonova, L. R. Batsanova, and E. A. Nekrasova, *Bull. Acad. Sci. USSR, Phys. Ser.* 31, 936 (1967).
- <sup>82</sup>L. Pauling, *The Nature of the Chemical Bond*, 3rd ed. (Cornell University Press, Ithaca, N.Y., 1960), p. 98.
- <sup>83</sup>T. E. Norwood and J. L. Fry, *Phys. Rev. B* 2, 472 (1970).
- <sup>84</sup>J. Zbasnik and L. E. Toth, *Phys. Rev. B* 8, 452 (1973).