

## Energy shift and structure of the *K*-absorption edge of vanadium in some vanadium compounds

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The energy shift of the *K*-absorption edge of vanadium and the associated fine structure have been investigated for the following chemical compounds: V, VO, V<sub>2</sub>O<sub>3</sub>, V<sub>2</sub>O<sub>4</sub>, V<sub>2</sub>O<sub>5</sub>, VC, VN, VB<sub>2</sub>, VSi<sub>2</sub>, VF<sub>3</sub>, and VS<sub>3</sub>. All measurements were made with an improved version of a single-crystal high-angle goniometer. All studied samples except V<sub>2</sub>O<sub>5</sub> exhibit an extended structure on the high-energy side of the absorption edge. Shoulders, on the absorption edge proper, were observed with several samples, and well-resolved "white" lines were found on the low-energy side of the edge of vanadium in the following compounds: VO, V<sub>2</sub>O<sub>3</sub>, and V<sub>2</sub>S<sub>3</sub>. The chemical energy shift of the *K*-absorption edge, which is found to be governed by the effective ionic charge on the absorbing atom and the structure in the vicinity of the edge are discussed on basis of the molecular-orbital theory.

### INTRODUCTION

The relative position of the *K*-absorption edge of an element is governed by the chemical state of that element. The energy shift of the edge is a result of the effective charge and the electronic configuration of the absorbing atom under investigation. The value of the energy shift yields information regarding the structure of the molecule and the energy liberated during its formation. This quantity may also be correlated with the relative stability of the molecules; of comparable systems, the one with the least free-energy content is the most stable.

The chemical energy shift of x-ray absorption edges was first observed some five decades ago,<sup>1</sup> and was then discussed on the basis of the potential at the absorbing atom due to its surrounding.<sup>2</sup> But until recently very little experimental work was done on the subject.<sup>3-5</sup>

This observed shift is primarily the result of the effective charge on the absorbing atom,<sup>6,7</sup> but its value is also sensitive to the detailed electronic configuration of the valence band and the relaxation effect in the absorbing atom.<sup>8</sup>

The pronounced structure on the high-energy side of the *K*-absorption edge, sometimes referred to as Kronig structure,<sup>9</sup> has been of considerable interest to physicists for some fifty years. And high-quality measurements and the detection of fine structure in the vicinity of the edge began with the pioneer work of Parratt<sup>10</sup> and Beeman and Friedman,<sup>11</sup> and was continued through the effort of Cauchois and Mott<sup>12</sup> and Hanson.<sup>13</sup> Recently, an extensive survey of the *K*-absorption edges and associated structures of the elements of the second transition series was made by Kostroun *et al.*<sup>14</sup>

In the absence of a sound and reliable theory, attempts with variable degrees of success were made to explain the observed fine structure. In the immediate vicinity of the edge, the shape of the structure is characteristic of the density distribution of the empty or partially empty molecular orbitals.<sup>12,15</sup> In the intermediate energy region, some 50–150 eV above the edge, multiple-scattering effect becomes important,<sup>16</sup> and at extremely high energies, more than 200 eV above the edge, the shape of the extended fine structure is governed by the crystal or amorphous structure that surrounds the absorbing atom.<sup>16</sup>

### EXPERIMENTAL

The *K*-absorption edge of vanadium was studied for the following compounds: V, VO, V<sub>2</sub>O<sub>3</sub>, V<sub>2</sub>O<sub>4</sub>, V<sub>2</sub>O<sub>5</sub>, VC, VN, VB<sub>2</sub>, VSi<sub>2</sub>, VF<sub>3</sub>, and V<sub>2</sub>S<sub>3</sub>. With the possible exception of V<sub>2</sub>O<sub>5</sub>, whose coordination is closer to 5 than 6, all these samples are crystals having octahedral symmetry. The studied samples were fine powder of better than 98% purity. The thickness and uniformity of each sample were checked visually and in the x-ray beam. The mass per unit area of each specimen was adjusted to provide maximum intensity discontinuity ratio at the absorption edge.

To reduce the possibility of any chemical effect due to moisture in the air, each sample was freshly prepared prior to its bombardment. All the compounds studied are relatively chemically stable; essentially no hygroscopic effect was ever noticed. For each chemical compound, measurements were made using different samples. No distortion in the shape of the spectrum was ever observed, and the position of the midpoint of the discontinuity and those of the various

structures remained, within experimental errors, unchanged. The detailed description of sample preparation has already been published.<sup>5</sup>

The x-ray beam was provided by a copper tube whose emission spectrum is relatively constant in the energy region of the vanadium *K*-absorption edge. An initial check showed that the overall variation in the incident beam intensity was considerably less than the statistical fluctuation in the intensity of the transmitted beam when the samples were under investigation.

The x-ray tube was activated by an industrial x-ray unit connected in series with a voltage regulator and ripple suppressor. This arrangement provides an output with less than 0.2% ripple at a load of 40 keV and 15 mA. This was the power load used all through the present work.

The transmitted radiation was analyzed using an improved version of a single-crystal, high-angle goniometer. At the studied energy, the overall equipment resolution  $\Delta\lambda/\lambda$  is approximately  $5 \times 10^{-5}$ , and the statistical fluctuations in the recorded data is less than 40 counts/min. This amounts to a standard deviation of less than 1.4% in  $I_0/I$ , where  $I$  and  $I_0$  are the measured intensities with and without the sample in the beam, respectively.

Figure 1 is a plot of the transmitted intensity versus the Bragg's angle; this is the actual raw data taken with a  $\text{VF}_3$  sample. The indicated error bars are purely statistical, and the "white" line and additional structure on the high-energy side of the absorption edge are clearly observed.

Such raw data may readily be converted into graphs of absorption coefficient versus photon energy. But for simplicity  $\ln(I_0/I) = \rho\mu\chi$  was plotted as a function of the energy in the remaining diagrams. For comparison, all data was normalized so that the change in the value of  $\ln(I_0/I)$  across the edge, for all samples studied, is the same. All subsequent measurements were made relative to the data obtained with pure vanadium metal.

In principle, an absorption edge may be fitted with an arctangent curve,<sup>5</sup> and the point of inflection corresponds to the midpoint of the absorption discontinuity, and therefore to the energy position of the edge. However, the structures on the edge proper and in its immediate vicinity make such fitting too cumbersome and frivolous as far as the analysis of the present data is concerned.

To determine the energy position of the midpoint of the discontinuity and of the "white" lines, the absorption spectra of the various compounds were normalized and then unfolded by comparing them with the smooth *K*-absorption spectrum of pure vanadium (Fig. 2). The energy positions of

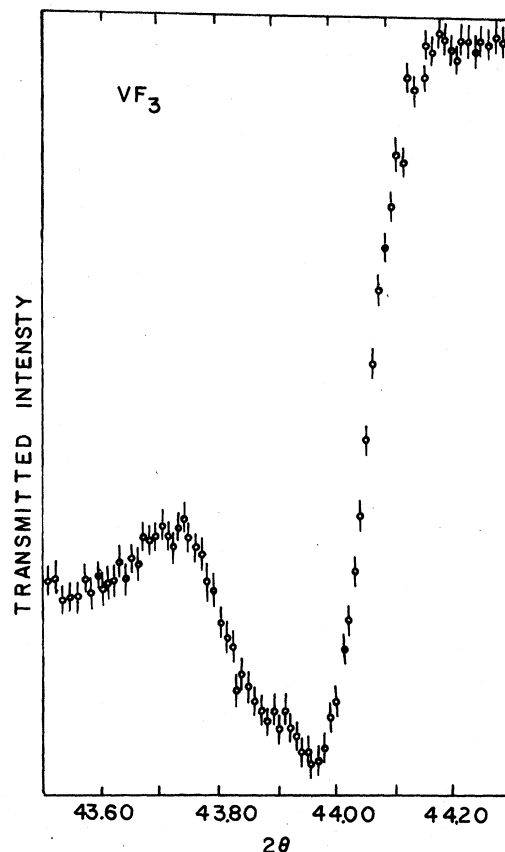


FIG. 1. X-ray intensity transmitted through a sample of  $\text{VF}_3$ , showing fine structure on the high-energy side of the *K*-absorption edge of vanadium. (The error bars are purely statistical.)

the absorption edge and lines were then read directly from the unfolded curves.

All the studied spectra are shown in Fig. 3 for the vanadium oxides and in Fig. 4 for other vana-

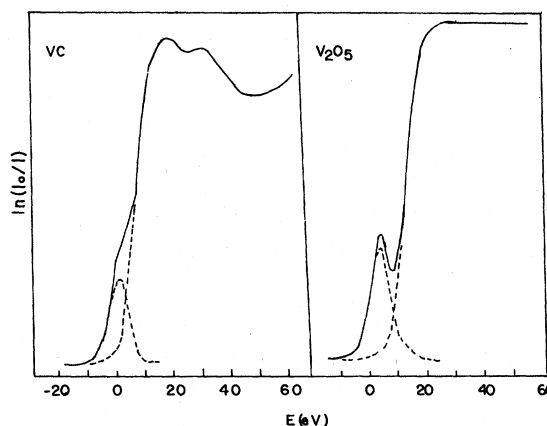


FIG. 2. Absorption spectra of VC and  $\text{V}_2\text{O}_5$  (solid curves) are unfolded into smooth edges and "white" lines (dashed curves).

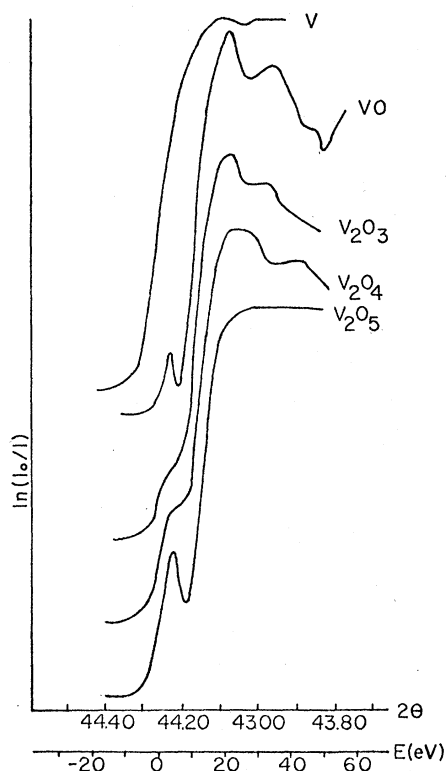


FIG. 3. Absorption spectra of a vanadium from the indicated vanadium oxides. They were obtained by drawing smooth curves through the experimental points.

dium compounds. The average measured chemical energy shifts of the different compounds of vanadium and the energy separation between the absorption edge and the major structures are listed in Table I.

#### CHEMICAL ENERGY SHIFT

When an atom enters into a chemical compound, a change in the charge distribution of its valence band takes place. This change primarily governs the observed energy shift of the *K*-absorption edge of the element.<sup>6,7</sup> The effective potential on the atom thus produced is related in varying degrees to all the electronic levels of that atom, resulting in an energy shift of both the absorption and the emission spectra.<sup>17</sup> Thus the value of the energy shift of the absorption edges corresponds to the energy of formation of the effective charge on the absorbing atom and the subsequent change in its screening factor.<sup>18</sup> The detailed electronic configuration of the valence band and the relaxation effect also contribute to the magnitude of the energy shift of the absorption edges.<sup>8</sup>

For a given bond in a compound, the average energy gap over all the bands  $E_g^\mu$ , may be written

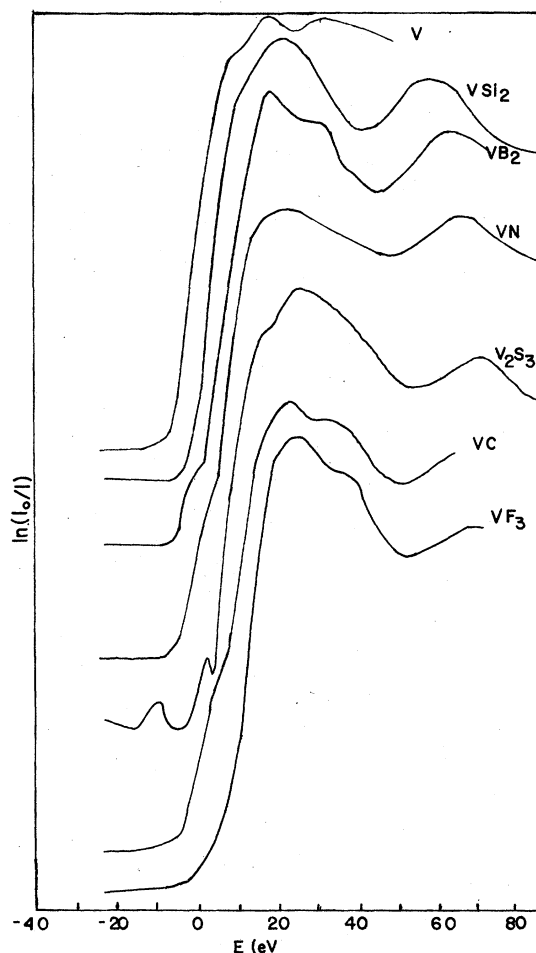


FIG. 4. Absorption spectra of vanadium from the indicated vanadium compounds. They were obtained by drawing smooth curves through the experimental points.

in terms of a homopolar part  $E_h^\mu$  and a heteropolar part ( $C^\mu$ ), thus<sup>19</sup>

$$(E_g^\mu)^2 = (E_h^\mu)^2 + (C^\mu)^2. \quad (1)$$

These quantities are related to the fractional ionicity  $f_i$  and to the fractional covalency  $f_c$  of a given bond as follows:

$$f_i = (C^\mu/E_g^\mu)^2, \quad f_c = (E_h^\mu/E_g^\mu)^2. \quad (2)$$

For a given element, the chemical energy shift of an absorption edge increases linearly<sup>7</sup> with  $E_g^\mu$ ,  $C^\mu$ , and  $f_i$ . Accordingly, assuming a constant ionic radius, the energy shift should vary linearly with the effective charge on the atom. This seems to be the case when the measured energy shifts for VC, VO, and VF<sub>3</sub> are compared with the effective charge on V calculated on the basis of molecular-orbital (MO) theory (Table II). But the energy shift with VN falls considerably below

TABLE I. Chemical energy shift of the *K*-absorption edge, and the position of the "white" line and that of the first peak above the edge of the indicated vanadium compound.

Chemical compounds	Energy shifts of <i>K</i> -absorption edge (eV)		Separation between the "white" line and the edge (eV)	Separation between the first peak above the edge and the edge (eV)
	Present work	Previous measurements		
V	0	0	...	19.11
VB <sub>2</sub>	6.82 ± 0.42	...	8.47	13.29
VC	9.38 ± 0.47	...	5.29	12.35
VN	7.06 ± 0.30	...	4.70	10.50
VO	11.28 ± 0.59	7.5 <sup>a</sup>	8.00	9.06
V <sub>2</sub> O <sub>3</sub>	10.75 ± 0.40	9.7 <sup>a</sup> , 14.1 <sup>b</sup>	7.65	11.18
V <sub>2</sub> O <sub>4</sub>	12.41 ± 0.47	10.1 <sup>a</sup>	7.54	11.87
V <sub>2</sub> O <sub>5</sub>	12.75 ± 0.28	15.5 <sup>a</sup> , 17.0 <sup>b</sup>	7.29	...
VF <sub>3</sub>	12.61 ± 0.35	...	...	9.32
V <sub>2</sub> S <sub>3</sub>	7.35 ± 0.30	7.7 <sup>a</sup>	5.29	22.94
VSi <sub>2</sub>	3.82 ± 0.30	...	...	22.06

<sup>a</sup> S. B. Hendricks and R. W. G. Wyckoff, *J. Phy. Chem.* **31**, 703 (1927).

<sup>b</sup> V. H. Sanner, Ph. D. thesis (University of Uppsala, 1941) (unpublished).

the straight line. It would be interesting if such calculations were performed on additional vanadium compounds.

#### FINE STRUCTURE

Recently, the physical mechanism responsible for the production of the extended x-ray absorption fine structure (EXAFS) received a great deal of attention. To a large extent, this was generated by the fact that the EXAFS could be a valuable tool for determining complicated crystal and amorphous structures.<sup>20</sup> Apparently, at different energies from the *K*-absorption edge, different mechanisms of EXAFS production pre-

vail.

For energies that extend more than 200 eV above the edge, the EXAFS is primarily due to the crystal structure or the amorphous structure that surrounds the absorbing atom.<sup>16</sup> In this high-energy region, theoretical results and experimental data from Cu and Ge samples seem to agree rather well.<sup>21</sup> For vanadium no such calculation is available.

For the region between 50 and 200 eV above the *K*-absorption edge, the multiple-scattering effect becomes important.<sup>22</sup> Calculations of this type are performed by constructing a scattering matrix for each atomic layer and then adding up all possible propagation from layer to layer.<sup>23</sup> But the

TABLE II. Electron configurations and effective charge of the metal ions in the indicated compounds.

Chemical compounds	Electron configuration of the metal ion <sup>a</sup>	Effective charge on the ion calculated on the basis of MO theory <sup>a</sup>	Energy shift of <i>K</i> -absorption edge (eV)
VC	3d <sup>4.05</sup> 4s <sup>0.1979</sup> 4p <sup>0.3508</sup>	0.394	9.38 ± 0.47
VN	3d <sup>3.9139</sup> 4s <sup>0.2134</sup> 4p <sup>0.3278</sup>	0.544	7.06 ± 0.30
VO	3d <sup>3.9684</sup> 4s <sup>0.1542</sup> 4p <sup>0.2189</sup>	0.660	11.28 ± 0.59
VF <sub>3</sub>	3d <sup>3.77</sup> 4s <sup>0.2134</sup> 4p <sup>0.3278</sup>	1.02	12.61 ± 0.35
MnCl <sub>2</sub>	3d <sup>6.03</sup> 4s <sup>0.24</sup> 4p <sup>0.36</sup>	0.37	5.84 ± 0.52 <sup>b</sup>
MnF <sub>2</sub>	3d <sup>5.89</sup> 4s <sup>0.10</sup> 4p <sup>0.16</sup>	0.85	7.57 ± 0.52 <sup>b</sup>
FeCl <sub>2</sub>	3d <sup>7.01</sup> 4s <sup>0.27</sup> 4p <sup>0.38</sup>	0.34	7.57 ± 0.24 <sup>b</sup>
FeCl <sub>3</sub>	3d <sup>6.92</sup> 4s <sup>0.27</sup> 4p <sup>0.42</sup>	0.39	9.97 ± 0.24 <sup>b</sup>

<sup>a</sup> Calculation based on the {Mulliken-Wolfsberg-Helmholz} method with self-consistency on charges and configurations. VC, VN, and VO were obtained by Gubanov *et al.* (Ref. 26). The rest were obtained by Basch *et al.* (Ref. 28).

<sup>b</sup> From Ref. 5.

main features of the EXAFS oscillations  $\chi(k)$  are due to back scattering from atoms that surrounds the absorbing atom,<sup>21</sup>

$$\chi(k) = \sum_j 2|\bar{Z}_j| \cos(2kr_j + \bar{\Phi}_j + 2\delta'_1), \quad (3)$$

where  $|\bar{Z}_j|$  is the amplitude of the matrix  $Z$  that contains information needed in the computation of the EXAFS,  $k$  is the photoelectron wave vector,  $r$  is the distance from the absorbing atom,  $\bar{\Phi}$  is the scattered wave, and  $\delta'_1$  is the central phase shift.

The Fourier transform of  $\chi(k)$ ,

$$F(r) = \int \frac{dk}{2\pi} e^{-ikr} \chi(k), \quad (4)$$

does peak at different values of  $r$ , providing information concerning the crystal structure surrounding the absorbing atom.

The structure within 50 eV above the absorption edge is governed by the characteristics and density distributions of the empty states just above the Fermi level,<sup>15,24</sup> and by the perturbation of these states generated by the core hole created in the absorbing atom.<sup>20,12</sup> Also, the angular momentum of these final states seems to have a significant effect on the shape of the absorption spectrum in this energy range.<sup>25</sup> These effects do interfere to generate the observed structure, and a thorough understanding of this phenomenon should incorporate all of these effects in a proper way. So far, the most successful approach is based on our understanding of the molecular orbital theory.<sup>13,26</sup>

The MO theory does satisfactorily account for the fine structure just above the absorption edge and just below it, and may be invoked to qualitatively explain the chemical energy shift of the absorption edge. When a vanadium atom enters into a chemical compound, its  $4p$  level interacting with the ligands  $2p$  orbitals splits into bonding and antibonding states<sup>27</sup> (Fig. 5). The electronic transition from the vanadium  $1s$  state to the  $4t_{1u}^*$  antibonding state gives rise to the large peak just above the  $K$ -absorption edge. The structure observed within this peak may be attributed to additional fine splitting of the antibonding state.

Higher oxidation states of vanadium result in stronger splitting of the  $4p$  state and raise the energy of the  $4t_{1u}^*$  level, thus qualitatively explaining the observed increase in the energy separation between the absorption edge and this peak as one goes from VO to  $V_2O_4$ , (Table I). All these oxides are crystals with good octahedral symmetry. The lack of such symmetry in the structure of  $V_2O_5$  explains the smoothness of its

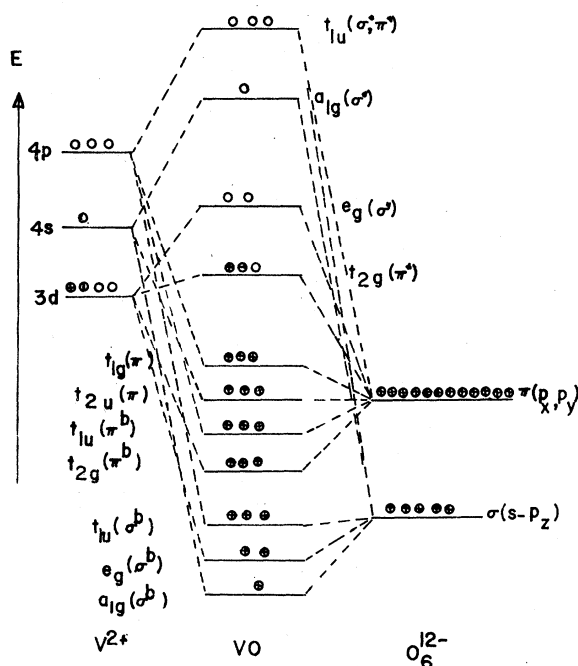


FIG. 5. MO levels of VO (from Ref. 27).

absorption spectrum above the  $K$ -absorption edge. As a matter of fact, the coordination number of  $V_2O_5$  appears to be closer to 5 rather than to 6.

The structure observed at or just below the low-energy side of the  $K$ -absorption edge may also be explained on the basis of the MO theory: sharp "white" lines have been reported below the  $K$ -absorption edges of some half a dozen compounds.<sup>5</sup> Although they are well resolved in the case of VO,  $V_2O_5$ , and  $V_2S_3$  their presence is easily detectable in all the vanadium oxides and in  $VB_2$  and VC. These "white" lines indicate that an empty or partially empty state, having a  $p$  character, exists below the continuum in these compounds.

Here the  $3d$  level of vanadium interacts with the ligands  $2p$  orbitals and splits into a  $2t_{2g}^*$  and a  $3e_g^*$  molecular level.<sup>28</sup> A transition from the  $1s$  state of vanadium to the  $2t_{2g}^*$  antibonding state, which lies below the continuum, gives rise to the "white" line observed at the low-energy side of the  $K$ -absorption edge. The measured separation between these "white" lines and the midpoint of the  $K$ -absorption edge decreases as the oxidation state increases from VO to  $V_2O_5$  (Table I). An increase in the degree of oxidation results in stronger interactions between the  $3d$  level of vanadium and the  $2p$  level of the ligands, and increases the energy level of the  $2t_{2g}^*$  state, bringing it closer to the continuum—hence the systematic decrease in energy separation between the "white"

lines and the absorption edges.

The intensity of these "white" lines is observed to increase from VO to  $V_2O_5$ . This is proportional to the number of vacancies in the  $2t_{2g}^*$  levels of these molecules: for VO the  $2t_{2g}^*$  level contains three electrons, for  $V_2O_3$  it has two electrons, and in  $V_2O_4$  it has only one; it is completely empty in the case of  $V_2O_5$ . Thus the transition probability for the  $1s$  to the  $2t_{2g}^*$  state increases with the availability of the vacancies in the  $2t_{2g}^*$ . A similar systematic change in the intensity of these "white" lines was observed in some compounds of manganese, and it was found to correspond to the number of vacancies in electronic levels below the continuum.

#### CONCLUSION

In this work the chemical energy shifts the K-absorption edge of some vanadium compounds were measured, and an attempt was made to interpret the results by pointing out that a correlation between the magnitude of the shift and the effective charge on the absorbing ion does exist.

The effective charge was calculated on the basis of the MO theory.

Second, an attempt was also made to interpret the observed fine structure in the vicinity of the edge on the basis of MO theory. The position and the relative intensity of the "white" lines on the low-energy side of the discontinuities are in qualitative agreement with the predictions of the MO theory, and only slight refinement may be needed to attain acceptable quantitative agreement. For the structure on the high-energy side of the edge, although reasonable agreement between theory and observations exists, one may have to consider additional contributing effects. It is of great interest that no such structure was observed with  $V_2O_5$ , which lacks the octahedral symmetry of the other studied crystals.

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