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CHEMICAL EFFECT ON X-RAY K-ABSORPTION EDGES OF MANGANESE, CHROMIUM, AND VANADIUM

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The narrow absorption peak appearing on the lower energy side of the K-absorption edges of manganese, chromium, and vanadium in the form of oxides has been specially investigated. The appearance of this peak depends on the oxidation number of metal atoms, rather than on their coordination number.

A narrow, sharp absorption peak appears on the lower energy side of the K-absorption edge when a transition metal atom forms a certain kind of chemical bond. A large number of research workers have observed this phenomenon and have attempted to explain the origin by applying an atomic orbital model, a molecular orbital model, or the Pauling valence-bond theory.

Most of the works in terms of the atomic orbital model endeavor to assign this peak to the 1s-3d transition, assuming that a relaxation of selection rules occurs due to hybridization of the 3d orbital 1, 2) or to asymmetric arrangement of the oxygen atoms.3) Nakamori and Tustumi showed the presence of a shoulder at roughly the same energy position as the peak in question in the case of MnP, and assigned it to the transition of the 1s electron to the empty d bands (related to the e$_g$ orbitals containing some s and p character).4) As for research using the molecular orbital model, it was reported that both low-energy peaks in the Na_2CrO_4 and $KCrO_3Cl$ spectra are attributed to 1s-3t$_2$5) according to the MO energy level diagrams for $(CrO_4)^{2-}$ shown by Wolfsberg and Helmholz.6) Fischer reported that the peak in the case of Na_3VO_4 corresponds to the transition of a 1s electron to 4t$_2$,7) which is based on the model shown by Ballhausen and Gray8) for tetrahedral transition metal complexes. He further cited the appearance of this absorption peak in the case of octahedral symmetry and assigned it to 1s-3e$_g$ and 1s-2t$_{2g}$.9) He stated that these transitions are forbidden but are possibly rendered observable because of crystallographic distortion.7)

On the other hand, the Pauling valence-bond theory traces the appearance of this peak to the 1s-4p (or 5p) transition.1, 10) According to this theory, the absence or presence of this peak depends upon whether or not the p orbital is occupied. The peak does not appear when a metal atom forms hybridization such as sp^3 or d^2 sp^3 and the 4p (or 5p) orbital is occupied, whereas the peak appears when the valence bond such as dsp^2 and sd^3 is formed; hence, the 4p (or 5p) orbital is partially or totally empty. Best discussed the sharp low-energy peaks in absorption spectra of transition atoms in $Na_3VO_4{}^{2-}$, and MnO_4^- in terms of a molecular orbital model. He mentioned that the peaks are due to the transition of 1s to an MO consisting largely of 4p metal wave function,[11)] and supported the results obtained by the Pauling valence-bond theory.

Van Nordstrand conducted a large number of measurements of the K-absorption edge, and after classification of the patterns observed, he stated that the sharp absorption peak appearing on the lower energy side is characteristic of tetrahedrally coordinated atoms.[12)]

On the basis of these two theories, namely the Pauling valance-bond theory and Van Nordstrand's empirical classification, the coordination number of transition metal atoms in their compounds has hitherto been determined depending on whether or not the peak in question appears.[13, 14)]

In recent years, however, White and McKinstry conducted measurements of the K-absorption edge on oxides of a series of transition metals, and unambiguously observed the low-energy peak in V_2O_5[15)] in which the vanadium atom is enclosed in a trigonal bipyramid of five atoms.[16)] Glen and Dodd also obtained similar results.[3)] If these experimental findings and discussions based on the atomic orbital model or the molecular orbital model mentioned above are considered collectively, the indiscriminate use of this sharp peak for determining the coordination number seems to present problems.

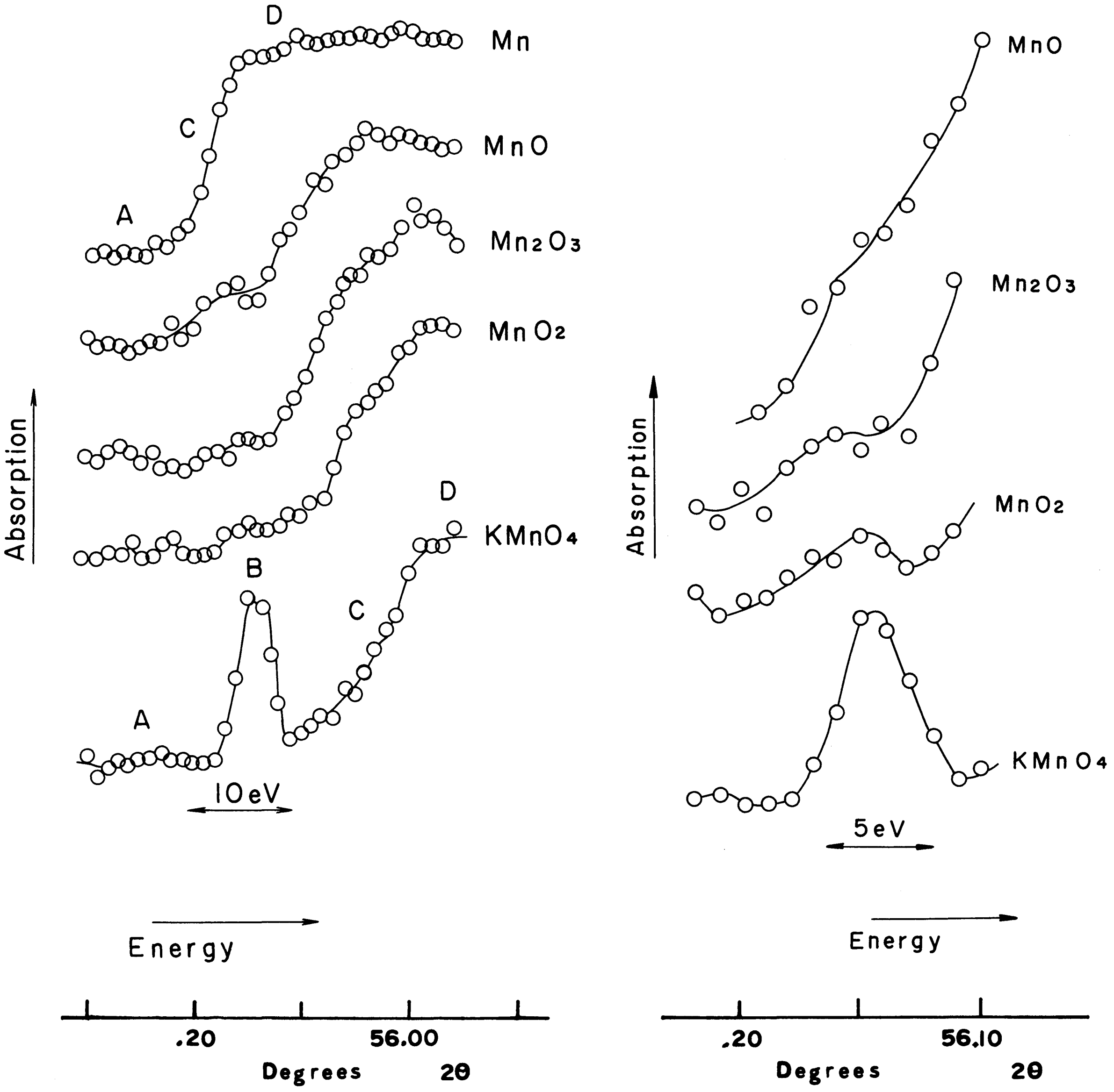
Having therefore felt a need for further studies on this sharp peak, we investigated the behavior of peaks appearing on the lower energy side of the K-absorption edges of Mn, Cr, and V in various oxides.

A commercial X-ray diffractometer was employed in all measurements, using a fine-focus Cu-target X-ray tube and the cleavage (200) planes of LiF as a monochromator. Counts for a preset time of 400 sec were taken automatically at regular intervals of 0.005° of arc in the Bragg angle. Detailed descriptions of the experimental procedure will be published elsewhere.

The K-absorption spectra obtained are shown in Figs. 1~3. The initial measurements for manganese (Fig. 1-a) showed the absorption peak B in question only in $KMnO_4$. However, other oxides of manganese also revealed something like a peak at the same energy position. Hence, this portion was further scanned several times and the mean values were plotted. As a result, MnO_2 showed a peak while Mn_2O_3 revealed a shoulder as shown in Fig. 1-b. The manganese atom in $KMnO_4$ is tetrahedrally coordinated, whereas MnO_2 and Mn_2O_3 are of the SnO_2 and Tl_2O_3 type respectively, and are both octahedrally coordinated with six oxygen atoms.[17)] Similarly, vanadium not in the tetrahedrally coordinated state also shows this absorption peak B. As mentioned above, V_2O_5 has the configuration of a trigonal bipyramid, and $V_2O_{4.34}$ also shows a peak while the V forms and octahedron VO_6.[16)] CrO_3 is known to form a crystal with a distorted tetrahedron of CrO_4.[17)] The coordination number of Cr is not yet known for Cr_3O_8 and Cr_2O_5.

It has thus been demonstrated that, in the above-mentioned cases, the narrow, sharp peak is not necessarily characteristic of tetrahedrally coordinated metal atoms.

A closer examination of this absorption peak B reveals that the peak height



(a) (b)

Fig.1. K-absorption spectra for manganese metal and oxides.

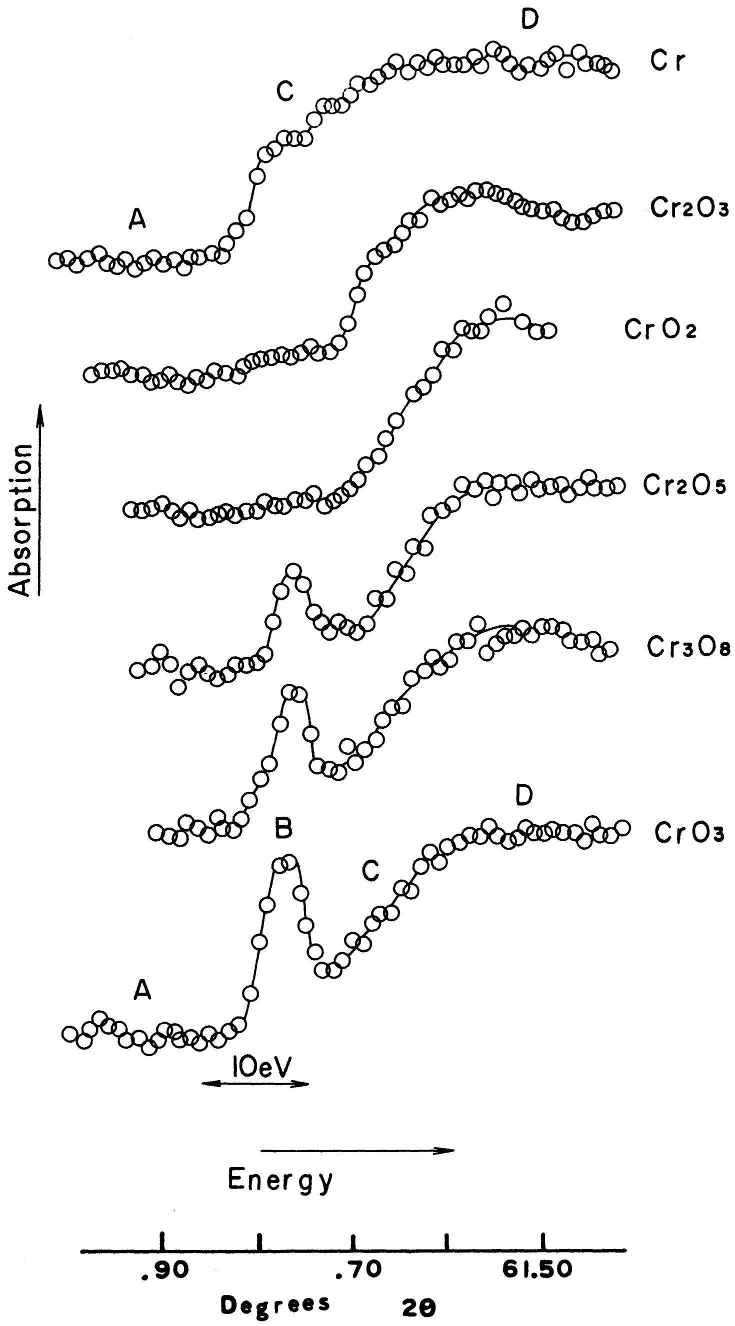


Fig.2. K-absorption spectra for chromium metal and oxides.

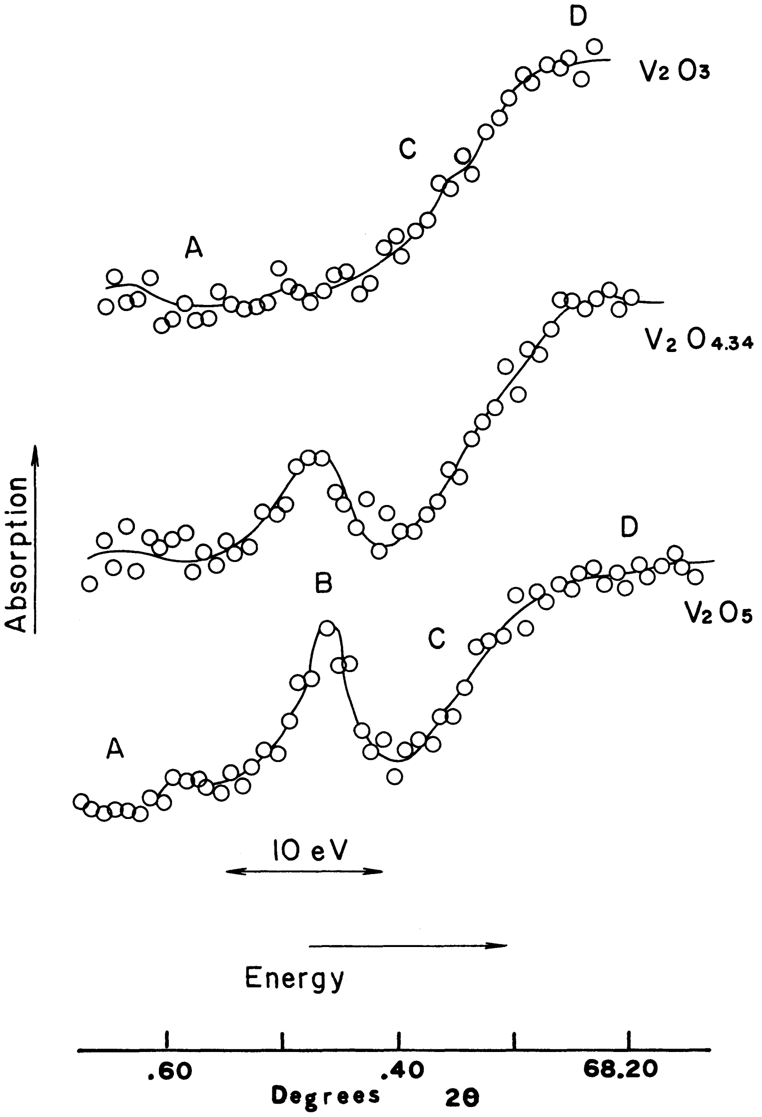


Fig.3 K-absorption spectra for vanadium oxides.

increases as the oxidation number increases. (Each figure is a standardized drawing, so that the space between A and D becomes constant.) It is apparent from the figures that the slope C shifts towards the higher energy side, rises steeply, and reduces tailing as the oxidation number of the metal atom increases. This contributes to a better separation of peak B and slope C, and coupled with the fact that the height of peak B increases with raising the oxidation number, assists in increasingly easier observation of the peak.

In the light of the above observation, it should be stated that the peak in question in the case of the oxides of manganese, chromium, and vanadium, rather than depending on the coordination number, apparently appears gradually as the oxidation number increases. Consequently, the oxidation state of the metal atom, in addition to the molecular or crystal symmetry reported so far,[3, 5, 7, 9~12] should be considered, in discussing the origin of the low-energy peak in K-absorption spectra of Mn, Cr, and V in oxides.

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