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Determination of metal atom positions in $CrVO_4$ by X-ray absorption spectroscopy.

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A feature in the X-ray absorption fine structure, characteristic of metal atoms tetrahedrally coordinated by oxygen in anions, is used to determine that in $CrVO_4$ the V atom is in the anion.

The metal atom positions in the compound $CrVO_4$ (sometimes written $VCrO_4$) have been in doubt because V and Cr have nearly the same X-ray scattering power. Brandt (1943) determined that the metal atom in the anion is surrounded tetrahedrally by oxygen atoms while the other metal atom is in octahedral coordination. The formula, $CrVO_4$, was deduced from consideration of ionic radii; however, Wells (1962) suggested that this reasoning may be incorrect since the degree of ionic or covalent character of the chemical bonds was ignored and bonds of intermediate type probably occur in $CrVO_4$. Wyckoff (1965) uses the compound as a structure type (written as $VCrO_4$) and cites only the paper by Brandt (1943).

Many authors have noted a low energy X-ray absorption maximum characteristic of metal atoms tetrahedrally coordinated by oxygen in anions as in VO_4^{3-}, CrO_4^{2-}, MnO_4^-. Recently Best (1966) reported X-ray absorption and emission data for these anions and used a molecular orbital treatment to assign spectral features to specific atomic or molecular electronic transitions. The easily identified X-ray *K*-edge absorption feature is used herein to determine experimentally the position of the metal atoms in $CrVO_4$.

$NiCrO_4$ and Na_3VO_4, in which the atomic positions are known, were chosen as reference compounds which would produce chromate and vanadate X-ray absorption spectra and were obtained from Alfa Inorganics, Beverly, Massachusetts. $CrVO_4$ was prepared as suggested by Brandt (1943) by heating together Cr_2O_3 and V_2O_5 at 750°C for 24 hours. All compounds were positively identified by their X-ray diffraction powder patterns. A second sample of $CrVO_4$ (labeled $VCrO_4$ when received) was obtained from K and K laboratories, Hollywood, California and found to be amorphous when examined by X-ray diffraction but had X-ray absorption fine structure identical with that produced above. Thin, uniform absorption specimens were prepared by grinding to a fine powder and casting in plastic cement. The X-ray spectrometer and experimental procedure have been described by Lytle (1965).

The experimental X-ray absorption fine structure curves are plotted in Fig. 1. From top to bottom the absorption curves refer to the *K*-absorption edges of Cr in $NiCrO_4$, Cr in $CrVO_4$, V in $CrVO_4$, and V in Na_3VO_4. The absorption feature which identifies the metal atom as being in anionic tetrahedral coordination is the first small peak in the absorption edge and is labeled *a* in each place it occurs. Since the peak *a* occurs for V and not for Cr in $CrVO_4$, I conclude the vanadium ion is tetrahedrally coordinated.

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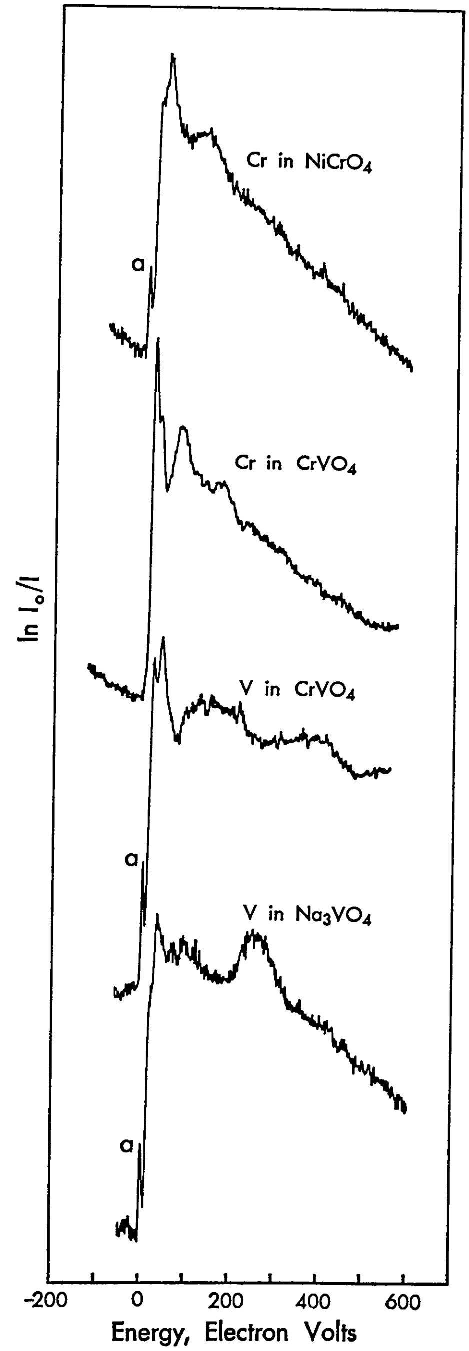

Fig. 1. X-ray absorption fine structure in chromates and vanadates where I_0 is the X-ray intensity of the incident X-ray beam and I the intensity after passing through the absorber. The energy scale is approximately the energy of the ejected photoelectron with zero energy customarily placed at the first inflection point of the absorption edge.