Acta Cryst. (1970). A**26**, 71

Determination of the Coordination Number of Yttrium in $YCrO_4$ by X-ray Spectroscopy*

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(*Received* 7 *August* 1969 *and in revised form* 9 *February* 1970)

The X-ray *K*-absorption edge of yttrium in $YCrO_4$ and YVO_4 has been investigated using a bent-crystal X-ray spectrograph. The shape of the absorption edge revealed that the yttrium ion in $YCrO_4$ is octahedrally coordinated.

Introduction

X-ray absorption spectroscopy is one of the interesting ways to study the nature of the chemical bond. The position and the fine structure of the X-ray absorption edge are determined by the immediate surroundings of the atom in question. Several investigators have used this structure to derive various solid-state properties such as valence state (Beeman, Forss & Humphry, 1945; Coster & Kiestra, 1948), coordination (Obashi, 1961; Lytle, 1967), bond lengths (Lytle, 1966) and so on. The elements of the first transition series and their compounds have been extensively studied. Recently, we have extended this study to the case of yttrium (Bhide & Bhat, 1968; Bhide & Bhat, 1969), the first member of the second transition series. The present paper describes further results regarding the shape of the *K*-absorption discontinuity of yttrium in yttrium orthovanadate and yttrium orthochromate.

Van Nordstrand (1960; 1967) has recently reported a large number of *K*-absorption curves of transition metal ions in different types of compounds. According to him these curves can be classified into four distinct categories (actually six). Of these, type IV curves, representing tetrahedrally surrounded ions, alone show splitting in the principal *K*-absorption edge. Such a splitting is known to be due to the ligand field and the nature of the bonding orbitals. Mitchell & Beeman (1952) have discussed Cr, Mn, Fe and Ni complexes and have shown that the low-energy absorption (at '*a*', Fig. 1) is determined by the coordination in question. Their expectation of low energy absorption for planar and tetrahedral complexes, involving at least some sd^3 bonding from the orbital assignments, has been confirmed by some experimental results. On this basis, no low-energy absorption line is expected for octahedral complexes.

Experimental

A 400 mm bent-crystal transmission spectrograph using a mica crystal oriented to reflect from (100) planes was employed for recording the absorption spectra. The dispersion of the spectrograph was about 12·5 x.u./mm. The yttrium *K*-absorption edge was photographed in the second order where it could be bracketed between the first order Cu $K\alpha_1$ and Cu $K\beta_1$ lines. Other experimental details have been described earlier (Bhide & Bhat, 1968). The spectrograms were microphotometered by a Hilger and Watts microphotometer coupled with a Honeywell strip chart recorder.

Yttrium orthovanadate was prepared by heating a mixture of Y_2O_3 and V_2O_5 in stoichiometric proportions in a tungsten crucible. The sample was heated for about 5 hours at 900 °C, and then cooled slowly. The sample was examined by X-ray diffraction methods, using Cr $K\alpha_1$ radiation and a Debye–Scherrer camera 11·4 cm in diameter. The observed values of interplanar spacings were found to be in agreement with the data of Milligan, Watt & Rachford (1949). The intensity ratios of the corresponding diffraction lines were determined visually. Yttrium orthovanadate is white in body colour and crystallizes in the tetragonal system with the zircon structure (Wyckoff, 1963).

Yttrium orthochromate, $YCrO_4$, is greenish in body colour and little information is available about its structure. Our sample was obtained from Bhabha Atomic Research Center, Trombay, Bombay. Yttrium oxide was mixed with ammonium chromate such that equimolar quantities of Y and Cr were present (Nigam, 1969). The samples were annealed at 800° for 5 hours. A detailed X-ray diffraction analysis is in progress in this laboratory.

However, our preliminary studies showed that the phase is indeed $YCrO_4$. None of the lines on a powder photograph corresponds to the diffraction data for $YCrO_3$ as described in ASTM diffraction data cards, thus showing clearly that the compound studied did not contain any trace of the obvious contaminant $YCrO_3$ (orthochromite). Further study regarding the crystal structure of $YCrO_4$ will be reported later.

Results and discussion

The experimental X-ray *K*-absorption edges of yttrium in yttrium orthovanadate and yttrium orthochromate are shown in Fig. 1. A recent survey (Bhat, 1968) re-

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* This work was performed in part while the author was working as a Research Fellow at National Physical Laboratory, New Delhi, India.

garding the shape of the *K*-absorption edge of yttrium in a number of complexes has clearly indicated that the classification pointed out by Van Nordstrand (1960, 1967) does hold good even in the case of yttrium compounds. The two curves closely resemble type IV and type I curves of Van Nordstrand respectively. (It should be pointed out that the curves given by Van Nordstrand are absorption coefficient *versus* energy curves, whereas our curves show the variation of transmitted intensity with energy). The curve for YVO_4 shows the splitting of the principal absorption edge into two components and the appearance of peak '*a*'. Such a low-energy absorption line '*a*' is to be expected for YVO_4 as it is known to crystallize in the zircon structure (Wyckoff, 1963) with yttrium ions being surrounded by oxygen tetrahedra. However, the coordinations of the metal atoms, yttrium and chromium, in $YCrO_4$ are not exactly known. The absorption spectrum of $YCrO_4$ does not have the low energy absorption line '*a*', indicating that the yttrium ion in this compound is not tetrahedrally coordinated. This conclusion is further supported by the fact that the fine structure appearing on the high-energy side of the yttrium *K*-absorption edge of $YCrO_4$ has broad maxima in contrast to sharper ones in that of YVO_4. The appearance of broader maxima is a characteristic feature of octahedral coordination. Moreover, the comparison of the absorption spectrum of $YCrO_4$ with that of Y_2O_3 shows that there is a great resemblance between the two (Fig. 1) and that the yttrium ion in $YCrO_4$ may be coordinated like that in Y_2O_3 (Wyckoff, 1963), that is, octahedrally. Thus it is concluded that yttrium metal ion in $YCrO_4$ is octahedrally coordinated by oxygen.

The hybridization in YVO_4 is largely sd^3 (π bonding) and hence the 5*p* orbitals are empty and localized, giving rise to the appearance of absorption line '*a*'. In the case of $YCrO_4$ the bonding is presumably d^2sp^3, since the yttrium ion has octahedral coordination, and thus the 5*p* orbitals are full and non-localized. Thus the absence of low-energy absorption line '*a*' is explained.

The author expresses his sincere thanks to Professor V. G. Bhide for helpful discussions and valuable suggestions during the course of this work. He is very much indebted to Dr A. N. Nigam for supplying the compounds studied here. Thanks are also due to Professor M. R. Padhye for his help and encouragement.

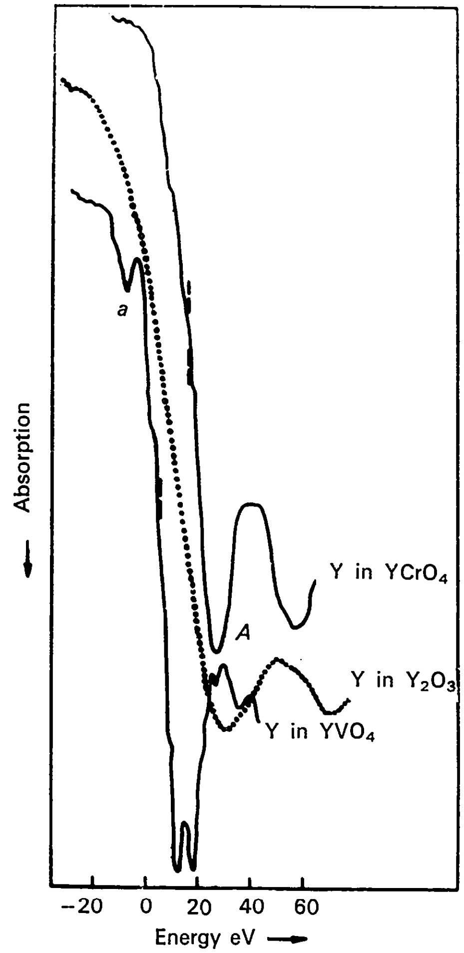

Fig. 1. The fine structure of X-ray *K*-absorption edge of yttrium in $YCrO_4$, YVO_4 and Y_2O_3. Zero energy is chosen at the main edge of pure yttrium metal.

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