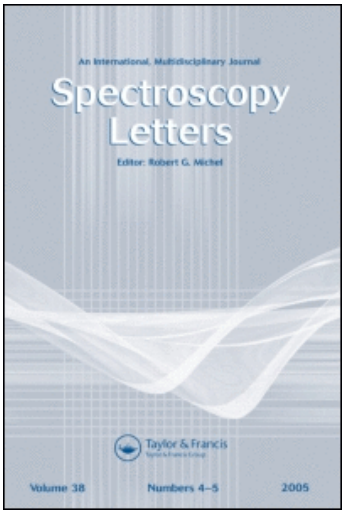

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An XPS Investigation of the Influence of Some Lanthanide Ions on the Bond Strength in $LnVO_4$ Compounds

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AN XPS INVESTIGATION OF THE INFLUENCE OF SOME LANTHANIDE IONS ON THE BOND STRENGTH IN $LnVO_4$ COMPOUNDS.

KEY WORDS : LANTHANIDE, BOND STRENGTH, ORTHOVANADATE

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ABSTRACT

The degree of covalency or thus bond strength between the vanadium and lanthanide ions in a series of lanthanide orthovanadates, seem not to be dependent on the lanthanide(III) ion sizes. The influence of the electronic properties are the major contributing factor to the bond strengths, as can be seen from the "tetrad" type of relation between the modified Auger parameter (α') and number of 4f electrons (or atomnumber, Z). The electronic properties influencing the bond strengths are due to interelectronic repulsion within the 4f energy levels.

INTRODUCTION

The lanthanide orthovanadates or $LnVO_4$, where Ln represents the series of lanthanide elements, are semiconductors and show interesting magnetic transformations [1,2]. It has been shown that

the zircon phase of these orthovanadates can easily be prepared from the high temperature reaction of the lanthanide oxide and either an alkali metal metavanadate (e.g. KVO_3 or $NaVO_3$) [3] or ammonium metavanadate [4]. Both the infrared and Raman spectra of this phase have been reported in the literature [5] and these can be used for characterization of samples. In this investigation a series of lanthanide orthovanadates ($LnVO_4$) was prepared and the influence of the lanthanide ions on the vanadium - lanthanide bond strength was investigated by means of X-ray photoelectron spectroscopy.

In the well-known lanthanide contraction the sizes of the Ln(III) ions decrease approximately linearly going from Ce(III) to Lu(III)[6]. It can be assumed that the size of the ion as well as the electronic properties of the ions will influence the bond strengths in the $LnVO_4$ compounds. It is the purpose of this study to evaluate the contributions of the ion size and the electronic properties to the vanadium - lanthanide bond strength in the lanthanide orthovanadates.

EXPERIMENTAL

Sample preparation

The zircon phase of $LnVO_4$ (Ln = La, Pr, Nd, Eu, Gd, Ho, Er and Tm) was obtained through the high temperature reaction of the lanthanide oxide with ammonium metavanadate (NH_4VO_3). A temperature of 1223 K was maintained on the stoichiometric mixtures for 12 hours [4]. Samples were identified by means of infra-red and Raman spectroscopy and X-ray powder diffraction patterns [4,5].

XPS Analysis

The X-ray photoelectron spectra were recorded on a VG Scientific ESCALAB Mk.II. Non-monochromated Mg Kα (1253.6 eV) radiation was used from a X-ray gun operated at 15 kV and 20 mA.

Table I : XPS data of the V 2p and V_{LMM} peaks of the prepared lanthanide orthovanadates.

Compound	V $2p_{3/2}$ eV	V $2p_{1/2}$ eV	V_{LMM} eV	α' eV
$LaVO_4$	517.05	524.45	787.75	982.9
$PrVO_4$	516.70	524.25	784.65	985.7
$NdVO_4$	516.50	524.75	786.00	984.1
$EuVO_4$	516.85	524.00	786.20	984.3
$GdVO_4$	517.10	525.70	786.60	984.1
$HoVO_4$	517.25	523.75	786.65	984.2
$ErVO_4$	516.70	523.70	785.80	984.5
$TmVO_4$	516.60	524.40	785.05	985.2

The base pressure was better than 7×10^{-9} mbar in the analyzer. All spectra were recorded using the same spectrometer parameters of 20 eV pass energy and 6 mm slit width. To obtained static-charged corrected values a 5 - 10 Angstrom gold layer was evaporated onto each sample. The Au $4f_{7/2}$ XPS peak at 84.0 eV was used as reference [7,8,9] and charging corrections varied between 1.70 and 7.35 eV.

RESULTS AND DISCUSSION

The binding energy values of some of the XPS and Auger peaks on the spectra of the prepared lanthanide orthovanadates are listed in table I. Figure I represents some of the V $2p_{3/2}$, V $2p_{1/2}$ and O 1s peaks and figure II some of the V_{LMM} Auger peaks.

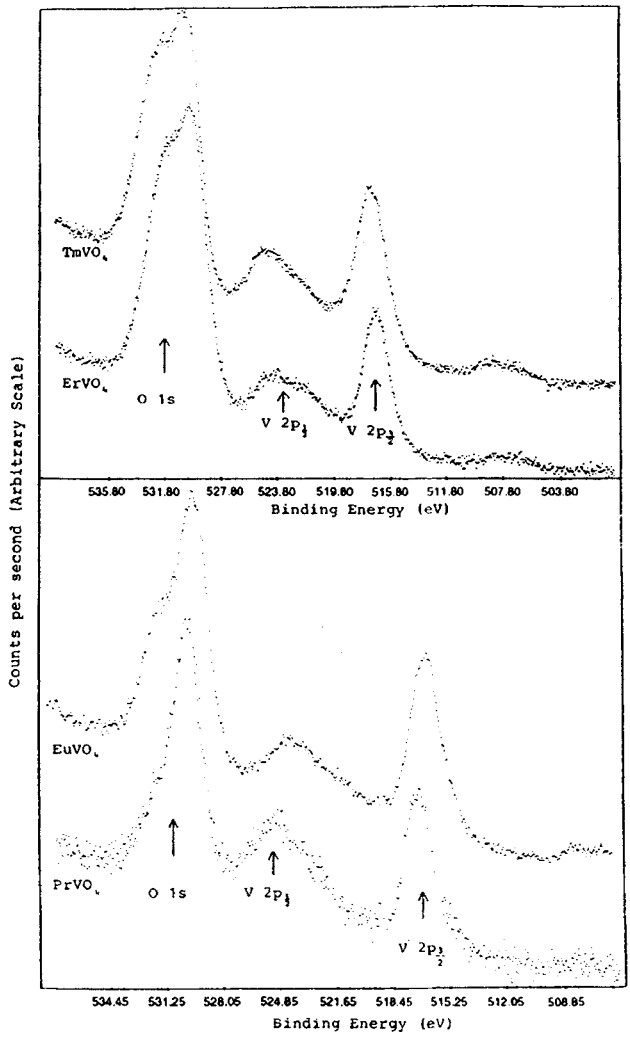

FIG 1 : The $V2p_{3/2}$, $V2p_{1/2}$ and O 1s XPS peaks of some of the lanthanide orthovanadates.

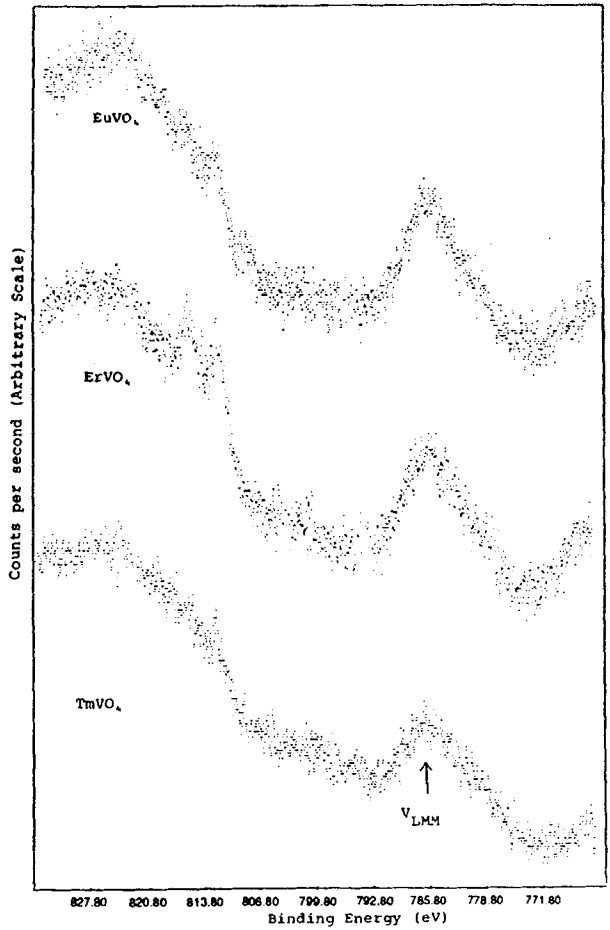

FIG II : The $V_{L3M23M45}$ Auger peaks of some of the lanthanide orthovanadates.

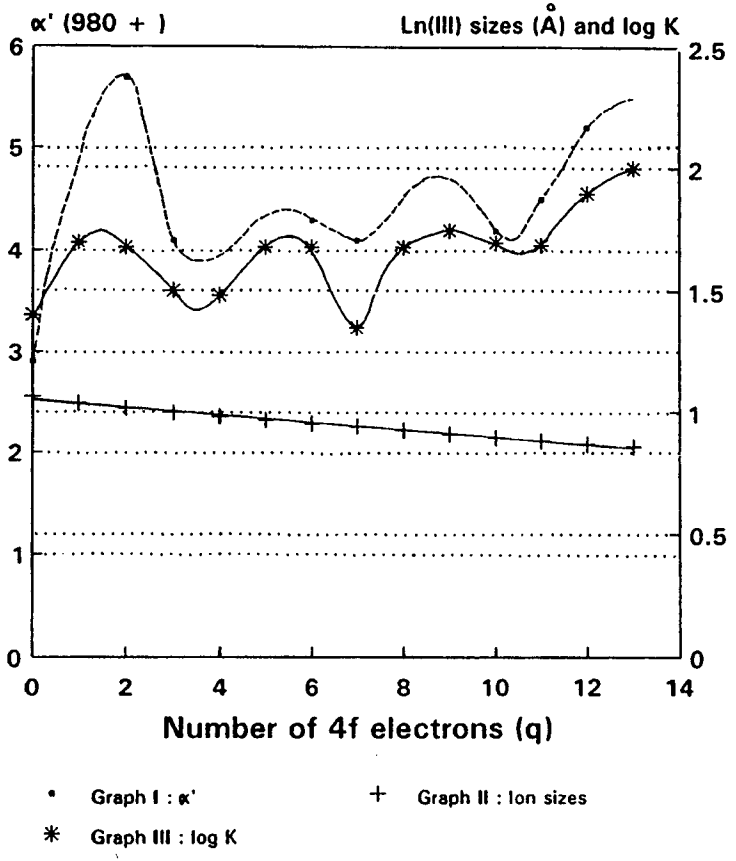

FIG III : The Auger parameter, Ln(III) ion sizes and log K as a function of the number of 4f electrons (q).

The modified Auger parameter

The modified Auger parameter (α') is defined as the sum of the binding energy of the major photoelectron peak ($V\ 2p_{3/2}$) and the kinetic energy of the major Auger peak ($V_{[illegible]}$) [10]. The modified Auger parameter also is independent of the charging on a sample and changes in its value is more pronounced than in the value of

any XPS peak. In the literature broad, but well defined V_{LMM} Auger peaks are reported to appear at 781.4 eV for the metal [11]. In solids the changes in the modified Auger parameter are due principally to changes in the polarization energy [12,13]. The greater the modified Auger parameter within a series of related compounds the more polarizable the compound. In the lanthanide orthovanadate compounds the changes in the V Auger parameters were used to determine the relative covalency of the vanadium - lanthanide bonds, thus also the strength of the V - Ln bonds. Figure III gives the modified Auger parameter versus the number of Ln f electrons (q). From this graph it can be seen that the relation between α' and q is not a simple one.

Also included in figure III is the variation in lanthanide ion size with number of f electrons (or atomnumber - Z). No clear relation between the lanthanide ion size and the modified Auger parameter can be determined from the graph and it thus seems that the ion sizes are not the major factor that contributes to the bond strengths.

The third graph on this figure is a rough approximation of literature values found for the equilibrium distribution of the Ln(III) species between the solution di-2-ethylhexyl-chloromethylphosphonate in benzene and the aqueous solution of 11.4 F LiBr + 0.5 F HBr at 22 ± 2 °C [14]. The equilibrium constant K is the ratio of the concentration of the metal cation in the organic phase to that in the aqueous phase. The variation of log K with q (number of f electrons) follows the so-called tetrad effect. The tetrad effect involves the following hypothesis : " In systems involving the lanthanide(III) ions, the points on a plot of the logarithm of a suitable numerical measure of a given property of these elements vs. Z may be grouped, through the use of four smooth curves without inflections, into four tetrads with the gadolinium point being common to the second and third tetrads and the extended smooth curves intersecting, additionally, in the 60 - 61 and 67 - 68 Z regions."[15,16]

Comparing graph I to graph III similarities are clearly evident, while clearly the sizes of the different lanthanide(III) ions do not seem to influence the modified Auger parameter and thus bond strength to a great extend. The tetrad effect observed in the Z or q dependence of properties of the lanthanide(III) series originates mainly from quantum mechanical interelectronic repulsion energy of the q electrons in each $4f^q$ electronic configuration, as described by Nugent [16]. Discontinuity at the 1/2 point is attributed to the half-filled shell effect in the electronic structure of Gd(III). The discontinuity at 1/2 point is the result of variations in the spin-pairing energy with q, that is one of the terms that influence the value of the inter electronic repulsion energy (H_{ee}). The 1/4 (between Nd(III) and Pm(III)) and 3/4 (between Ho(III) and Er(III)) points with their corresponding 1/4 and 3/4 shell fillings are the result of the further refining of the terms describing the spin-pairing energies as described by Nugent [16].

CONCLUSIONS

The repulsion and spin-pairing energies of the 4f electrons seem to influence the vanadium - lanthanide bond strength to a much greater extend than the lanthanide(III) ion sizes. This results in the so-called tetrad effect that was also observed for a number of other physical and chemical properties concerning the lanthanide(III) series [15,16]. The order of increasing covalency (thus strength) of the vanadium - lanthanide bond as visually represented in figure III graph I, is as follows for the compounds prepared in this study :

$PrVO_4 < TmVO_4 < ErVO_4 < EuVO_4 < HoVO_4 < GdVO_4 < NdVO_4 < LaVO_4$

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