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INVESTIGATION OF SOME STRUCTURAL AND VALENCE PROBLEMS IN THE PRASEODYMIUM OXIDES BY X-RAY ABSORPTION SPECTROSCOPY*

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Summary

The L_{III} and $M_{IV\text{-}V}$ spectra of the fluorite-structure-based praseodymium oxides ($Pr^{3+} \rightarrow Pr^{4+}$) have been studied. These spectra clearly demonstrate the evolution of Pr valence in these oxides. The various spectral features of tetravalent Pr are compared with the corresponding absorption structures of CeO_2. The results indicate that one f electron participates in bond formation in CeO_2 and PrO_2. The present observations reveal the importance of the character of f symmetry states and their admixture with the valence states on Pr_6O_{11} or PrO_2 tetravalent sites.

Introduction

The rare earth oxides RO_x ($R \equiv Ce, Pr, Tb$), ($1.5 \leqslant x \leqslant 2$) are classical examples of non-stoichiometric systems characterised by the existence of several compounds with well defined x. These compounds are difficult to obtain in large amount and some of their physico-chemical properties are not yet well known [1 - 5]. The basic structure of these compounds is the fluorite type (CaF_2). The RO_x ($x = 2$, $R \equiv Ce, Pr, Tb$) is cubic and the rare earth valence is considered to be 4+. On the other side of the system, for $x = 1.5$ the R_2O_3 structure is of the bixbyite type. This corresponds to a fluorite structure in which 1/4 of the anionic sites are vacant. R_7O_{12} ($x = 1.714$) is the only intermediate compound the structure (rhombohedral) of which is reasonably well established. The other compounds in the system are structurally not well identified. The oxygen vacancy order is probably a

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factor which governs the occurrence of different phases. As far as the two cations R^{3+} and R^{4+} are concerned, it seems that there is no structural order among themselves. Thus the RO_x non-stoichiometric oxides are considered to form a variable-valence system.

The electrical transport behaviour in RO_x systems as a function of temperature, oxygen pressure, and x has been extensively studied [6]. From these studies and the available structural information, the behaviour of ionic conductivity in these compounds is understood in terms of hopping mechanism, the ordering of oxygen vacancies, and the concentration of R^{3+} and R^{4+} cations in the basic fluorite lattice. The role of average, $R^{3.5+}$, valence sites is considered to be important in the transport properties. These results suggest that the 4f electrons contribute to electrical conduction in these oxides.

The results of a few experiments on direct probing of the R cation in these systems are now available, however. Recently, the case of insulating and non-magnetic CeO_2 has attracted much interest. The evidence of intermediate valence (I.V.) in the ground state from earlier L_{III} edge [7] and XPS [8] data on CeO_2 led to some controversial opinions, obtained from optical and magnetic measurements, concerning its ground state description [9]. The intermediate valency and the insulating and non-magnetic behaviour were reconciled [10] by considering the presence of 4f electrons and configuration mixing (4f-ligand with $4f^0$ states). By contrast, the recent band structure calculations [11] on CeO_2 and PrO_2 show that there is an appreciable admixture of 4f states in the oxygen 2p band with a band gap of 6 eV for both compounds. These calculations predict a partial covalent bonding. This picture is supported by photoemission and BIS (Bremsstrahlung Isochromat Spectroscopy) experiments [12]. Recently spectroscopic evidence of localised and extended f-symmetry states in CeO_2 has been published [13]. These results definitely exclude a mixed valence in CeO_2 and correspond well with a many-body-states calculation (Gunnarsson–Schonhammer model [14]) taking into account the presence of f-symmetry admixture in the valence band.

The response of the RO_x systems to deeper level probes such as X-ray absorption spectra (XAS) is expected to give information on the character of certain vacant states. It is interesting to investigate the evolution of the character of the 4f-symmetry and the conduction states for well-defined stable phases in the fluorite structure as the oxygen concentration is increased. In this respect the PrO_x system is interesting. In normal trivalent compounds Pr contains two 4f electrons. At the end of the system, for PrO_2, the tetravalent Pr is expected to contain only one 4f electron.

The aim of the present work is to study Pr valency evolution in the fluorite-based structure in the PrO_x system. A comparative study of these Pr compounds by the two absorption probes (2p and 3d) is motivated by the fact that they give information on the sd symmetry and the 4f vacant states. In this way we have studied the $2p \rightarrow 5d$ (L_{III} edge) and $3d \rightarrow 4f$ ($M_{IV,V}$ edges) XAS of Pr in:

(i) trivalent compounds A-(hexagonal), C-(cubic) Pr_2O_3 and Pr oxalate;
(ii) intermediate oxides such as Pr_6O_{11} ($Pr_{12}O_{22}$ or $PrO_{1.833}$);
(iii) tetravalent oxides such as PrO_2.

Experimental details

The starting compound for the preparation of the various oxides was 99.9%-pure, commercial (Rhone Progil S.A.) Pr_6O_{11}. The cubic Pr_2O_3 was obtained by reducing Pr_6O_{11} in a current of pure hydrogen at 520 °C for 10 h. The hexagonal form was obtained by similar reduction at 920 °C for the same time. The Pr_6O_{11}, free from carbonate, was prepared by calcination of the commercial Pr_6O_{11} in an electric furnace at 1100 °C for 18 h. The PrO_2 was obtained by continuous agitation of a suspension of pure Pr_6O_{11} in a 5% solution of acetic acid for 8 days. The final product was filtered and dried.

The Pr oxalate was prepared by precipitation using pure oxalic acid and a solution of Pr hydrochloride.

The purity of all the compounds thus prepared was checked by X-ray diffraction diagrams.

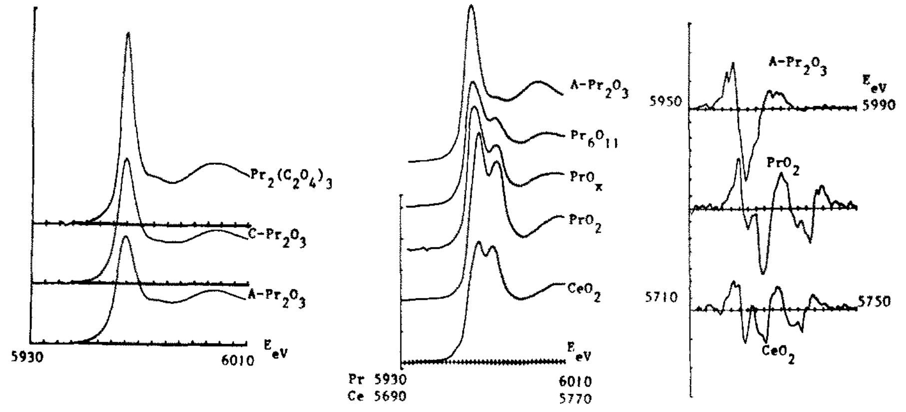
The L_{III} absorption measurements were performed at DCI, LURE, Orsay, which provides X-radiation emitted by 1.72 GeV electrons in the storage ring. A silicon double monochromator (311) with a band pass of 2 eV was used to measure the absorption of the sample powder under atmospheric pressure. The 3d spectra were obtained at ACO, LURE by using the radiation emitted by 537 MeV electrons in the storage ring. A beryl double-crystal monochromator [15] was used to obtain the yield spectra [16] from sample powder spread over an aluminum plate. The overall resolution in this case was about 0.4 eV. The yield measurements were carried out under a vacuum of the order of 10 - 5 Pa.

Results

The results of absorption measurements on the L_{III} edge of Pr in $Pr_2(C_2O_4)_3$, A-Pr_2O_3, C-Pr_2O_3, Pr_6O_{11}, $PrO_x (1.83 \leqslant x \leqslant 2)$ and PrO_2 are given in Fig. 1(a) and (b). For comparison, we have included in this Figure the corresponding L_{III} spectrum obtained from CeO_2. In order to show clearly the details of the weak structures and shoulders we give in Fig. 1(c) some of these spectra in a second derivative form. The corresponding $M_{IV\text{-}V}$ yield spectra are given in Fig. 2(a) and (b).

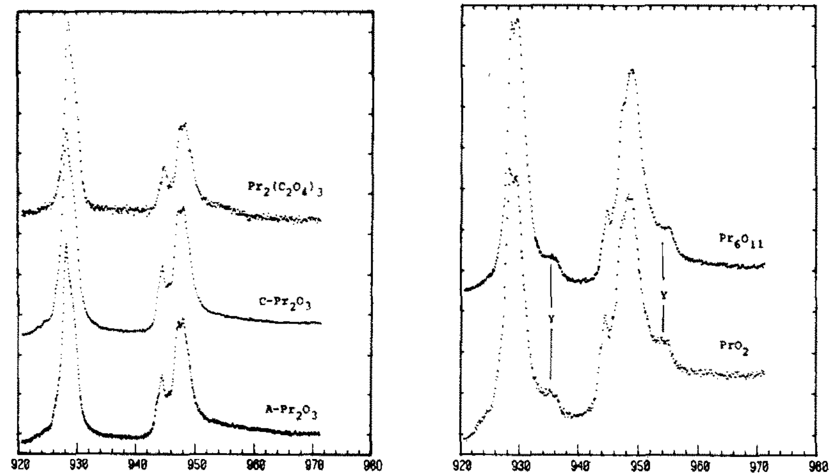
Discussion

The L_{III} absorption spectra (normalised to the absorption jump) for trivalent Pr in $Pr_2(C_2O_4)_3$, Pr_2O_3-A and Pr_2O_3-C (Fig. 1(a)) show a single absorption line. Its position in these compounds does not vary. A change in its



(a) (b) (c)

Fig. 1. (a) L_{III} absorption edges of trivalent Pr compounds. (b) L_{III} absorption edges of fluorite-structure-based Pr oxides. For comparison, the L_{III} edge of CeO_2 is also included. Two different scales for Pr (5930 - 6010 eV) and for Ce (5690 - 5770 eV) are given. (c) Second derivative L_{III} spectra of C-Pr_2O_3, PrO_2 and CeO_2 with different energy scales for Pr and Ce.



(a) (b)

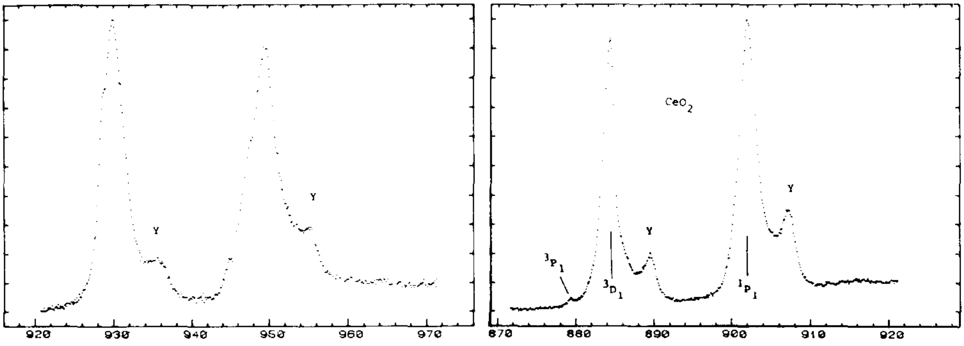
Fig. 2. (a) M_{IV}-$_V$ yield spectra of trivalent Pr compounds. (b) M_{IV}-$_V$ yield spectra of Pr_6O_{11} and PrO_2.

relative intensity and width is noticed, however. This is due to the fact that the band structure of these compounds is different in each case. From Pr_2O_3 to PrO_2 (Fig. 1(b)) it is evident that (i) the first peak shifts 3 eV towards the higher energies; (ii) a second peak more and more intense and invariant in energy appears. For PrO_2, as in CeO_2, the two peaks are well separated by 7 eV, but some change in their relative intensities (the second peak particularly is less intense) is observed.

The L_{III} spectra of the PrO_x system clearly demonstrate the evolution of Pr valence for different oxygen concentrations. These observations clearly show that the trivalent Pr compounds yield a single absorption line whereas the typical doublet in PrO_2 ($x = 2$) is characteristic of tetravalency. The second-derivative spectra (Fig. 1(c)) clearly show the trivalent and tetravalent spectral contributions in A-Pr_2O_3, PrO_2 and CeO_2. The Pr_6O_{11} and $PrO_x(1.83 \leqslant x \leqslant 2)$ spectra were found to be formed by trivalent (C-Pr_2O_3-like) and tetravalent (PrO_2-like) constituents in appropriate proportion.

The M_{IV-V} spectra from trivalent $Pr_2(C_2O_4)_3$, A-Pr_2O_3 and C-Pr_2O_3 (Fig. 2(a)) are identical. They are characteristic of the $3d^94f^3$ multiplet structures separated into two spin-orbit groups 19 eV apart. For Pr_6O_{11} and PrO_2 (Fig. 2(b)) several additional intense features appear. The structures due to the $3d^94f^3$ final configuration can easily be recognized by comparison with the spectra from trivalent Pr compounds. The additional structures clearly indicate the presence of tetravalent Pr in Pr_6O_{11} and PrO_2. It is interesting to note that the observed M_{IV-V} yield spectra of Pr_6O_{11}, PrO_x and PrO_2 contain a substantial amount of trivalent spectral weight. This may be due to the presence of contaminants at the surface which are easily detected in yield measurements. One of the important contaminants, as revealed sometimes in X-ray diffraction patterns, is $Pr(OH)_3$, which is purely trivalent. By contrast, CeO_2 is less prone to contaminants and the yield spectrum attests to the purity of the sample.

In an ideal case the valence change, trivalence → tetravalence, in Pr would correspond to a delocalization of one 4f electron from the initial f^2 configuration. Thus the M_{IV-V} spectra in this case will correspond to the transitions $3d^{10}4f^1 \rightarrow 3d^94f^2$, as in the case of trivalent Ce. In order to identify the various spectral features in the spectra from Pr_6O_{11} and PrO_2 we subtracted from these spectra, by trials, the contribution of the trivalent spectrum. In Fig. 3(a) we give the result of subtracting 50% spectral weight of C-Pr_2O_3 from the Pr_6O_{11} spectrum. The visual estimation of the residual contribution of C-Pr_2O_3 and its complete elimination is subject to an error of



(a) (b)

Fig. 3. (a) M_{IV-V} spectrum of tetravalent Pr obtained by subtraction procedure as described in the text. (b) M_{IV-V} yield spectrum of CeO_2.

about 10% in the spectral weight. The resulting spectrum was found to have shifted as a whole by 2 eV on the higher energy side with respect to that of C-Pr_2O_3. The main $M_{IV\text{-}V}$ lines in this spectrum show multiplet structures which are similar to those observed for Ce^{3+} compounds. In addition to the multiplet structures on the main $M_{IV\text{-}V}$ lines, we observed two weaker structures on the higher energy side. They are labelled Y in Figs. 2(b) and 3(a).

Considering the difficulties encountered in the Pr oxides sample preparation, their transfer to the vacuum chamber, and our inability to obtain the required surface purity, we reconcile the resultant spectrum given in Fig. 3(a) with that of tetravalent Pr. This is justified by the fact that on subtracting the C-Pr_2O_3 L_{III} spectral contribution from that of Pr_6O_{11} we obtain a PrO_2-like spectrum, as shown in Fig. 1(b).

The results of our tentative identification of the Pr absorption spectra need some discussion of the corresponding Ce spectra of CeO_2 and other I.V. Ce compounds. We will discuss the $M_{IV\text{-}V}$ spectra in more detail. To this end, for comparison, we give the $M_{IV\text{-}V}$ spectrum of CeO_2 in Fig. 3(b).

For CeO_2 (Fig. 3(b)) one can unambiguously identify the three lines at 879.2, 884.1 and 901.8 eV. They correspond to the transitions:

$$3d^{10}4f^0({}^1S_1) \longrightarrow 3d^94f^1({}^3P_1,\ {}^3D_1,\ {}^1P_1)$$

as occurring in La^{3+} [17].

The ${}^3D_1$ line is seen to be Lorentzian in shape, whereas the ${}^1P_1$ line is asymmetric and has a Fano-like profile [18]. Their observed widths (1.7 and 2.3 eV, respectively) are greater than the 1.2 and 1.8 eV widths observed, respectively, for the ${}^3D_1$ and ${}^1P_1$ lines in La compounds [18]. This implies that the vacant 4f states in CeO_2 are in a narrow band and still keep a discrete character in the presence of a 3d hole.

In addition to the La-like lines we observe, in CeO_2, two weaker structures, Y, at 5.3 eV on the higher energy side of the ${}^3D_1$ and ${}^1P_1$ lines. The CeO_2 spectrum as a whole shows a shift of about 2 eV towards the higher energy with respect to the normal trivalent Ce compounds.

In I.V. Ce compounds similar weaker structures following the main lines are also observed [19, 20]. However, the main lines show the multiplet structures which can be easily identified [17] with the $3d^94f^2$ final configuration. In such a case the weaker structures are attributed to initial $(f^0) \rightarrow f^1$ transitions.

Thus we see that the major difference between the $M_{IV\text{-}V}$ spectra of CeO_2 and the I.V. Ce compounds lies in the identity of the main lines. The most important information which we derive from these spectra is that the local 4f electron, which is responsible for the f^2 final multiplet in the $M_{IV\text{-}V}$ spectra of I.V. Ce compounds, is delocalized to form a chemical bond in CeO_2. Thus the local 4f states remain vacant. This is clearly demonstrated by the observation of La-like ($3d^{10}4f^0 \rightarrow 3d^94f^1$) lines in the spectrum of CeO_2.

The above mentioned observations, and consideration of the order of the final f^1 and f^2 energies in I.V. Ce compounds, suggest that the origin of the weaker Y structures in CeO_2 is different. This implies that Y features are due to different types of final states. The presence of Y structures in CeO_2 indicates that the delocalized f electron is still under the influence of the central Ce atom. This situation can easily be visualized as occurring in a covalent bond. The low energy La-like features in CeO_2 reflect a better screening provided by a local 4f electron in the final state. The transition of a 3d electron in the extended covalent states leading to a poorer screening may be the origin of the Y-type structures.

By analogy, the above mentioned arguments can be extended to the interpretation of Y-type structures in the M_{IV-V} spectra of Pr_6O_{11} and PrO_2. However, we see in Fig. 3(a) that the Y structures are observed on the higher energy side of the $4f^2$ type of multiplet. From a chemical point of view it is rather difficult to reconcile the assignment of Y structures as f^1 final states with the possibility of pentavalence of Pr in the ground state. Moreover, the L_{III} spectra of CeO_2 and PrO_2 are similar, and no additional feature is observed in the PrO_2 spectrum. This implies that, in both cases, the valence is changing by one unit. So the Y structures observed in the M_{IV-V} spectrum of tetravalent Pr can be attributed to the transitions to the extended covalent states, as in CeO_2.

The L_{III} absorption spectra of CeO_2 and PrO_2 are very similar. The absorption lines in these complex spectra may be due to the transitions:

$$2p^6f^n(V) \longrightarrow 2p^5f^n(V)d, s$$

(where $n = 0$ or 1, respectively, for CeO_2 and PrO_2; V is the valence band formed by the ligand and 5d6s-derived (4f-derived) rare earth orbitals).

For the free ion Ce(V)(Ce^{4+}), the spectroscopic data [21] show that the $5p^55d$ and $5p^56s$ configurations are almost degenerate, exhibiting two groups of levels separated by roughly 6 or 7 eV. On an equivalent core basis we expect a similar separation of the outer levels for the transition of a 2p level electron. It may be possible that, in the present case, the f electrons are only spectator electrons, and that we are seeing a complex spectrum on both Ce^{4+} and Pr^{4+} ions due to configuration interaction between the $2p^5f^n(V)d$ and $2p^5f^n(V)s$ configurations. It is rather difficult to reconcile this argument with the observed M_{IV-V} spectra of these compounds. The observation of the Y-type structures indicates that the presence of an f electron in the valence band has some influence on the 3d → 4f transitions. The relative positions of the spectral features in L_{III} and in M_{IV-V} spectra can easily be explained by considering the 4f screening mechanism.

Conclusion

The evolution of Pr valence in the $PrO_x (1.5 \leqslant x \leqslant 2)$ system has been demonstrated by the study of the L_{III} and M_{IV-V} absorption spectra. The L_{III} edge of Pr in PrO_2 shows two absorption lines of comparable intensity. This edge structure is found to be similar to that observed for Ce in CeO_2.

By considering the multiplet structure of the main lines in the $M_{IV\text{-}V}$ spectrum of CeO_2 and the tetravalent Pr, we deduce that by the participation of a 4f electron in bond formation the localized f states remain vacant. The weaker Y structures observed on the high-energy side of the main lines are thought to be due to the transitions to vacant f symmetry extended states. These results indicate that the metal–oxygen bonding in CeO_2 and PrO_2 has a partially covalent character.

With the present data, it is rather difficult to give a quantitative estimate of the extended and localized f character in CeO_2 and PrO_2. For this estimation we need to undertake similar studies on the TbO_x system and an actinide oxide like UO_2, which are expected to be two extreme cases of the f character in these compounds.

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