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X-ray absorption studies of CeO_2, PrO_2, and TbO_2. I. Manifestation of localized and extended *f* states in the 3*d* absorption spectra

R. C. Karnatak and J. -M. Esteva
Laboratoire pour l'Utilisation du Rayonnement Electromagnétique, Bâtiment 209d, Université Paris-Sud, 91405 Orsay, France and Laboratoire de Spectroscopie Atomique et Ionique, Bâtiment 350, Université Paris-Sud, 91405 Orsay, France

H. Dexpert
Laboratoire pour l'Utilisation du Rayonnement Electromagnétique, Bâtiment 209d, Université Paris-Sud, 91405 Orsay, France and Laboratoire des Elements de Transition dans les Solides, 1 Place A Briand, 92195 Meudon Cedex, France

M. Gasgnier, P. E. Caro, and L. Albert
Laboratoire des Elements de Transition dans les Solides, 1 Place A Briand, 92195 Meudon Cedex, France

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The 3*d* x-ray absorption spectra of CeO_2, PrO_2, and TbO_2 show some interesting features. The main lines in these spectra are unusually broad. They are identified by comparison with the 3*d*-4*f* atomiclike multiplets observed in $Z-1$ elements. In these oxides, the positions and the similar form of a weaker structure which is systematically observed at about 3–5 eV above each main line indicate that it is due to the transitions to the extended *f* type of states. These observations demonstrate a specific behavior of the outermost *f* electron which differentiates these oxides from other intermediate-valence materials and from the Ce intermetallic compounds.

INTRODUCTION

The insulating and nonmagnetic material CeO_2 possesses the fluorite structure and is a member of the RO_x (R =Ce,Pr,Tb; $1.5 \le x \le 2$) system.[1] It has recently attracted much interest in relation to the fascinating studies of the intermediate-valence (IV) compounds. The description of the ground state of CeO_2 from its spectral response to high-energy probes[2–9] such as x-ray photoelectron spectroscopy (XPS), bremsstrahlung isochromat spectroscopy (BIS), electron-energy-loss spectroscopy (EELS), and x-ray absorption spectroscopy (XAS) is still a subject of active research. The interpretation of the optical and magnetic measurements and the earlier L_{III}-edge[6] and XPS (Ref. 2) data on CeO_2 led to some controversial opinions concerning its valence and the description of its ground state.[10] In fact the valence behavior, the ground-state properties, and various spectral features of CeO_2 are reconciled within the framework of the existing Anderson impurity model in the zero-bandwidth[11] or finite-bandwidth[12,13] limits. Moreover, calculations[13] based on this model, by taking into account the 4*f*-2*p* oxygen hybridization, can distinguish between f^0, f^1, and f^2 character or their admixture in the ground and final states involved in the core-level spectra of CeO_2. Due to their complexity, multiplet effects are not included in the model. Recently Willoud *et al.*[3] applied the Gunnarsson-Schönhammer (GS) many-body state calculations[12] to reproduce the outer-level and 3*d* excitation spectra. These calculations yield 4*f* spectral weights for a choice of parameters corresponding to 0.5 4*f* electrons in the ground state. The two low-binding-energy peaks of appreciable intensity observed below the isolated f^0 peak in the 3*d* XPS of CeO_2 were found to be due to the close and strongly mixed f^1 and f^2 final configurations and band excitations. The observation of a large intensity due to states of this type was considered to be a consequence of the existence of the $4f^1$ initial population of extended states which was thus indirectly demonstrated. Other impurity calculations[13] leading to a similar description of the 3*d* XPS of CeO_2 consider the f^0 and f^1 admixture in the ground state as a precursor of mixed valence.[14] The 4*f* occupancy (n_f) thus obtained was found to be in agreement with the band calculations on CeO_2,[15] which show considerable mixing of 4*f* Ce states into the oxygen 2*p* band corresponding to about 0.5 electrons. The present summary shows that the difference in opinions over the valence state of CeO_2 concerns whether the population of *f* electrons is in localized or in extended states.

In the present context, 3*d* XAS offers some advantage over other core-level spectroscopies. In contrast to XPS, x-ray absorption transitions are governed by dipole selection rules, and the reduction in the number of accessible final states[16] facilitates the identification of spectral features. Thus the study of valence transitions in the rare-earth (RE) materials by 3*d* XAS seems to be advantageous. The signature of the multiplet structure associated with the $3d^9 4f^{n+1}$ final configuration provides an unambiguous identification of the localized state. The identification of the additional weaker structure observed in the 3*d* XAS of these materials may lead to a clearer understanding of the nature of the 4*f* electron at RE sites.

In order to gain such insight into the CeO_2 valence problem in relation to the study of localized and extended 4*f* states, we performed $M_{\text{IV,V}}$ XAS measurements on the fluorite-structure-related Pr and Tb homologs. So far, to our knowledge, no 3*d* XAS measurements on pure PrO_2 (Ref. 17) and TbO_2 have been reported.

EXPERIMENTS

CeO_2 free from carbonate and other trivalent contaminants was prepared by calcination of commercial CeO_2 in an electric furnace at 1100 °C for 18 h. PrO_2 and TbO_2 were prepared by continuous agitation of a suspension of their stable oxides, Pr_6O_{11} and Tb_4O_7, respectively, in a 5% aqueous solution of acetic acid for several days. Details of the sample preparation will be given elsewhere.[18] The $3d$ spectra were obtained at Anneau de Collision d'Orsay (ACO), Laboratoire pour l'Utilisation du Rayonnement Electromagnetique (LURE) by using the radiation emitted by 537-MeV electrons in the storage ring. A beryl double-crystal monochromator[19] was used to obtain the yield spectra[20] 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 AND DISCUSSION

The $M_{IV,V}$ yield spectra of CeO_2, PrO_2, and TbO_2 are given in Fig. 1. The two $3d$ spin-orbit groups of lines and structures are found to be separated by 17.7, 19.5, and 31.5 eV, respectively, for CeO_2, PrO_2, and TbO_2. In these spectra additional weaker features (labeled Y in Fig. 1) at about 3–5 eV on the higher-energy side of the main line in each spin-orbit group are systematically observed. For brevity we do not give the corresponding spectra of the trivalent oxides. We indicate by vertical arrows (Fig. 1) the positions of the main peaks in the $3d^94f^{n+1}$ multiplets of the corresponding trivalent oxides. The CeO_2, PrO_2, and TbO_2 spectra are found to be shifted as a whole towards higher energy by 1.7, 1.7, and 1.2 eV, respectively, as compared to those for the corresponding trivalent oxides or compounds. It is interesting to mention that in the $3d$ XAS of fluctuating-valence Sm, Eu, and Tm compounds, the separation between two types of final multiplets is observed[8] to be 2.5–3 eV. In fact, these spectral shifts correspond well to the magnitude of the energy difference between the $4f^n$ and $4f^{n+1}$ final spectroscopic states relevant to a valence change, and are in good agreement with those obtained from the results of the recent theoretical calculations[21] on the $3d^94f^{n+1}$ multiplets.

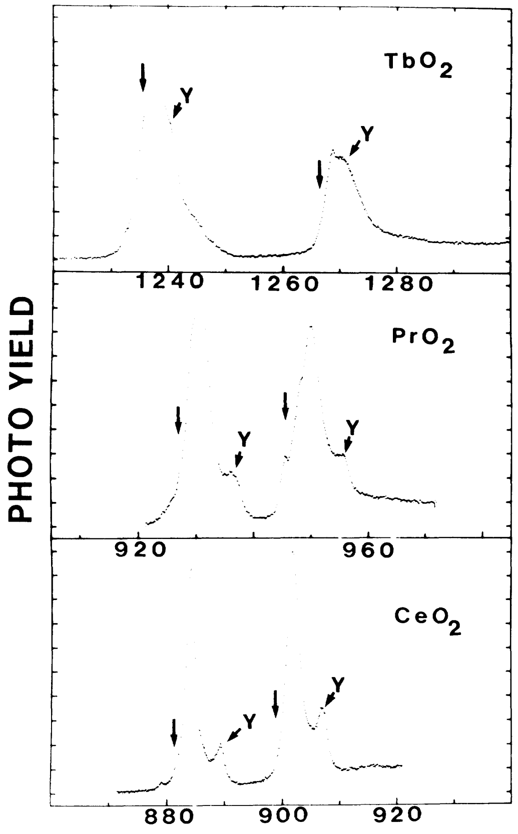

FIG. 1. $M_{IV,V}$ absorption spectra of CeO_2, PrO_2, and TbO_2. The main lines of PrO_2 and TbO_2 show multiplet splitting. The additional weaker features Y are well separated from the main lines in CeO_2 and PrO_2. Note that in TbO_2 these are within the main multiplets.

One expects a diminution of the local f count at a given RE atom in a tri- to tetravalence charge for a RE oxide. Thus the $3d$ XAS transitions in RO_2 can be compared with the corresponding transition in $Z-1$ elements (where Z is the atomic number of R). In order to identify the main line features of these oxides, we compared them with the $M_{IV,V}$ spectra of the trivalent compounds of the corresponding $Z-1$ elements. The M_{IV}-M_V intensity ratios observed in the present cases are similar to those for the corresponding $Z-1$ element spectra. As expected we observe an increase in the $3d$ spin-orbit separation between the two main features of these spectra with respect to those obtained for $Z-1$ elements. In Fig. 2(a) we have presented on a relative energy scale the M_V and M_{IV} spectra of CeO_2 and PrO_2 comparative to those of La_2O_3 and Ce oxalate. In Fig. 2(b) the M_V and M_{IV} spectra of TbO_2, which are wider than the other oxide spectra, are separately compared to those of Gd_2O_3. The correspondence between the various lines and the multiplet structures of RO_2 and the trivalent $Z-1$ compounds is indicated by dashed connecting lines. The CeO_2 main lines in Fig. 2(a) are similar to the three $3d^94f^1$ lines (the weak $^3P_1$ line and the intense $^3D_1$ and $^1P_1$ lines) observed for La_2O_3. The PrO_2 broad main line features resemble closely the $3d^94f^2$ (trivalent Ce-like) multiplet. Finally, we find for TbO_2 the $3d^94f^8$ (Gd-like) multiplets [Fig. 2(b)] which are broad, and the structures can easily be recognized by comparison with the Gd_2O_3 spectra. We therefore identify the main lines of CeO_2, PrO_2, and TbO_2, respectively, as transitions from the atomiclike f^0, f^1, and f^7 ground-state configurations.

The most interesting fact about these oxide spectra is the observation of unusual broadening of the constituent main multiplet lines. The broad RO_2 and the corresponding trivalent-compound spectra [Figs. 2(a) and 2(b)] were obtained with the same resolution. A comparison between the individual structures within the multiplets of RO_2 and those observed in the corresponding $Z-1$ elements reveals (1) an increase in the widths of the $^3D_1$- and $^1P_1$-like lines in CeO_2, (2) an increase in the separation between the structures within the multiplets of RO_2, and (3) a correspondence between the relative intensity of RO_2 structures and those for $Z-1$ elements. In Table I, we give the measured full width at half maximum (FWHM) of the $3d$-$4f$ lines or multiplets for RO_2 and those for the corresponding $Z-1$ elements in trivalent compounds. The 40–50% increase in the line or multiplet width in these oxides with respect to that observed in the corresponding $Z-1$ element is found to be too high to be explained by invoking the increase in the spin-orbit separation. These broadened multiplets roughly keep their usual forms as observed for the normal RE elements. A careful examination of the $^3D_1$- and $^1P_1$-like lines of CeO_2 show deviations from the usual Lorentzian or Fano profiles. A detailed analysis of the line broadening requires a suitable function to take into account the interactions of excited $4f$ electrons with the complex conduction states in RO_2. Such interactions may also explain the further line splitting within the multiplets which leads to an unusual increase in the FWHM of the multiplets. Thus a detailed analysis of the complex multiplets in PrO_2 and TbO_2 is presently difficult.

TABLE I. Measured full width at half maximum (FWHM) of the $3d$-$4f$ lines or multiplets for RO_2 and those for the corresponding $Z-1$ elements in trivalent compounds.

		Width (eV)	
RO_2	$Z-1$ element	M_V	M_{IV}
CeO_2		1.7	2.6
	La[a]	1.2	1.8
PrO_2		4.1	5.0
	Ce[b]	2.4	3.2
TbO_2		4.8	6.8
	Gd[a]	2.6	4.6

[a] FWHM obtained from the spectra in Ref. 23.

[b] FWHM obtained from the spectra in Ref. 24.

The structures labeled Y (Fig. 1) appearing at about 5 eV above the main lines of CeO_2 and PrO_2 have similar forms, and the M_{IV} Y structures are somewhat higher in intensity than the M_V ones. They are asymmetric and appear to extend up to the bottom of the main lines. In TbO_2 these structures are found to be within the wide Gd-like multiplets. The Y-type structure at about 3 eV above the main M_V line can easily be recognized as a feature [Fig. 2(b)] contributing to the enhancement in the intensity between the main line and the high-energy weaker structures of the Gd-like multiplet. For the M_{IV} [Fig. 2(b)] it is probably overlapping the high-energy main line structure. In the M_V spectrum of TbO_2 we observe a weak shoulder S at about 1.5 eV below the main line [Fig. 2(b)]. Its position corresponds approximately to the expected energy of the main M_V peak of the trivalent oxide. The presence of such a low-energy shoulder on the M_{IV} line corresponding to the trivalent component is not observed. So the identification of the weak low-energy shoulder S becomes doubtful. Moreover, the $3d$-$4f$ multiplet calculations predict 16 closely spaced, more or less intense lines within the main M_{IV} peak. Due to increased splitting of such multiplet lines in TbO_2, under the present resolution, some modification in the line shape and the appearance of a weaker shoulder are also expected. At present, calculations which take into account the interaction leading to increased line splitting are not available.

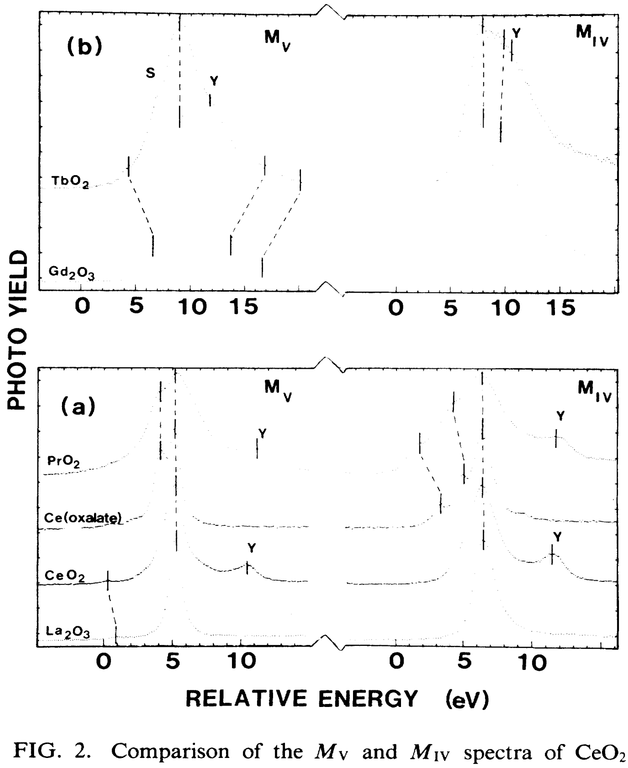

FIG. 2. Comparison of the M_V and M_{IV} spectra of CeO_2, PrO_2, and TbO_2 with those from corresponding $Z-1$ elements in trivalent compounds. (a) M_V and M_{IV} spectra of CeO_2 and PrO_2 are presented with those of La_2O_3 and Ce oxalate on a relative energy scale. (b) M_V and M_{IV} spectra of TbO_2 are compared with those from Gd_2O_3. The connecting dashed lines show the correspondence between the multiplet structures in $Z-1$ elements and the structures in RO_2. The structures due to transitions to the extended type of f states are labeled Y.

The signatures of the $3d^94f^{n+1}$ multiplets and their positions in R_2O_3 as compared to those in the corresponding RO_2 indicate that on valence transition a diminution of the f count in the ground-state local occupancy is taking place. Our identification that the main lines in CeO_2 are due to transitions from the f^0 ground state implies that the Y structures in CeO_2 cannot be due to another localized configuration. In PrO_2 and TbO_2, such a possibility can easily be excluded as it would lead to an improbable higher-valence state in Pr and Tb.

Thus we see that the Y structures in CeO_2 and PrO_2 do not correspond to any known multiplet features of nearly RE elements. The systematic increased separation (3–5 eV) between RO_2 atomic main lines and the Y structures as compared to RO_2-R_2O_3 multiplet separation and the similar form of the Y structures indicate that the origin of these structures is closely related to the degree of the core-hole screening by the excited f electron. These considerations suggest that the Y structures in RO_2 originate from transitions to the $4f$ admixture in the conduction states. The interaction of an excited $4f$ electron with a finite f-admixture continuum may lead to further broadening of the $3d$-$4f$ lines in these oxides. In what follows, we define a localized f electron as an electron which attaches to the inner reaches of the RE atom, and a delocalized electron as one which overlaps with the valence band.

The picture of the ground state of the rare earth atom in RO_2 emerging out of the present study is that in each case, due to RE-oxygen bonding, only a fraction c of the delocalized $4f$ electron remains on the RE site. Its presence is detected in XAS by transitions to the $4f$ admixture within the conduction continuum. The remaining fraction $(1-c)$ is used up in a partial ionic type of bonding and, as a result, appears as a vacant localized f state. The present description of this specific valence state in the dioxides is different from that of the Ce intermetallics obtained by $3d$ XAS (Ref. 24) and other high-energy spectroscopies.[3,25] In these materials, nearly one electron occupies the localized f orbital and only a small fraction of this electron is delocalized in the valence band. In contrast to the La-like lines observed in CeO_2, the observation of the f^2-type atomic multiplet lines in Ce-based intermetallics[24] confirms the presence of a localized f electron in the ground state. The Y-type structures similar to those observed in RO_2 with varying relative intensity with the f-level hybridization are also observed at about 5 eV above the main f^2 lines in the Ce intermetallics. In fact this separation corresponds well to the 4–6-eV difference observed in XPS between a well-screened f^2 peak and a valence-electron-screened f^1 peak. The descriptions of the final states giving rise to f^1 and f^2 peaks in XPS and the f^2 multiplet and the Y structures in $3d$ XAS are now essentially similar.

The impurity model calculations on the Ce materials provide a reasonable description of the positions of the various $3d$ XAS structures and $4f$ occupancy. However, the distinction between the $4f$ occupancies related to an f electron occupying a localized state and that in extended states is not so clear in this model. Similar calculations[13] for CeO_2 yield a ground state in which the f^0 and f^1 configurations are strongly mixed with comparable weights. We do observe the presence of a local f^0 component in the $3d$ XAS of CeO_2. But surprisingly the f^1 component does not show any observable $3d^9f^2$ multiplet. Instead we observe structures due to transitions to the extended states. Thus we see that the $3d$ XAS can distinguish a quasiatomic f state from extended states by multiplet identification. An estimate of the occupancy of the last $4f$ electron in PrO_2 and TbO_2 from the present $3d$ XAS is difficult to obtain due to complexity of the broad multiplets and the overlapping Y structures. Such estimate can easily be obtained from L_{III} edge measurements on RO_2 and will be presented in a following paper.[26]

CONCLUSION

The main spectral features of CeO_2, PrO_2, and TbO_2 which distinguish them from those of Ce intermetallic compounds on one hand and the Sm, Eu, and Tm fluctuating-valence compounds on the other hand are summarized as follows.

1. (a) The $3d$-multiplet identification in Ce intermetallic compounds indicates the presence of a localized f electron in the ground state. In the dioxides the recognizable multiplet corresponds to the $3d$ multiplets of a $Z-1$ element.

(b) The $3d$-multiplet widths are observed to be 40–50 % higher in dioxides than the corresponding $Z-1$ elements. In Ce intermetallic compounds no such dramatic change in the multiplet width is observed. However, some change in the relative intensity of the multiplet lines arising from population of the spin-orbit-split $f_{7/2}$ state occurs due to $4f$-level hybridization.[27]

2. In the fluctuating-valence Sm, Eu, and Tm compounds, two types of $3d$-$4f$ atomic multiplets separated by 2.5–3 eV corresponding to two distinct valence configurations are observed.[8]

The present results demonstrate the $4f$-$2p$ oxygen hybridization even in a heavier RE oxide like TbO_2. The relative decrease in the $4f$-$2p$ overlap in TbO_2 as compared to that in CeO_2 and PrO_2 is apparent from the decrease in the separation between the main line and the Y structures.

The observation of the atomiclike main multiplet lines and the absence of any recognizable multiplet feature on the Y structures in RO_2 suggest the coexistence of the localized atomic with the extended type of f states in RO_2. In this context, the double-valley-potential theory which may include atomic[28] and solid-state effects[29] seems to be attractive for the interpretation of the spectral features of RO_2.

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[1] L. Eyring, in *Nonstoichiometric Oxides*, edited by O. T. Sorensen (Academic, New York, 1981), p. 337.

[2] P. Burrough, A. Hamnett, A. F. Orchard, and G. Thorton, J. Chem. Soc. Trans. **17**, 1686 (1976).

[3] E. Wuilloud, B. Delley, W. Schneider, and Y. Baer, Phys. Rev. Lett. **53**, 202 (1984); W.-D. Schneider, B. Delley, E. Wuilloud, J.-M. Imer, and Y. Baer, Phys. Rev. B **32**, 6819 (1985).

[4] J. W. Allen, J. Less-Common Met. **93**, 183 (1983); J. Magn. Magn. Mater. **47&48**, 168 (1985).

[5] G. Strasser and F. P. Netzer, J. Vac. Sci. Technol. A **2**, 826 (1984).

[6] K. R. Bauchspiess, W. Boksch, E. Holland-Moritz, H. Launois,

R. Pott, and D. Wohlleben, in *Valence Fluctuations in Solids,* edited by L. M. Falicov, W. Hanke, and M. B. Maple (North-Holland, Amsterdam, 1981), p. 417.

[7] E. Beaurepaire, Docteur Ingenieur thesis, Institut Polytechnique, Nancy, 1983.

[8] G. Kaindl, G. Kalkowski, W. D. Brewer, B. Perscheid, and F. Holtzberg, J. Appl. Phys. **55**, 1910 (1984); G. Kaindl, G. Kalkowski, W. D. Brewer, E. V. Sampathkumaran, F. Holtzberg, and A. Schavch v.Wittenau, J. Magn. Magn. Mater. **47&48**, 181 (1985).

[9] R. C. Karnatak, M. Gasgnier, H. Dexpert, J. M. Esteva, P. E. Caro, and L. Albert, J. Less-Common Met. **110**, 377 (1985).

[10] P. Watchter, in *Valence Instabilities,* edited by P. Wachter and H. Boppart (North-Holland, Amsterdam, 1982), p. 145.

[11] A. Fujimuri, Phys. Rev. B **28**, 2281 (1983).

[12] O. Gunnarsson and K. Schönhammer, Phys. Rev. B **28**, 4315 (1983).

[13] A. Kotani, H. Mizuta, T. Jo, and J. C. Parlebas, Solid State Commun. **53**, 805 (1985); T. Jo and A. Kotani, *ibid.* **54**, 451 (1985).

[14] The term "mixed valence" characterizes the fractional occupation of localized states in the metallic phase [C. M. Varma, Rev. Mod. Phys. **48**, 219 (1976)].

[15] D. D. Koelling, A. M. Boring, and J. H. Wood, Solid State Commun. **47**, 227 (1983).

[16] J.-M. Esteva, R. C. Karnatak, J. C. Fuggle, and G. A. Sawatzky, Phys. Rev. Lett. **50**, 910 (1983).

[17] The $3d$ spectrum of PrO_2 given in Ref. 9 was obtained by subtracting a Pr_2O_3 spectrum from that of Pr_6O_{11}.

[18] L. Albert, M. Gasgnier, and P. E. Caro (unpublished).

[19] M. Lemonier, O. Collet, C. Depautex, J.-M. Esteva, and D. Raoux, Nucl. Instrum. Methods **152**, 109 (1978).

[20] J.-M. Esteva, R. C. Karnatak, and J. P. Connerade, J. Electron Spectrosc. Relat. Phenom. **31**, 1 (1983).

[21] B. T. Thole, G. van der Laan, J. C. Fuggle, G. A. Sawatzky, R. C. Karnatak, and J.-M. Esteva, Phys. Rev. B **32**, 5107 (1985).

[22] C. Bonnelle, R. C. Karnatak, and J. Sugar, Phys. Rev. A **9**, 1920 (1974).

[23] R. C. Karnatak, J.-M. Esteva, and J. P. Connerade, J. Phys. B **14**, 4747 (1981).

[24] J. C. Fuggle, F. U. Hillebrecht, J.-M. Esteva, R. C. Karnatak, O. Gunnarsson, and K. Schönhammer, Phys. Rev. B **27**, 4637 (1983); O. Gunnarsson, K. Schönhammer, J. C. Fuggle, F. U. Hillebrecht, J.-M. Esteva, R. C. Karnatak, and B. Hillebrand, *ibid.* **28**, 7330 (1983).

[25] J. C. Fuggle, F. U. Hillebrecht, Z. Zolnierek, R. Lässer, Ch. Freiburg, O. Gunnarsson, and K. Schönhammer, Phys. Rev. B **27**, 7330 (1983).

[26] H. Dexpert *et al.*, Phys. Rev. B **36**, 1750 (1987).

[27] G. van der Laan, B. T. Thole, G. A. Sawatzky, J. C. Fuggle, R. C. Karnatak, J.-M. Esteva, and B. Lengeler, J. Phys. C **19**, 817 (1986).

[28] J. P. Connerade, J. Phys. C **15**, L367 (1982).

[29] M. Schlüter and C. M. Varma, Helv. Phys. Acta **56**, 147 (1983).