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Position of the 4f level in γ -cerium

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Résumé. — Nous présentons les mesures de spectroscopie photoélectronique effectuées soit dans la bande ultraviolet (UPS He II), soit dans la bande X (XPS MgK_{α}) sur des films de cérium pur et de cérium exposé à l'oxygène à la température ambiante. La comparaison des spectres UPS et XPS des deux types de films permet de conclure que le niveau 4f dans le cérium γ est situé à $(1,9 \pm 0,2)$ eV par rapport au niveau de Fermi. Ces résultats montrent que la transition γ - α est liée à une transition de Mott des électrons 4f et à une hybridation subséquente avec la bande sd.

Abstract. — The present paper concerns ultraviolet photoelectron spectroscopy (UPS) (He II) and X-ray photoelectron spectroscopy (XPS) (MgK_{α}) measurements on clean cerium films, and on cerium films exposed to oxygen at room temperature. From comparison of the UPS and XPS spectra on clean and oxidized cerium the 4f level binding energy in γ -cerium is concluded to be (1.9 ± 0.2) eV relative to the Fermi level. Our results indicate that the γ - α transition is due to a Mott transition of the 4f electron and a subsequent hybridization with the sd band.

1. Introduction. — In different pictures, accounting for the γ - α phase transition of cerium, the energy and width of the 4f level of γ -cerium are of crucial importance. It is therefore highly desirable that experimental determinations of these parameters be undertaken.

In photoelectron spectroscopy on cerium the electron emission due to the 4f level and the 5d 6s band are overlapping. Therefore the proposed value of the 4f binding energy shows some scatter: 1.8 eV [1], 0.9 eV [2], and 0.5 eV [3].

However, by studying the oxidation of cerium by UPS and XPS we have in the present work found strong experimental evidence for a correct identification of the 4f level photoelectron emission.

The measurements were performed in an ion-pumped ultrahigh vacuum chamber ($p \leq 10^{-8}$ Pa) using a retarding field electron spectrometer with differential output [4]. A more detailed description is given elsewhere [5].

2. Results and discussion. — The valence band spectra excited from clean cerium films by He II and MgK_{α} radiations are quite similar (figure 1). The UPS spectrum of the valence band shows a kind of shoulder (B) at 2 eV. On the other hand, in XPS the valence band spectrum forms a more symmetrical peak, and it is in fair agreement with previous reports [1-3]. In neither spectrum can the f level emission be separated from the sd band emission. However, the relative photoemission cross sections of the f level and the sd band (σ_{4f}/σ_{sd}) increase with increasing photon energy, when going from He II to MgK_{α} radiation. Thus, from a comparison of the

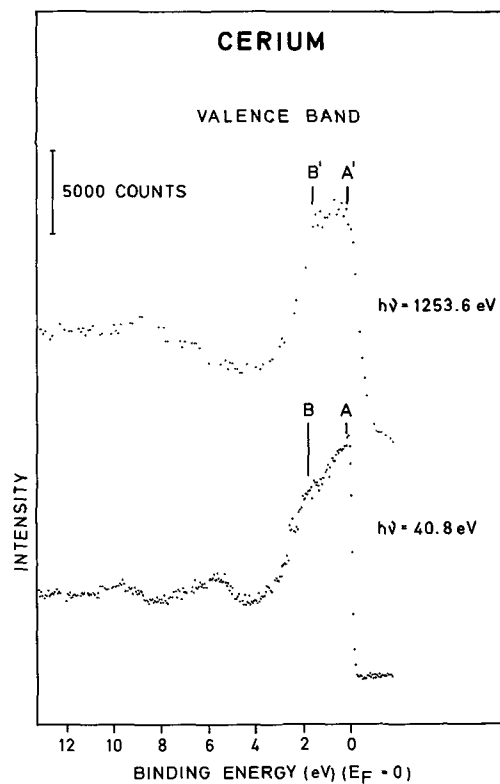


Fig. 1. — XPS ($h\nu = 1253.6$ eV) and UPS ($h\nu = 40.8$ eV) valence band spectra of γ -cerium. The analyzer resolution was set to 0.33 eV in XPS and 0.13 eV in UPS. To normalize the spectra to about the same step height at the Fermi edge, the UPS spectrum is multiplied by 4.5.

two spectra, we interpret structures A and A' as being due to the sd band emission and structures B and B' as being due to the f level.

Subsequent oxygen exposures were found to change the He II induced spectra (figure 2) in the following manner: 1) A broad peak appears at 6 eV due to oxygen 2p emission from chemically bound oxygen. 2) The intensity near the Fermi edge is reduced with increasing exposure to oxygen. 3) After an exposure of 100 L (1 L = 10^{-6} torr.s), the emission from the Fermi edge has disappeared. 4) The structure at 2 eV does not depend on oxygen exposure apart from a small shift to higher binding energies. Similar results were obtained from the MgK $_{\alpha}$ induced valence band spectra.

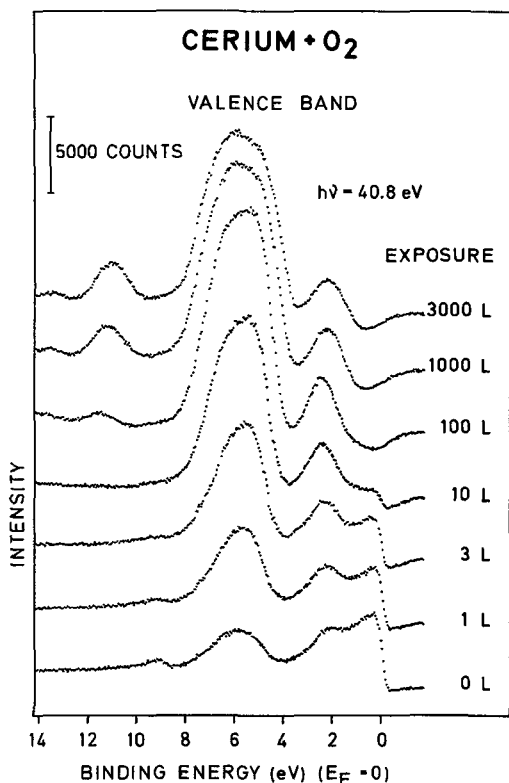


Fig. 2. — UPS ($h\nu = 40.8$ eV) valence band spectra of cerium after various exposures to oxygen. The analyzer resolution was set to 0.21 eV.

Thus, we draw following conclusions: The oxide phase formed depletes the sd band but does not affect the 4f level emission intensity. Assuming that the photoemission cross section does not depend strongly on the chemical environment, a 4f level position of (1.9 ± 0.2) eV in γ -cerium is consistent with all UPS and XPS spectra obtained.

To test the latter assumption XPS spectra from praseodymium (electron configuration $4f^2(5d\ 6s)^3$) were recorded immediately after evaporation (0 L) and after exposure to oxygen (1 000 L), see figure 3. The emission due to the Pr 4f level, at 3 eV, is twice as high as in the case of Ce, when compared to the sd band emission, as expected. As in cerium, oxidation is leading to a vanishing of the emission due to the sd

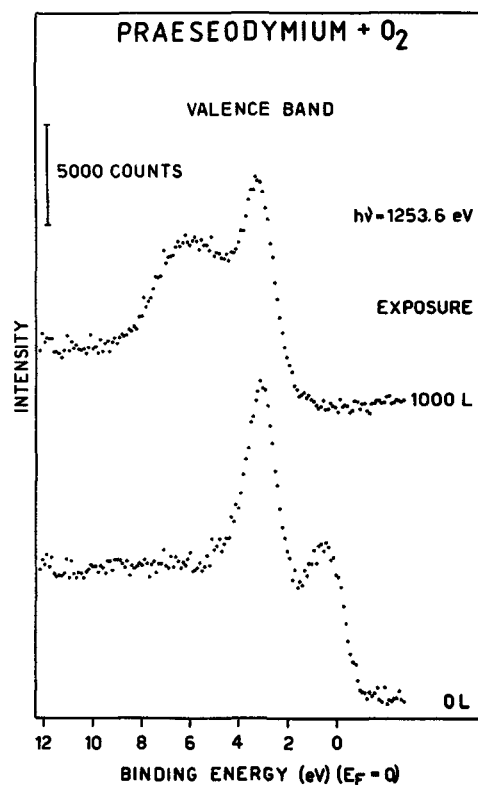


Fig. 3. — XPS ($h\nu = 1\ 253.6$ eV) valence band spectra of clean and oxidized praseodymium.

band, while the emission due to the 4f level shows a nearly unchanged intensity accompanied by a small shift not exceeding the measurement uncertainty (0.2 eV).

3. Conclusion. — We believe that we have given experimental evidence for a correct identification of the 4f level in γ -cerium metal. The position and width of the f level agree fairly well with the theoretical calculations by Herbst *et al.* [6]. Comparing with the XPS spectra on Pr and its oxide, our result, the finding of a 4f binding energy of 1.9 eV in γ -cerium, is much more plausible than a position direct at the Fermi edge would be. The value for the 4f level position reported here is in fact close to that first reported by Baer and Busch [1] and also agrees with that advanced by Johansson [7-9] on thermodynamic reasons.

In the promotion model and its various extensions [10-14] as well as in the sd-f hybridization model [15], it is required that the 4f level is situated just below the Fermi energy in the cerium γ -phase. However, in the model describing the γ - α transition as a Mott transition within the 4f shell [7], such a close proximity of the 4f level to the Fermi level is not required. Therefore, our results give evidence for the view that the γ - α transition is due to a Mott transition of the 4f electron with a subsequent hybridization with the sd electrons.

References

- [1] BAER, Y. and BUSCH, G., *Phys. Rev. Lett.* **31** (1973) 35.
- [2] BAER, Y. and BUSCH, G., *J. Electron Spectrosc.* **5** (1974) 611.
- [3] STEINER, P., HÖCHST, H. and HÜFNER, S., *J. Phys. F : Metal Phys.* **7** (1977) L 145.
- [4] LINDAU, I., HELMER, J. C. and UEBBING, J., *Rev. Sci. Instr.* **44** (1973) 265.
- [5] PLATAU, A. and KARLSSON, S. E., *Phys. Rev.* **B 18** (1978) 3820.
- [6] HERBST, J. F., LOW, D. N., WATSON, R. E., *Phys. Rev. B* **6** (1972) 1913.
- [7] JOHANSSON, B., *Phil. Mag.* **30** (1974) 469.
- [8] JOHANSSON, B., *Phys. Rev. B* **12** (1975) 3253.
- [9] JOHANSSON, B., *J. Phys. F : Metal Phys.* **7** (1977) 877.
- [10] ZACHARIASEN, H. W., quoted by Lawson and Tang (1949), *J. Inorg. Nucl. Chem.* **35** (1973) 3487.
- [11] PAULING, L., quoted by SCHUCK, A. F. and STURDIVANT, J. H., *J. Chem. Phys.* **18** (1950) 145.
- [12] COOBLIN, B. and BLANDIN, A., *Adv. Phys.* **17** (1968) 281.
- [13] RAMIREZ, R. and FALICOV, R. M., *Phys. Rev. B* **3** (1971) 2925.
- [14] HIRST, L. L., *J. Phys. Chem. Solids* **35** (1974) 1285.
- [15] HILL, H. H. and KMETKO, E. A., *J. Phys.* **5** (1975) 1119.