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Electronic structure of Sm surface studied by synchrotron-radiation-excited-photoelectron spectroscopies

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Résumé. — Nous avons utilisé le rayonnement synchrotron entre 50 et 250 eV pour faire des mesures photoélectriques de grande sensibilité de surface pour Sm. Pour les photons de 150 eV, la distribution d'énergie des électrons de la bande de valence montre les caractéristiques aussi bien de 4f5 que de 4f6. Si l'absorption optique correspondant à la transition 4d → 4f est déterminée par le spectre du rendement photoélectrique (avec l'énergie de l'état initial fixée dans la structure 4f6) le résultat diffère remarquablement de celui obtenu pour l'absorption 4d10 4f5 → 4d9 4f6 intervenant en le volume. Nous attribuons le nouveau spectre à la présence à la surface d'atomes de Sm 4f6, permettant une transition 4d10 4f6 → 4d9 4f7.

Abstract. — We have utilized synchrotron radiation in the 50-250 eV range to make surface sensitive photoelectron measurements on Sm. For 150 eV photons the valence band photoelectron energy distribution shows both 4f5 and 4f6 structure. By constant initial state photoelectron yield spectroscopy we have measured separately the 4d → 4f photon absorption of 4f5 and 4f6 surface Sm atoms (see résumé).

Text. — Wertheim and coworkers [1, 2] have presented evidence from X-ray photoelectron spectroscopy (XPS) studies that Sm metal is mixed valent on its surface. In this XPS work, surface sensitivity was induced geometrically by changing the electron collection take-off angle away from the normal to the surface [2]. Greater surface sensitivity can be achieved more directly by choosing photon energies so that electrons are emitted with kinetic energies for which the escape depth is very short. Such is the case for a broad range of kinetic energies around 100-150 eV [3], and so we have made photoelectron spectroscopy measurements on Sm using synchrotron radiation in the range 50-250 eV. In this paper we summarize briefly the results of these measurements, which provide very direct spectroscopic evidence of both 4f5 and 4f6 surface atoms.

The measurements made are of three types; the photoelectron energy distribution for various photon energies, the photon absorption coefficient given by the partial photoelectron yield, and the photon absorption coefficient given by the constant initial state (CIS) yield. The two yield measurements differ in that the kinetic energy window is fixed for the partial yield, but is varied with the photon energy to maintain a constant photon energy-electron energy difference in the CIS yield. It is important to note that of the three measurements only the partial yield at low kinetic energy is bulk sensitive because inelastic electrons from deeper in the solid are a large fraction of those collected.

The experiments were performed at the Stanford Synchrotron Radiation Laboratory at the 4° beam line and the Sm films were prepared in situ by evaporation. The evaporation pressure was < 2 × 10⁻⁸ torr and the pressure during measurements was < 5 × 10⁻¹⁰ torr.

The experimental results are summarized below. (a) The valence band photoelectron energy distribution obtained with 150 eV photons (figure 1) shows spectral features characteristic of both 4f5 and 4f6 emission, as determined by comparison with the 4f spectra of solids with the Sm valence known [4]. The XPS spectrum of Sm [5] does not show the 4f6 cha-

![Fig. 1. — Valence band photoemission spectrum of Sm from 150 eV photons.](http://dx.doi.org/10.1051/jphyscol:19795120)
characteristic structure clearly [1]. We attribute the difference to the greatly enhanced surface sensitivity obtained in this range of kinetic energy.

(b) The 4d photoelectron emission obtained for our photon energies (not shown in a figure) is very weak, too much so for useful study of the primary emission process. The reason is that rare earth 4d photon absorption [6-8] in this energy range is dominated by the process $4d^{10} 4f^n \rightarrow 4d^{10} 4f^{n+1}$, with very tightly bound final states. The nature of the final state is known because the spectrum displays rich structure which is accounted for in detail as the multiplet splitting of the final state $4d^{9} 4f^{n+1}$ configuration [9].

(c) The partial yield spectrum using a kinetic energy window at 60 eV (figure 2a) is identical in detail with the bulk photon absorption spectrum of Sm [6-8]. We conclude that the partial yield is measuring a bulk photon absorption coefficient and that in the bulk there are Sm $4f^3$ atoms only.

(d) The CIS spectrum obtained with the initial state set in any of the valence band structure attributed to $4f^6$ emission (figure 2b) is new and quite different compared to the bulk absorption (figure 2a). We assign the new spectrum to $4d^{10} 4f^6 \rightarrow 4d^9 4f^7$ absorption by $4f^6$ surface Sm atoms. The $4d^9 4f^7$ state decays by elastic electron-electron scattering to $4d^1 4f^2 + \text{electron}$, the same final state as for direct $4f^6$ photoemission.

(e) The CIS spectrum obtained with the initial state set in the valence band $4f^5$ structure (figure 2c) is like that of figure 2a but with a contribution from the spectrum of figure 2b. The spectrum of figure 2a is expected because the absorption and decay processes $4d^{10} 4f^5 \rightarrow 4d^9 4f^6 \rightarrow 4d^{10} 4f^4 + \text{electron}$ produce the same final state as for direct $4f^5$ photoemission. The (2b) contribution is due to inelastic scattering of electrons emitted from $4f^6$ states, and possibly to some overlap of the $4f^3$ and $4f^6$ photoemission spectra.

We believe these results constitute strong direct spectroscopic evidence that on the surface of evaporated Sm films there are both $4f^3$ and $4f^6$ atoms. They also demonstrate that making photoelectron studies of rare earth metals or compounds using a continuum photon source in this energy range is a powerful technique for investigating surface valence change effects.

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