

Surface $4d \rightarrow 4f$ Photon Absorption and Surface Mixed Valence in Sm Metal

J. W. Allen

Xerox Palo Alto Research Center, Palo Alto, California 94304

and

L. I. Johansson

Stanford Synchrotron Radiation Laboratory, Stanford, California 94305

and

R. S. Bauer

Xerox Palo Alto Research Center, Palo Alto, California 94304

and

I. Lindau

Stanford Synchrotron Radiation Laboratory, Stanford, California 94305

and

S. B. M. Hagström

Xerox Palo Alto Research Center, Palo Alto, California 94304

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By constant-initial-state photoelectron-yield spectroscopy in the 50–250-eV photon energy range, we have measured separately the $4d \rightarrow 4f$ photon absorption of $4f^5$ and $4f^6$ Sm atoms on the surface of evaporated Sm films. The $4f^6$ and $4f^5$ electron emission shows two spectrally distinct enhancements corresponding to $4d^{10}4f^5 \rightarrow 4d^9 4f^6$ and $4d^{10}4f^6 \rightarrow 4d^9 4f^7$ transitions. Since bulk photon absorption and constant-final-state yield shows only the first spectrum, surface and bulk electronic configurations can be distinguished.

In this Letter we present experimental results from photoelectron-yield and energy-distribution measurements on Sm metal using photon energies between 50 and 250 eV, a range not used previously for photoelectron studies of rare-earth metals. The results provide very direct spectroscopic evidence for a surface mixed-valent state in Sm, and also reveal some intrinsically interesting photoelectron phenomena which combine to enable us, by means of constant-initial-state photoelectron-yield spectroscopy, to measure the $4d \rightarrow 4f$ photon absorption by atoms with a particular valence in the first layer of the Sm surface, and to distinguish this absorption from the bulk absorption.

Wertheim and co-workers^{1,2} have very recently presented evidence from x-ray photoelectron spectroscopy (XPS) studies for a surface mixed-valent layer in Sm. Wertheim and Campagna¹ observed that the $4d$ XPS spectrum of Sm metal films shows spectral features characteristic of both $4f^5$ and $4f^6$ Sm atoms, but also pointed out that the structure in the XPS spectrum of the $4f$ electrons themselves was ambiguous as to the presence of $4f^6$ atoms or their location relative to the surface. Wertheim and Crecelius² then showed by varying the takeoff angle in XPS meas-

urements that the spectral features ascribed to Sm $4f^6$ atoms increase in intensity relative to those of the Sm $4f^5$ atoms as the surface sensitivity of the XPS measurement is increased. Although these measurements are very persuasive, the identification of the surface valence states has not been made by means of a clear spectroscopic "fingerprint" obtained in a direct probe of the $4f$ electrons themselves. Our results fill this gap.

We have made three types of photoelectron spectroscopy measurements on Sm, utilizing synchrotron radiation in the photon energy range 50–250 eV. These measurements are the photoelectron energy distribution excited with various photon energies, the photon absorption coefficient given by the partial photoelectron yield,³ and the photon absorption coefficient given by the constant-initial-state (CIS) yield.³ The two yield measurements differ in that the kinetic energy of the collected electrons is fixed for the partial yield, but is varied with the photon energy to maintain a constant photon-energy-kinetic-energy difference, and hence a constant initial state, in the CIS yield. It is an important distinction in our three measurements whether or not inelastically scattered electrons are collected because

elastic electrons with kinetic energies in a broad range around 150 eV have very short escape depths, $\approx 4 \text{ \AA}$, providing excellent surface sensitivity.⁴ Thus, for our range of photon energy, the partial yield at low kinetic energy is the most bulk-sensitive measurement of the three because inelastic electrons from deeper in the solid are a large fraction of those collected. Similarly, the most surface-sensitive measurement of the three is the CIS yield with the initial state set just below the Fermi energy because almost no inelastically scattered electrons are collected. The CIS measurement, which has proven to be very useful in other contexts,³ here provides a means of selectively studying the electronic states in the surface layer.

The experiments were performed at the Stanford Synchrotron Radiation Laboratory at the 4^o beam line⁵ using a double-pass cylindrical-mirror energy analyzer. The Sm films were prepared *in situ* by evaporation onto various substrates. After a number of slow evaporations to outgas the Sm source a sample film was made by rapid evaporation during which the pressure was $\leq 2 \times 10^{-8}$ Torr. After the deposition the pressure dropped immediately to 2×10^{-9} Torr and decreased further to 5×10^{-10} Torr within two minutes. Valence-band photoemission spectra were taken periodically to check for oxygen *2p* emission or a deterioration of sharpness of spectral features. When this occurred a new film was prepared.

The valence-band photoelectron energy distri-

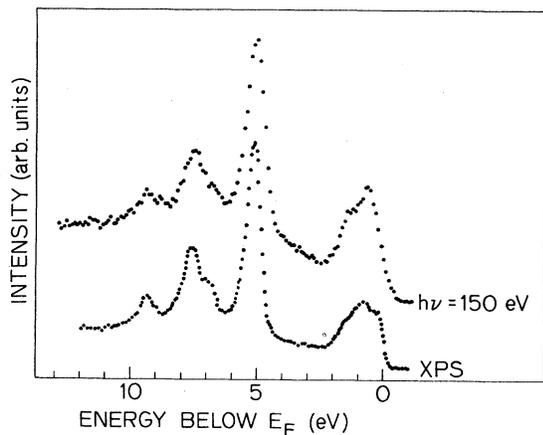


FIG. 1. Valence-band photoelectron energy distribution of Sm excited with 150-eV photons. Final-state multiplets of both $4f^5$ and $4f^6$ emission appear. Also shown is the XPS valence-band spectrum of Sm from Ref. 6; photon energy is 1487 eV ($Al K\alpha$).

bution obtained with 150-eV photons, shown in Fig. 1, is qualitatively similar to the XPS spectrum,⁶ also shown in Fig. 1. In both spectra the $4f^5$ emission with its $4f^4$ final-state multiplet structure⁷ is evident in the range 5–10 eV below the Fermi level. However, for the structure near the Fermi level, spectral features typical of $4f^6$ emission appear clearly in the 150-eV spectrum, in contrast to the ambiguity of the XPS spectrum. We attribute this difference to the enhanced surface sensitivity obtained for this range of electron kinetic energy, which permits observation of $4f^6$ emission from surface Sm atoms less obscured by bulk $5d$ emission. The $4f$ emission may also be increased relative to $5d$ emission by the resonant enhancement processes detected in our yield measurements, which are described next.

Very striking effects are obtained in the yield spectra. It is well known from bulk absorption measurements that $4d^{10}4f^n \rightarrow 4d^94f^{n+1}$ absorption occurs for the rare-earth metals in the photon energy range 100–200 eV.^{8,9} This absorption is highly structured, and the structure has been ac-

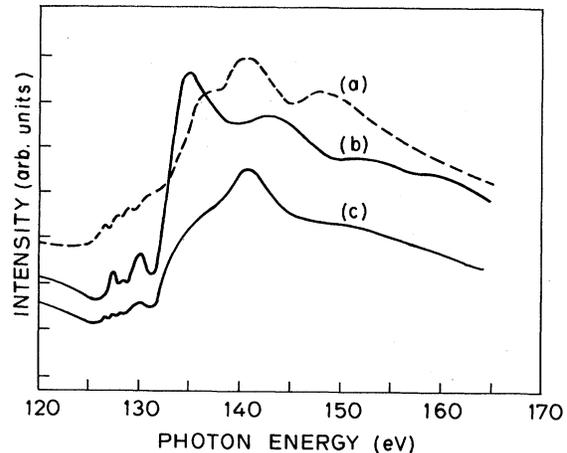


FIG. 2. Curve *a*: $4d \rightarrow 4f$ photon absorption measured by partial yield with 60-eV kinetic-energy window. The spectrum is identical to the bulk $4d^{10}4f^5 \rightarrow 4d^94f^6$ photon absorption spectrum of Fig. 3. Curve *b*: $4d \rightarrow 4f$ photon absorption given by constant-initial-state yield with the initial state set in the valence-band $4f^6$ structure. The spectrum is assigned to $4d^{10}4f^6 \rightarrow 4d^94f^7$ absorption. Curve *c*: $4d \rightarrow 4f$ photon absorption given by constant-initial-state yield with the initial state set in the valence-band $4f^5$ structure. The spectrum is that of curve *a* with a contribution from curve *b* due to inelastically scattered electrons. The vertical scales of the three curves are arbitrary, different, and offset from zero.

counted for in detail, including the relative intensities, by calculations of the $4d^9 4f^{n+1}$ multiplet spectrum.¹⁰⁻¹² Because the final $4f^{n+1}$ states are tightly bound and highly localized, direct $4d$ photoemission for these photon energies is too weak to be usefully studied. However, the lack of $4d$ emission is more than compensated for spectroscopically by a large contribution of elastic Auger decay of the $4d^9 4f^{n+1}$ state to emission of valence-band electrons.¹³ The partial-yield spectrum using a kinetic energy window at 60 eV is shown in Fig. 2, curve *a*, with the Sm bulk absorption spectrum⁹ shown for comparison in Fig. 3, curve *a*. It is obvious that, apart from a difference in resolution, the two spectra agree even in the details of the fine structure, as shown in Figs. 3, curves *b* and *c*. We conclude that the partial yield is measuring a bulk photon absorption due to $4d^{10} 4f^5 - 4d^9 4f^6$ transitions and that in the bulk there are Sm $4f^5$ atoms only.

Figure 2, curve *b*, shows the CIS yield spectrum obtained with the photon-energy-kinetic-energy difference fixed to place the initial state in the very first peak (below the Fermi energy) of the valence band. Recall that this peak is part of the structure attributed above to emission from surface $4f^6$ atoms. Although this CIS spectrum shows the general features observed for $4d - 4f$ transitions into less-than-half-filled $4f$ shells (weak sharp structure followed by strong broader structure) the details of the structure differ completely from those of the spectrum of Fig. 2,

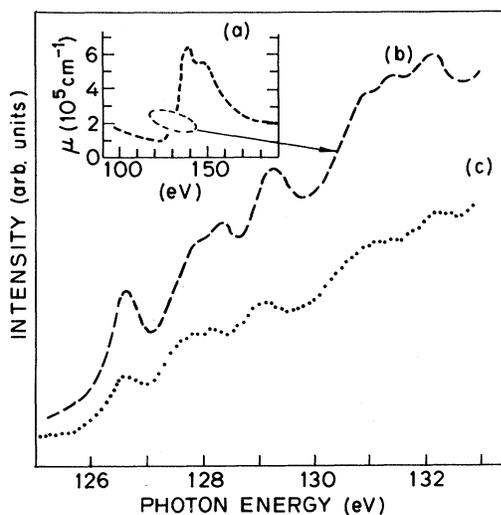


FIG. 3. Curves *a* and *b*: The bulk $4d \rightarrow 4f$ absorption spectrum of Sm (Ref. 9). Curve *c*: Fine structure of curve *a* of Fig. 2, for comparison with curve *b*.

curve *a*. Keeping in mind the fingerprint character of a particular multiplet spectrum, we conclude from the observation of a new spectrum in this photon energy range that a different $4f$ valence state is present, and we assign the spectrum to $4d^{10} 4f^6 - 4d^9 4f^7$ transitions in $4f^6$ surface Sm atoms. The $4d^9 4f^7$ state decays elastically via the Coulomb interaction to $4d^{10} 4f^5 + \text{electron}$. Thus, the same final state is obtained as for direct photoemission from the $4f^6$ initial state. Placement of the initial state in any of the $4f^6$ valence-band peaks yields a CIS spectrum with the same spectral features. We note that the $4d - 4f$ absorption process preserves the number of electrons on a Sm atom, implying that the two $4d - 4f$ absorption spectra are separated not by a Coulomb correlation energy as with the $4f^n$ and $4f^{n-1}$ photoemission spectra, but by differences in correlation energies, the most important probably being that between the $4f - 4d$ and $4f - 4f$ energies, $U_{fd} - U_{ff}$. From the observed absorption thresholds' separation this difference is only 1-2 eV.

The arguments of the preceding paragraph imply that if the initial state is placed in the valence-band $4f^5$ structure, the CIS spectrum should again have the appearance of the $4d^{10} 4f^5 - 4d^9 4f^6$ absorption spectrum as a result of the elastic decay process $4d^9 4f^6 - 4d^{10} 4f^4 + \text{electron}$, the same final state as for direct photoemission from the $4f^5$ initial state. This is almost the case, as shown by the CIS spectrum of Fig. 2, curve *c*, for which the initial state is the first of the $4f^5$ peaks below the Fermi energy. The spectrum is mainly like that of Fig. 2, curve *a*, but with a contribution from the spectrum of curve *b*. This contribution results from unavoidable inelastic scattering processes which allow electrons emitted from $4f^6$ states to leave the solid with the lower kinetic energy corresponding to the deeper initial state used. The $4f^5$ valence-band emission and the $4f^5$ CIS spectrum, both of which result from a surface-sensitive measurement, lead us to conclude that there are also $4f^5$ Sm atoms on the surface, so that the surface has both divalent and trivalent Sm. Whether the valence mixing is homogeneous or inhomogeneous cannot be determined by a high-energy probe such as photoemission.

It is a possible argument that, for unknown reasons, the two CIS spectra could differ simply because the states near the Fermi level have $5d$ character and not because of a new $4f$ valence state. We have rejected this possibility on the

basis of our measurements on Tm metal films. In Tm our valence-band spectra are essentially identical to XPS spectra,⁶ showing weak $5d$ emission near the Fermi energy and $4f^{12}$ emission at higher binding energy. The partial-yield and CIS spectra with either $4f$ or $5d$ initial states are all similar to bulk $4d-4f$ absorption spectra.^{8,9} Thus, the $4d^9 4f^{13} (5d6s)^3$ final state of the photon absorption can decay either to $4d^{10} 4f^{11} (5d6s)^3 + \text{electron}$ or to $4d^{10} 4f^{12} (5d6s)^2 + \text{electron}$. These results also show that Tm has no unusual surface valence changes, a possibility raised by Wertheim and Crecelius.²

Finally, we note that a complete experimental demonstration of our assignment entails comparison with a known $4d^{10} 4f^6 - 4d^9 4f^7$ absorption spectrum. Such a spectrum is not obtainable from any bulk rare earth, and will require further measurements on Sm compounds in which Sm is known to be divalent. Ours is the first observation of this particular $4d-4f$ absorption spectrum.

In summary, we have presented the results of photoelectron spectroscopy measurements on Sm (and Tm) metal using photon energies in the range 50–250 eV, a range not previously used for any rare-earth metal. We find strong contributions to valence-band emission from $4d-4f$ absorption, followed by elastic Auger decay. By CIS spectroscopy we are able to isolate and observe the $4d-4f$ absorption spectra of both $4f^5$ and $4f^6$ surface Sm atoms, providing strong, direct spectroscopic evidence of surface valence mixing in evaporated Sm films. More generally, it appears that photoelectron spectroscopy using photon energies in the 50–250-eV range will be a powerful tool for studying the very interesting

phenomenon of rare-earth surface-valence-change effects.

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Transition from Type-II to Type-I Superconductivity with Magnetic Field Direction

H. W. Weber, J. F. Sporna, and E. Seidl

Atominstytut der Österreichischen Universitäten, A-1020 Vienna, Austria

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We report on a new effect in superconductivity and demonstrate experimentally that, because of the correlation of the upper critical field H_{c2} with crystal directions in single-crystalline TaN samples (anisotropy effect), at certain fixed temperatures the material is a type-I superconductor near the [100] and a type-II superconductor near the [111] directions.

Previous experimental work on the magnetic properties of superconductors has shown that high-purity type-I superconductors ($\kappa < 1/\sqrt{2}$, ρ_n

$\propto 1/l - 0$) may be converted into type-II superconductors ($\kappa > 1/\sqrt{2}$), e.g., by alloying thallium to lead¹⁻³ or by introducing nitrogen into tantalum.⁴