Possible interpretation of the photoelectron spectrum for americium metal

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An interpretation of the valence-band photoelectron spectrum for americium metal is attempted. This involves a bulk as well as a surface $f^6 \rightarrow f^5$ photoionization process. The surface contribution is shifted by 0.6 eV relative to the bulk peak. Furthermore, the experimental peak at 1.8 eV is interpreted as originating from divalent americium atoms at the surface.

Many properties suggest that americium metal has localized $5f$ electrons and essentially behaves like a normal trivalent rare-earth element. Examples of these properties are atomic volume,[1] crystal structure,[1] compressibility,[2] cohesive energy,[3] magnetic properties,[4] superconductivity,[5] high-pressure behavior,[6] specific heat,[7] and melting temperature.[8,9] Also detailed theoretical calculations strongly support this localized picture of the $5f^6$ configuration.[10]

Recent photoelectron spectra for americium[11] have shown that the $5f$ level is totally withdrawn from the Fermi energy and the spectra show strong similarities to the spectra of the lanthanide metals.[12] This is in contrast to the case of plutonium,[11] the element preceding americium in the actinide series, where the $5f$ emission extends all the way up to the Fermi level. This drastic change in behavior is indeed a strong confirmation of $5f$ localization in americium. Realizing that between plutonium and americium one witnesses a tremendous change in the $5f$ properties, which as a function of atomic number can be considered a Mott transition,[13] it becomes most important that the $5f$ emission in americium is understood in detail.[11,14,15] In the present contribution we propose a *possible identification* of the various contributions to the photoelectron spectrum for americium metal. Unfortunately, it is at present not possible to give a totally unequivocal interpretation of all the observed features. Nevertheless, due to the importance of the americium spectrum it is worthwhile to present a tentative identification scheme, which could be helpful as a guide for future experimental and theoretical work. A previous paper[15] in this direction was devoted to the energy position of the $5f$ level in bulk americium metal. Here we will extend this treatment so that we consider the complete multiplet contribution and not just the lowest-lying energy level.

Figure 1 shows the He II—($h\nu = 40.8$ eV) excited photoelectron spectrum of Am metal.[11] The sample was cleaned by argon-ion etching. However, due to segregation of oxygen from the bulk, no annealing of the sample could be performed. The spectrum is dominated by a broad double structure at 2—3-eV binding energy. Furthermore, a relatively sharp feature at 1.8 eV is clearly resolved.

Trivalent americium will have an electronic configuration $5f^6(6d\,7s)^3$, where the $5f$ electrons are localized. In the ground state the $5f$ electrons couple to give a nonmagnetic $J = 0$ state. The three $(6d\,7s)^3$ electrons form the conduction band just like the $(5d\,6s)^3$ electrons in the trivalent rare-earth metals. In the valence-band spectrum for americium we therefore expect a contribution from
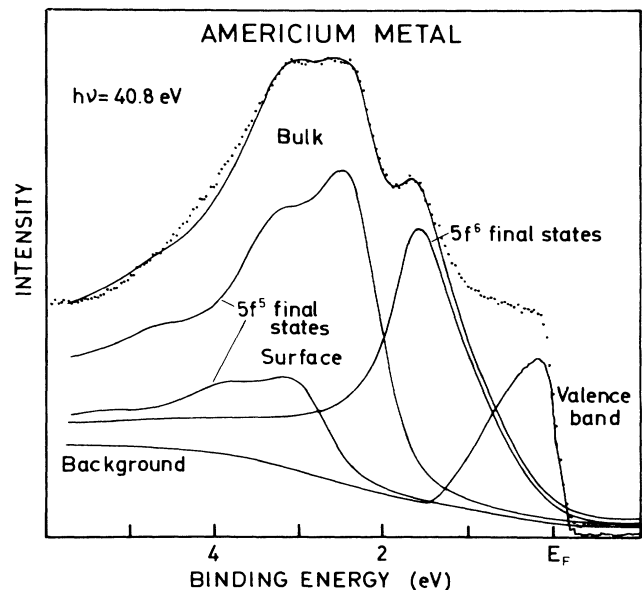

FIG. 1. The He II—excited photoelectron spectrum from Am metal is analyzed in terms of two shifted and broadened $5f^5$ final-state multiplets representing bulk and surface emission, respectively, and a broadened $5f^6$ final-state structure (see text). Subtraction of these contributions yields a 1.5-eV broad feature at E_F which is interpreted as the Am d-band emission. The inelastic background is assumed to be proportional to the integrated intensity at higher kinetic energies.

the $(6d\,7s)^3$ electrons as well as from the localized $5f^6$ electrons. The conduction-electron contribution will, due to differences in cross sections, be dominated by $6d$ electrons. This d band extends somewhat more than 2 eV below the Fermi energy[10] and might give rise to rather sharp features in high-resolution spectra. Such features have, for example, been observed in the valence-band spectra for ytterbium and lutetium.[16,17]

The contribution from the $5f^6 \rightarrow 5f^5$ ionization will also be rather extended in energy due to the energy separations between the final-state multiplet levels.[17] The spectral shape for the $f^6 \rightarrow f^5$ photoionization process has been calculated by Gerken and Schmidt-May.[18] From its form (see curve denoted $5f^5$ final states in Fig. 1) it is clear that this contribution alone *cannot* account for the experimental spectrum.[11]

Due to the high surface sensitivity obtained with He II excitation it is clear that the observed spectrum contains not only contributions from bulk americium atoms, but also a substantial contribution from surface atoms. Theoretical considerations for the rare-earth elements showed that a surface shift of about $+0.4$ eV is to be expected for these metals.[19,20] Experimentally one has found shifts varying from about 0.4 eV in the early lanthanides up to 0.7 eV in lutetium.[21] For americium one would on the same theoretical grounds expect a surface shift of similar magnitude. If a surface contribution (shifted by 0.6 eV) with 30% of the bulk intensity is added, one reproduces quite well the spectrum in the 2—3-eV range (compare Fig. 1).

The remaining unexplained feature is located at 1.8 eV below the Fermi energy. Since americium is the sister element to europium one certainly expects tendencies towards divalency in this actinide element.[15] This tendency should be enhanced at the surface, something which has actually been observed for samarium metal.[22] Samarium is a trivalent metal in the bulk and has on its surface a divalent layer.[19,23,24] Assuming that at least part of the americium surface atoms are divalent we include also a calculated $f^7 \rightarrow f^6$ contribution to the interpretation of the spectrum. As seen in Fig. 1, such a contribution can very well explain the 1.8-eV peak. Furthermore, the lowest multiplet level of the final f^6 configuration is then situated only 0.1 eV below the Fermi level, consistent with a just barely stable divalent state at the surface. However, in Ref. 15 doubts were raised about whether a planar surface of americium could indeed become divalent. Only for a very rough surface should one expect some divalency. However, the experimental spectrum in Fig. 1 was obtained after argon sputtering and without annealing, a treatment which is known to produce rough surfaces.

Furthermore it cannot be totally excluded that the 1.8-eV signal is extrinsic, namely due to some impurities which at the surface facilitate the formation of some divalent americium.

A divalent state should also be observable in the core-level spectrum. The experimental $4f$ spectrum of americium[11] contains a main line as well as a weak contribution at 4-eV less binding energy. This peak has been interpreted as a shakedown satellite,[11,15] similar to what has been observed for lanthanum, cerium, praseodymium, and neodymium.[25] However, a divalent americium atom would have a $4f$ binding energy close to this satellite position. Thus, unfortunately, it is not possible to use the $4f$ core-level spectrum to answer the question about a partly divalent americium surface.

Another possible interpretation of the 1.8-eV feature can be obtained from a comparison with the $4f$ contribution in the valence-band spectrum for cerium metal.[26] In cerium one observes two features, one d-screened $4f$ signal located quite far from the Fermi energy and a $4f$ screened hole close to the Fermi energy.[27-29] Thus the 1.8-eV feature in americium could be looked upon as a $5f$ screened final state, i.e., $5f^6 \rightarrow 5f^5 5f^1$. Unfortunately, nothing is presently known about the distribution among the various final-state multiplets for such a process, which makes it impossible to judge if this is a reasonable interpretation or not. In the low-photon-energy spectra He I ($h\nu = 21.2$ eV), there are also structures observed rather close to the Fermi surface.[11] Again, this might be due to a $5f$ screened state. However, it might also originate from $6d$ conduction-band states which are now more clearly seen in the spectrum because of less dominance of the $5f$ contribution at these low-photon energies. The He I spectrum was furthermore recorded at better resolution. We also note in Fig. 1 that after subtracting the $5f$ emission features which are used to explain the peaks at 1.8 and 2—3 eV, one obtains a 1.5-eV broad structure closest to the Fermi level which has the shape expected for the d emission from a trivalent metal.

In summary we have tried to give an interpretation of the experimental valence-band photoelectron spectrum for americium metal. This involved a bulk and a surface $f^6 \rightarrow f^5$ contribution. Furthermore, a divalent surface peak was also proposed ($f^7 \rightarrow f^6$) but for which much less certainty could be achieved. The lowest-level position for the bulk $f^6 \rightarrow f^5$ ionization was found to be 2.3 eV, which agrees quite well with the theoretical calculation in Ref. 15.

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