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Localization of 5f Electrons in Americium: A Photoemission Study

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X-ray and high-resolution uv photoemission spectroscopy of the conduction band of Am metal directly reveal that the 5f electrons in Am are localized, in contrast to the 5f electrons in the lighter actinide metals. The observed 5f final-state multiplet structure arises from a trivalent $5f^6$ Am ground state. The withdrawal of the 5f electrons from the Fermi level is also manifested in the core-hole screening mechanism: The 4f core-level spectrum shows the poorly screened peak (s,d electrons) to be the most intense one.

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It has been suggested[1,2] that the 5f electrons for the lighter actinides are itinerant and take part in the chemical bond whereas the 5f electrons of the heavier actinide metals are localized. The solid-state properties of Am indicate that Am is the first rare-earth-like metal in the actinide series.[3] Theoretical calculations[4] have also supported the localized picture for Am. The ground-state electron configuration is assumed to be $5f^6$ (nonmagnetic). Previous valence-band photoemission spectra of U metal[5-9] provided clear evidence for the itinerant character of the 5f electrons, which were identified to be at the Fermi level. Mainly because of the radiation hazard of the heavier actinide metals, only for Pu metal[10-12] have low-resolution x-ray photoemission spectroscopy (XPS) measurements been published supporting the itinerant description of the 5f states.

To examine where the 5f electrons become localized in the actinide series we modified a Leybold-Heraeus LHS-10 photoemission spectrometer, enclosed in glove boxes to enable XPS and, in particular, high-resolution ultraviolet photoemission spectroscopy (UPS) measurements on highly radioactive material.[13] In this Letter, we present photoemission spectra of the 4f core levels (XPS) and of the conduction band (XPS, UPS) of Am metal, which holds a key position in the actinide series.

Polycrystalline films of Am metal (5 μm thick) were condensed by evaporation on W substrates[14] and afterwards transferred to the photoemission spectrometer. The surface Am oxide layer was removed *in situ* by Ar-ion sputtering. Conduction-band data were recorded at room temperature with an energy resolution of 1.30 eV (XPS, Mg $K\alpha$ line) and 0.12 to 0.17 eV (He I and He II lines, respectively); the Am 4f core levels were recorded with an energy resolution of 1.0 eV (XPS, Mg $K\alpha$ line). The base pressure was in the low 10^{-9} Pa range. After repeated sputtering cycles no oxygen surface contamination was detectable in XPS (O 1s emission), but was in UPS (O 2p emission); the O 2p signal was slowly growing in time as a result of segregation of oxygen to the surface. To improve statistics several sets of spectra were recorded directly after sputter cleaning. By calculating the difference spectra the weak oxygen contribution was determined and finally subtracted.

The conduction-band spectra of Am metal (Fig. 1) show for increasing photon energy that the emission at the Fermi energy E_F becomes less important compared to that of the structured peak around 2.8-eV binding energy (for Mg $K\alpha$ excitation, Fig. 1, curve d, the structures are not resolved). The photon-energy–dependent excitation probability for f electrons in the UPS regime[15] and the order-of-magnitude–higher probability for 5f electron excitation compared to that for 6d and 7s electrons in the XPS regime[16] give unambiguous evidence of the 5f character of the emission around 2.8 eV; i.e., the 5f electrons are withdrawn from the Fermi level. This is a direct verification of 5f electron localization in Am, and confirms that Am metal is indeed the first rare-earth-like metal in the actinide series.

Because of localization of the electrons in the partially filled 5f shell, a fingerprintlike final-state multiplet structure is expected in the photoemission spectrum, as for rare-earth metals.[17,18] Final-state photoemission intensities for actinides have been calculated including spin-orbit interaction ($5f^3$ through $5f^8$, and $5f^2$, $5f^3$, and $5f^{13}$ initial configuations, Veal *et al.*[19] and Beatham *et al.*,[20] respectively). The results for the $5f^3$ state disagree considerably. One calculation[20] yields a slight intensity rearrangement when changing the main quantum number or the coupling. The other calculation[19] produces many intense multiplet lines even at high binding energies, extending, e.g., for the $5f^6$

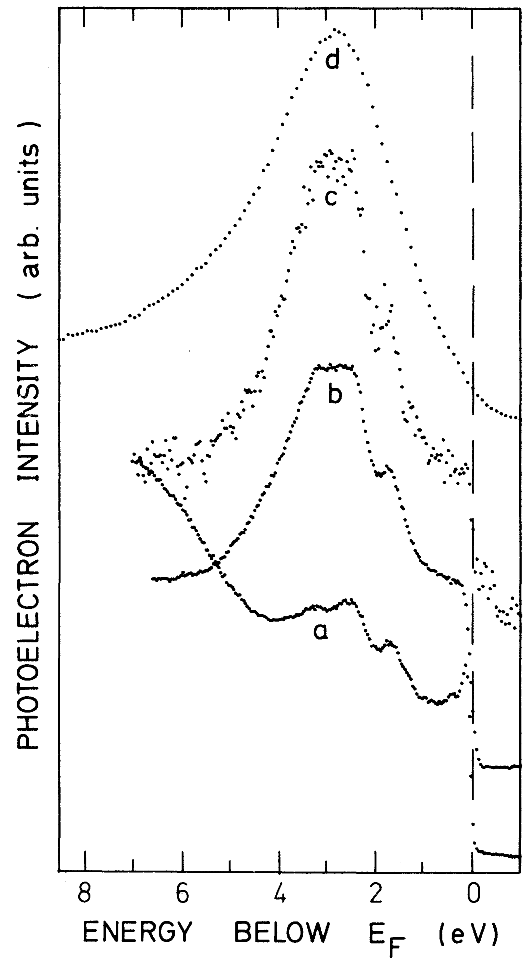

FIG. 1. UPS/XPS conduction-band spectra of Am metal for (a) 21.1, (b) 40.8, (c) 48.4, and (d) 1253.6 eV excitation energy.

configuration, to energies as high as 15 eV. High-resolution UPS valence-band spectra of actinide oxides,[21] exhibiting localized $5f$ electrons, do not display high-energy multiplet components but a single broad $5f$ emission close to E_F. We therefore compare in Fig. 2 the UPS conduction-band spectra of Am to that of Sm[22] which displays a final-state multiplet quartet for the "trivalent" bulk ($4f^5$ initial configuration) and a triplet for the "divalent" surface ($4f^6$ initial configuration). Optical absorption spectra of $PuCl_3$ ($5f^5$ state) reveal an energy separation between the ^6H and ^6P levels of 2.4 eV[23] (Sm metal, 4 eV). A surface-induced energy shift and broadening of the triplet or even a contribution from divalent surface ($5f^7$ initial configuration, broad single line) may modify the relative intensity of the multiplet structure of Am. The energy position of the $5f$ electrons for "trivalent" Am metal has been recently calculated[24] under the assumption of electron screening of the photoionized Am atom ("tetravalent" Am) in a "trivalent" surrounding. The value of 2.0 eV for the energy position of the ^6H final-state multiplet component is in good agreement with the experimental value of 1.8 eV.

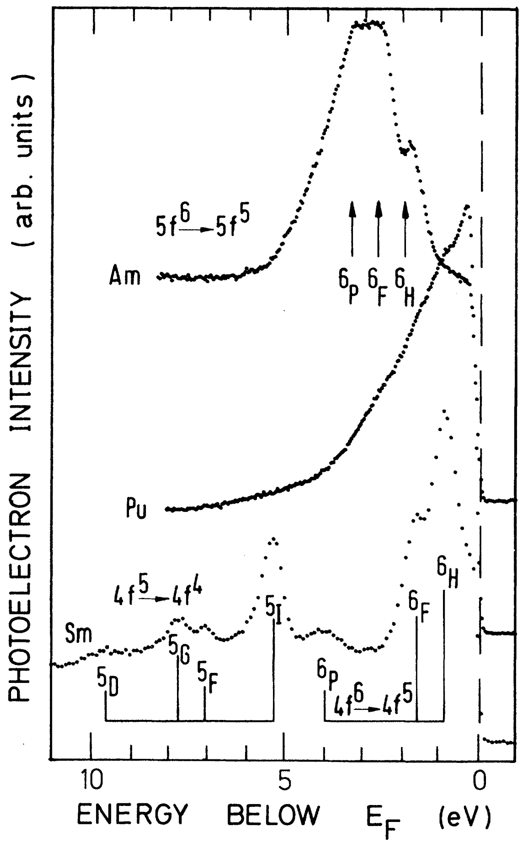

FIG. 2. Conduction-band spectra of Am, Pu, and Sm metal for 40.8-eV excitation.

To show the different character of the $5f$ electrons the UPS valence-band spectrum of Pu[25] has been added in Fig. 2. In contrast to Am the strongest emission for Pu is just found at E_F and is due to itinerant $5f$ electrons. No final-state multiplet structures representative of localized $5f$ electrons (f^5 initial configurations as for trivalent Sm) can be detected; structures at 0.8, 1.5, and 2.5 eV are difficult to attribute either to electron density of states or to beginning $5f$ electron localization.

The actinide $4f$ core levels also reflect the degree of $5f$ electron localization by the screening mechanism[26,27]: The $4f$ core-hole potential pulls screening levels, that are not occupied in the ground state (i.e., above E_F), down below E_F into the occupied part of the conduction band. The occupation of these levels, either by $5f$ or by $\{6d, 7s\}$ electrons,

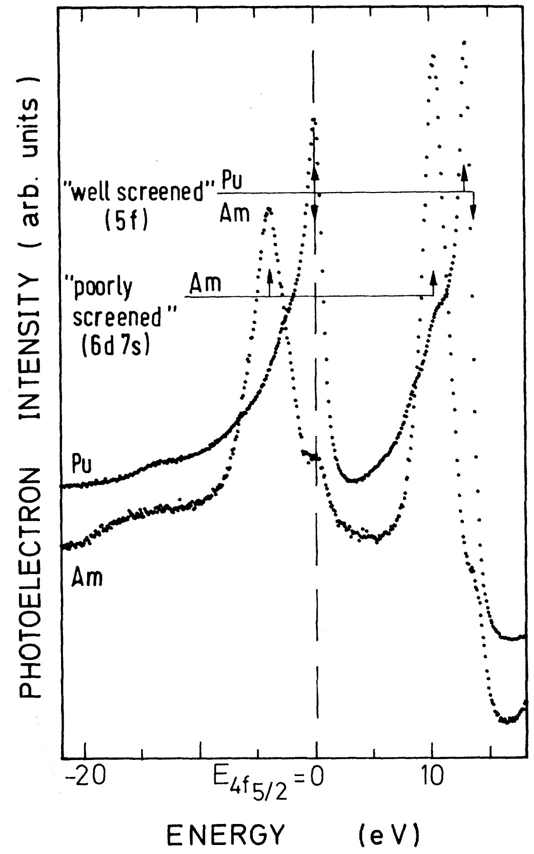

FIG. 3. XPS $4f$-core-level spectra of Am and Pu metal.

lowers the total energy of the final state characteristically; the occupation probability depends critically on the hybridization with the conduction states in the initial state ($5f$ states delocalized, $4f^{13}5f^7\{6d,7s\}^3$ final state: "well screened" peak at low binding energy; $5f$ states localized, $4f^{13}5f^6\{6d,7s\}^4$ final state: "poorly screened" peak at high binding energy). The $4f$ core levels of Am metal are shown in Fig. 3. The spectrum is dominated by nearly symmetric $4f_{5/2}$ and $4f_{7/2}$ lines; each line is accompanied by a satellite at 4 eV lower binding energy which has not been previously observed for any actinide. The main peak is attributed to "poor screening" by $\{6d, 7s\}$ conduction electrons. The satellite is due to "good screening" by $5f$ electrons; its intensity is weak since the $5f$ hybridization is poor, i.e., the $5f$ states are almost completely localized. The energy position of the satellite has been recently calculated[24] to be 3.8 eV, in good agreement with the experimental result.

For comparison the $4f$ core levels of Pu metal are also shown in Fig. 3. The spectrum is dominated by a very asymmetric $4f$ doublet corresponding to good screening by bandlike $5f$ electrons. Because of the very high density of $5f$ states at E_{F} a large number of low-energy electron-hole pairs are generated along with the photoemission process, inducing the strong asymmetry[28] of the $4f$ core lines. The origin of the 2.5-eV satellite on the high-binding-energy side of the Pu $4f_{5/2}$ line is not quite clear at the moment. It may be either induced by a very weak oxygen contamination[29] or due to poor screening by $\{6d, 7s\}$ electrons. Even if the small structure is a genuine satellite due to poor screening, the dominant screening is by itinerant $5f$ electrons.

Thus photoemission conduction-band as well as $4f$-core-level spectra show clearly that Am is the first elemental metal in the actinide series that has localized $5f$ electrons like a rare-earth metal. The comparison of Am and Pu metal proves that the transition from delocalized to localized $5f$ behavior in fact takes place between Pu and Am.

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[1] A. J. Freeman and D. D. Koelling, in *The Actinides: Electronic Structure and Related Properties,* edited by A. J. Freeman and J. B. Darby, Jr. (Academic, New York, 1974).

[2] B. Johansson, Phys. Rev. B. **11**, 2740 (1975).

[3] See, e.g., H. L. Skriver, O. K. Andersen, and B. Johannsson, Phys. Rev. Lett. **44**, 1230 (1980).

[4] H. L. Skriver, O. K. Andersen, and B. Johansson, Phsy. Rev. Lett. **41**, 42 (1978).

[5] J. C. Fuggle, A. F. Burr, W. Lang, L. M. Watson, and D. J. Fabian, J. Phys. F **4**, 335 (1974).

[6] Y. Baer and J. K. Lang, Phys. Rev. B **21**, 2060 (1980).

[7] H. Grohs, H. Höchst, P. Steiner, S. Hüffner, and K. H. J. Buschow, Solid State Commun. **33**, 573 (1980).

[8] M. Iwan, E. E. Koch, and F.-J. Himpsel, Phys. Rev. B **24**, 613 (1981).

[9] G. C. Allen, I. R. Trickle, and P. M. Tucker, Philos. Mag. B **43**, 689 (1981).

[10] D. T. Larson, J. Vac. Sci. Technol. **17**, 55 (1980).

[11] L. E. Cox and J. W. Ward, Inorg. Nucl. Chem. Lett. **17**, 265 (1981).

[12] R. Baptist, D. Courteix, J. Chayrouse, and L. Heintz, J. Phys. F **12**, 2103 (1982).

[13] J. R. Naegele, to be published.

[14] J. C. Spirlet and W. Müller, J. Less-Common Met. **31**, 35 (1973).

[15] D. E. Eastman and M. Kuznietz, Phys. Rev. Lett. **26**, 846 (1971).

[16] J. H. Scofield, J. Electron Spectrosc. **8**, 129 (1976).

[17] J. K. Lang, Y. Baer, and P. A. Cox, J. Phys. F **11**, 121 (1981).

[18] F. Gerken, J. Phys. F **13**, 703 (1983).

[19] B. W. Veal, D. J. Lam, H. Diamond, and H. R. Hoekstra, Phys. Rev. **15**, 2929 (1977).

[20] N. Beatham, P. A. Cox, A. F. Orchard, and I. P. Grant, Chem. Phys. Lett. **63**, 69 (1979).

[21] J. R. Naegele and L. Manes, Lawrence Berkeley Laboratory Report No. 12441, 1981 (unpublished), p. 69.

[22] J. R. Naegele, unpublished results; a thin film of Sm metal was evaporated at a base pressure of 2×10^{-8} Pa; after short *in situ* sputter cleaning the photoemission spectra were recorded showing the multiplet structures as reported previously for an excitation energy of 35 eV [F. Gerken, J. Barth, R. Kammerer, L. I. Johansson, and A. Flodström, Surf. Sci. **117**, 468 (1982)].

[23] W. T. Carnall, P. R. Fields, and R. G. Pappalardo, J. Chem. Phys. **53**, 2922 (1970).

[24] B. Johansson, to be published.

[25] J. R. Naegele, K. Richter, L. Manes, and W. Müller, Douzièmes Journées des Actinides, Orsay, France, 1982 (unpublished).

[26] J. C. Fuggle, M. Campagna, Z. Zolnierek, R. Lässer, and A. Platau, Phys. Rev. Lett. **45**, 1597 (1980).

[27] F. U. Hillebrecht and J. C. Fuggle, Phys. Rev. B **25**, 3350 (1982).

[28] S. Doniach and M. Sunjic, J. Phys. C **3**, 285 (1970).

[29] This may be the case even if no oxygen $1s$ signal is observed because the Pu $4f$ core levels indicate an oxygen contamination with much higher sensitivity. The doublet satellite on the high-binding-energy side of the Pu $4f_{7/2}$ line is due to the $K\alpha_{3,4}$ satellite of the Mg x-ray source.