RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 30, NUMBER 6 15 SEPTEMBER 1984

Energy position of the $5f$ level in americium metal

Börje Johansson
Institute of Physics, University of Aarhus, DK-8000 Aarhus C, Denmark
(Received 4 June 1984)

The energy position of the $5f$ level relative to the Fermi energy is calculated for the trivalent actinide metals and compared with recent photoemission experiments for americium. Also, the energy position of the (shakedown) satellite relative to the main $4f_{7/2}$ core-level line in americium is calculated.

During the last decade it has become increasingly clear that the $5f$ electrons are itinerant (metallic) for the earlier actinide metals (protactinium, uranium, neptunium, and plutonium).[1-9] One important piece of evidence for such a behavior has been obtained from photoelectron spectroscopic experiments on U (Refs. 10–12) and Pu (Refs. 13 and 14), where the measured valence-band density of states clearly demonstrates that the occupied $5f$ orbitals have energies that extend all the way up to the Fermi level.[15] It has been suggested[4,7] that as a function of atomic number a Mott transition of the $5f$ electrons takes place between plutonium and americium, and that a localized rare-earth-like behavior of the $5f$ electrons begins in the actinide series for the metals beyond plutonium.[2,5] This picture led to the prediction of superconductivity in americium,[5] which was later verified experimentally by Smith and Haire.[16] Also detailed theoretical calculations have supported this localization picture for americium.[8,9] Very recently, photoelectron spectroscopic studies have been performed for the americium metal.[17] In these experiments it was found that the $5f$ level is indeed withdrawn from the Fermi energy. This type of electron spectrum is very well known from studies of the rare-earth metals,[18] and the results by Naegele, Manes, Spirlet, and Müller[17] provide a direct verification of the $5f$ localization in americium. In the present Rapid Communication we will present theoretical calculations for some of the features obtained from the americium x-ray and ultraviolet photoelectron spectroscopy (XPS and UPS) spectra.

When the $5f$ electrons are localized, they are expected to behave just as the $4f$ electrons in the lanthanide metals and should, therefore, be considered as inert as far as the cohesive properties are concerned. For the lanthanide metals the experimental position of the $4f$ level relative to the Fermi energy is now well understood.[19,20] This theoretical understanding has been achieved by application of the complete screening picture for the final state in the excitation of a localized core electron.[21,22] The meaning of this model is that the conduction electrons respond to the disturbance produced by the photoionization process in such a way as to give a screened charge-neutral final state at the core-excited site. Therefore, if the initial state of the metallic site to become photoionized has a $5f^n[6d7s]^3$ configuration (where the square brackets denote the metallic state of the "sd"-valence band and $5f^n$ stands for a localized configuration), the final state of this site after a $5f$ electron ionization becomes $5f^{n-1}[6d7s]^4$. Effectively the atom subject to $5f$ electron photoionization has become converted from a trivalent to a tetravalent metallic state. It should be kept in mind, however, that the tetravalent final state resides in a surrounding of trivalent metal atoms; i.e., it is an impurity in the otherwise perfect trivalent metal. Therefore, the $5f$ binding energy relative to the Fermi energy $\epsilon(f\rightarrow\epsilon_F)$ can be written as[20]

$$\epsilon(f\rightarrow\epsilon_F)=\Delta E_{\text{III,IV}}+E_{\text{IV}}^{\text{imp}}(\text{III}) \quad . \tag{1}$$

The first term $\Delta E_{\text{III,IV}}$ describes the energy required to transform the trivalent site (in a trivalent surrounding) into a tetravalent site (in a tetravalent surrounding). Since the final state is a tetravalent impurity in a trivalent host, we have to include the heat of solution, $E_{\text{IV}}^{\text{imp}}(\text{III})$, of a substitutional tetravalent metallic atom in the trivalent host. The formula for the f photoionization energy in Eq. (1) has been applied to the rare-earth metals and a very good agreement with experiments was found for all of them.[20] In that study it was also noticed that the impurity term in Eq. (1) only has a minor influence on the excitation energy and for the present investigation of the rare-earth-like trivalent actinides we will, to begin with, neglect this term. What remains to be calculated is then just the energy difference between the trivalent and the (hypothetical) tetravalent state, $\Delta E_{\text{III,IV}}$. In a different context, this quantity has been considered in some detail in Ref. 7, where it was found that $\Delta E_{\text{III,IV}}(\text{Am})\simeq 50$ kcal/mol, $\Delta E_{\text{III,IV}}(\text{Cm})\simeq 74$ kcal/mol, $\Delta E_{\text{III,IV}}(\text{Bk})\simeq 34$ kcal/mol, and $\Delta E_{\text{III,IV}}(\text{Cf})\simeq 56$ kcal/mol. From this we directly obtain from Eq. (1) the following position of the $5f$ level relative to the Fermi energy (for the lowest final-state multiplet level), $\epsilon(f\rightarrow\epsilon_F)(\text{Am})\simeq 2.2$ eV, $\epsilon(f\rightarrow\epsilon_F)(\text{Cm})\simeq 3.2$ eV, $\epsilon(f\rightarrow\epsilon_F)(\text{Bk})\simeq 1.5$ eV, and $\epsilon(f\rightarrow\epsilon_F)(\text{Cf})\simeq 2.4$ eV. The corresponding experimental value for Am was found to be 1.8 eV,[17] which is in fairly good agreement with our calculated value of 2.2 eV. The impurity term in Eq. (1) was for the trivalent rare-earth metals found to be about -0.2 eV,[20] and is likely to be very similar for the rare-earth-like trivalent actinide metals. Adding this correction to the calculated value for the $5f$ position in americium, we obtain a good agreement with the experimental data.

It should, however, be noted that the interpretation of the experimental UPS data for americium is not quite straightforward. Thus, the calculated line shape[23] for the $5f^6\rightarrow 5f^5$ photoionization process cannot directly be fitted to the UPS data. The low-resolution Mg $K\alpha$ XPS valence-band spectrum shows a strong $5f$ peak with a maximum at 2.8 eV. Accounting for the final-state multiplet distribution this would give the lowest level at approximately 2.2 eV, which is also in good agreement with our calculated value. In the high-resolution UPS valence-band spectrum a peak at 1.8 eV is clearly resolved. It has been suggested that this could be due to a signal from a divalent surface layer,[17,24] i.e., from a process of type $5f^7\rightarrow 5f^6$. The increased surface sensitivity of UPS relative to XPS supports this interpretation as well as the peak position. On the other hand, the cohesive energy for americium is 68 kcal/mol,[25] which should be compared with 49 kcal/mol for samarium and 56 kcal/mol for thulium.[26] Since samarium has a divalent surface[27] but thulium not,[28] this seems to suggest that americium should have a stable trivalent surface. As an alternative explanation for the 1.8-eV peak we propose that it might be due to a multiplet component of a $5f$ screened final state of similar nature as the low-energy structure obtained in photoemission experiments on γ cerium.[29] The remaining part of the $5f$ UPS spectra would then be due to a superposition of bulk and surface signals, where the surface-derived structures should have a higher binding energy of about 0.5 eV than the corresponding bulk features.[22,30]

It is of special interest to note the comparatively low value of $\Delta E_{\mathrm{III,IV}}$ for berkelium. Due to this, it was suggested[31] that under compression the berkelium metal will undergo a valence change from trivalent to tetravalent behavior for a pressure somewhat higher than 200 kbar and that only later the $5f$ electrons will delocalize. However, in recent high-pressure experiments[32] on berkelium the α-uranium structure has been identified above 250 kbar, and the general behavior of the pressure-volume curve suggests that the $5f$ delocalization transition precedes the valence change (which then loses any meaning). Apparently the pressure dependence of the energy position of the $5f$ level relative to the Fermi energy is less pronounced than hoped for in Ref. 31. The relatively low value of $\epsilon(f \rightarrow \epsilon_F)$ suggests that the electronic structure of berkelium intermetallic compounds with late d transition elements like rhodium or ruthenium might be of special interest.

Another most noticeable feature of the experimental XPS spectra for americium is the almost symmetric line shape of the $4f$ core levels,[17] which is in sharp contrast to the strongly asymmetric $4f$ line in the uranium metal.[11] This experimental finding strongly supports that the $5f$ level in americium has been withdrawn from the Fermi level. A similar behavior has, for example, been observed[33] for the $3d$ core-level line shape of Pd in $\mathrm{Cu}_{1-x}\mathrm{Pd}_x$ alloys, which in pure Pd is strongly asymmetric but becomes almost symmetric when $x < 0.5$. This is also the concentration for which the Pd $4d$ valence level has become essentially filled and no longer extends markedly up to the Fermi level.

A further very significant feature of the $4f$ core-level spectrum of Am is the observation of a "shakedown" satellite at 4-eV lower binding energy than the main $4f_{7/2}$ line. This is very similar to what has been observed for the $3d_{5/2}$ line in La, Ce, Pr, and Nd (Ref. 34) and again confirms the rare-earth-like behavior of americium. In contrast, one has for Th (Ref. 35), U (Ref. 36), and Pu (Ref. 14) observed shake-up satellites in the $4f$ core spectra. Thus, the proposed[37] change between main line and satellite as one proceeds through the actinide series seems to have been confirmed experimentally. Here, we will calculate the position of the satellite relative to the main line in Am. Doing this, we apply the same method as was previously used for the satellites in the earlier lanthanide metals.[38] For the main line with conduction electron screening the final-state configuration is $4f^{*}5f^{6}[6d7s]^{4}$, where the asterisk denotes a hole in the $4f$ core level. The shakedown satellite is assumed to be due to a complete screening in the $5f$ orbital instead of the "ds"-valence band. This then corresponds to a $4f^{*}5f^{7}[6d7s]^{3}$ final state. It follows immediately that the energy difference between the satellite and the main line is just the $5f^{7}[6d7s]^{3} \rightarrow 5f^{6}[6d7s]^{4}$ excitation in the presence of a $4f$ hole. It is, however, well known that the effect of a core hole might be quite well simulated by a $(Z+1)$ replacement. Therefore, the required energy difference has a direct correspondence to the $5f^{7}[6s7d]^{3} \rightarrow 5f^{6}[6d7s]^{4}$ excitation in the curium metal, which above was calculated to be 3.2 eV. This is in relatively good agreement with the experimental value of 4 eV for the satellite position in Am.[17] However, it is also possible to calculate a correction to the $(Z+1)$ approximation. This can simply be done by performing an *atomic* ΔSCF (self-consistent field) calculation for the excitation $5f^{7}6d7s^{2} \rightarrow 5f^{6}6d^{2}7s^{2}$ in curium and $4f^{*}5f^{7}6d7s^{2} \rightarrow 4f^{*}5f^{6}6d^{2}7s^{2}$ in americium. In the metals these excitation energies will become renormalized in an almost identical way. Thus, the correction calculated for the atom will be essentially the same for the metallic state. This method to improve on the $(Z+1)$ approximation was earlier successfully applied to the $3d$ satellites in the lighter lanthanide metals.[38] For the present case the atomic calculation shows that the $5f^{7}$ level is more bound in Am (with a $4f$ hole) than in Cm, the difference being about 0.8 eV. From this the relative position of the shakedown satellite to the main line in americium metal is calculated to be $3.2+0.8=4.0$ eV. Accounting for the impurity term of the tetravalent site, we should reduce this number somewhat, to about 3.8 eV, which is close to the experimental value.

In conclusion, we want to stress the significance of the experimental XPS and UPS photoemission spectra of americium[17] in that they clearly demonstrate the rare-earth type of electronic structure of this metal. The previously found superconductivity,[16] the low electronic specific heat,[39] and the double-hexagonal close-packed crystal structure and the comparatively high equilibrium volume[40] all have the same implication. These evidences taken together give a very consistent picture of the fact that the $5f$ electrons are localized in americium as opposed to the itinerant $5f$ electrons in plutonium. The presently found good agreement between some calculated electronic structure properties and experiments for americium gives additional support to this view. From the fundamental change in the $5f$ electron behavior between plutonium and americium it is evident that high-pressure experiments on americium are of particular importance.[7] Especially, high-pressure work in the low-temperature region should be most useful for the detailed understanding of the delocalization process (Mott transition) derived from the theoretical calculations in Ref. 9. High-pressure work at room temperature has already shown that above 110 kbar the crystal structure of americium becomes quite complex[41-43] and at 160 kbar it has been indexed as the α-uranium structure.[43,44] This gives strong evidence for that the $5f$ states have become itinerant in this pressure range.

---

[1] E. A. Kmetko and H. H. Hill, *Plutonium 70,* edited by W. N. Miner (AIME, New York, 1970), p. 233.

[2] A. J. Freeman and D. D. Koelling, *The Actinides: Electronic Structure and Related Properties,* edited by A. J. Freeman and J. B. Darby, Jr. (Academic, New York, 1974), p. 51.

[3] B. Johansson, Philos. Mag. **30**, 469 (1974).

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

[5] B. Johansson and A. Rosengren, Phys. Rev. B **11**, 2836 (1975).

[6] J. W. Ward and H. H. Hill, *Heavy Element Properties,* edited by W. Müller and H. Blank (North-Holland, Amsterdam 1976), p. 65.

[7] B. Johansson, J. Phys. Chem. Solids **39**, 467 (1978).

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

[9] H. L. Skrivr, O. K. Andersen, and B. Johansson, Phys. Rev. Lett. **44**, 1230 (1980).

[10] B. W. Veal and D. J. Lam, Phys. Rev. B **21**, 4902 (1974).

[11] Y. Baer, Physica B **102**, 104 (1980).

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

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

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

[15] There are no reasons to expect that this would not be the case for the metal between U and Pu, i.e., Np, as well as for the metal preceding U, i.e., Pa.

[16] J. L. Smith and R. G. Haire, Science **200**, 535 (1978).

[17] J. R. Naegele, L. Manes, J. C. Spirlet, and W. Müller, Phys. Rev. Lett. **52**, 1834 (1984).

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

[19] J. F. Herbst, R. E. Watson, and J. W. Wilkins, Phys. Rev. B **17**, 3089 (1978).

[20] B. Johansson, Phys. Rev. B **20**, 1315 (1979).

[21] J. F. Herbst, D. N. Lowy, and R. E. Watson, Phys. Rev. B **6**, 1913 (1972).

[22] B. Johansson and N. Mårtensson, Phys. Rev. B **21**, 4427 (1980).

[23] F. Gerken and J. Schmidt-May, J. Phys. F **13**, 1571 (1983).

[24] A. Zangwill (private communication).

[25] J. W. Ward, J. Less-Common. Met. **93**, 279 (1983).

[26] L. Brewer, Lawrence Berkeley Laboratory Report No. LBL-3720, 1975 (unpublished).

[27] G. K. Wertheim and G. Creselius, Phys. Rev. Lett. **40**, 813 (1978).

[28] L. I. Johansson, J. W. Allen, and I. Lindau, Phys. Lett. **86A**, 442 (1981).

[29] N. Mårtensson, B. Reihl, and R. D. Parks, Solid State Commun. **41**, 573 (1982); D. M. Wieliczka, C. G. Olson, and D. W. Lynch, Phys. Rev. B **29**, 3028 (1984).

[30] B. Johansson, Phys. Rev. B **19**, 6615 (1979).

[31] B. Johansson, H. L. Skriver, and O. K. Andersen, in *Physics of Solids Under High Pressure,* edited by J. S. Schilling and R. N. Shelton (North-Holland, Amsterdam, 1981), p. 245.

[32] U. Benedict, J. R. Peterson, R. G. Haire, and C. Dufour, J. Phys. F **14**, L43 (1984).

[33] N. Mårtensson, R. Nyholm, H. Calén, J. Hedman, and B. Johansson, Phys. Rev. B **24**, 1725 (1981).

[34] G. Creselius, G. K. Wertheim, and D. N. E. Buchanan, Phys. Rev. B **18**, 6519 (1978).

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

[36] W. D. Schneider and C. Laubschat, Phys. Rev. Lett. **46**, 1023 (1981).

[37] B. Johansson, H. L. Skriver, N. Mårtensson, O. K. Andersen, and D. Glötzel, Physica B **102**, 12 (1980).

[38] B. Johansson and N. Mårtensson, Phys. Rev. B **24**, 4484 (1981).

[39] J. L. Smith, G. R. Stewart, C. Y. Huang, and R. G. Haire, J. Phys. (Paris) Colloq. **40**, C4-138 (1979); G. R. Stewart (private communication).

[40] D. B. McWhan, B. B. Cunningham, and J. C. Wallman, J. Inorg. Nucl. Chem. **24**, 1025 (1962).

[41] J. Akella, Q. Johnson, W. Thayer, and R. N. Schock, J. Less Common Met. **68**, 95 (1979).

[42] J. Akella, *Report on the Workshop "Actinides under Pressure", Karlsruhe, 21–22 April 1983* (European Institute for Transuranium Elements, Karlsruhe, 1983).

[43] R. B. Roof, Z. Kristallogr. **158**, 307 (1982); J. Appl. Cryst. **14**, 447 (1981).

[44] R. B. Roof, R. G. Haire, D. Schiferl, L. Schwalbe, E. A. Kmetko, and J. L. Smith, Science **207**, 1353 (1980).