$5f$-Electron Localization in PuSe and PuSb

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Thin layers of PuSb and PuSe were studied by photoelectron spectroscopy. X-ray photoelectron spectroscopy and high-resolution valence-band ultraviolet photoelectron spectroscopy spectra show localization of the $5f$ states and a low density of states at E_F in PuSb. In PuSe, which can be classified as a heavy fermion system with low carrier density, we observed three narrow peaks in the valence band, which can be related to the $5f$ emission. These three features are very sensitive to stoichiometry deviations and disappear for PuSe prepared at $T = 77$ K.

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A crossover from itinerant to localized behavior of the $5f$ states occurs in the sequence of actinide metals between plutonium and americium [1]. The great potential of transuranium studies for the physics of strongly correlated electron systems has not been used extensively because of severe safety precautions. With few exceptions, photoelectron spectroscopy data thus exist only for pure elements Np, Pu, Am, and some oxidic materials [2].

One of the major technical difficulties in actinide photoelectron spectroscopy is the fast segregation of oxygen diffusing from the bulk, which leads to a surface degradation. The surface sensitivity of the photoemission thus restricted all studies to the region in which the segregation processes are slowed down by low temperatures, although temperature variations of photoelectron spectra can yield valuable information on various many-body phenomena. To overcome this difficulty we prepared thin layers of actinide materials deposited on a Si substrate. This method enables one to extend the useful temperature range up to $T = 350$ °C. Here we present results obtained on two plutonium compounds, namely, PuSb and PuSe.

PuSb and PuSe crystallize in the NaCl type of structure. Magnetic measurements [3] and neutron-diffraction experiments [4,5] showed that PuSb orders magnetically below $T = 85$ K. The Pu magnetic moment of $0.75\mu_B$ in PuSb is consistent with the $5f^5$ ground state. Both static and dynamic magnetic properties [6] could be understood in the model assuming localized $5f$ states and a weak hybridization with conduction electron states, in analogy to, e.g., CeSb [7].

The weakly paramagnetic behavior of PuSe (and very similar PuS and PuTe) [8] is much less understood, because the $5f^6$ ground state with $J = 0$, $S = L = 3$ is excluded using the lattice parameter considerations. A qualitative explanation was provided by electronic structure calculations [9], yielding a plausible picture of a "relativistic semiconductor," in which the $5f$ states form two bands characterized by quantum numbers $j = \frac{5}{2}$ and $\frac{7}{2}$. The lower band, accommodating $2j + 1 = 6$ electrons (Se contributes here by one p electron due to the $5f$-p hybridization) is split off due to a strong spin-orbit interaction from the $j = \frac{7}{2}$ band, and the Fermi level is placed in the gap between these bands. This picture explained also qualitatively a semiconducting or semimetallic behavior of electrical resistivity of all three Pu monochalcogenides [10], whereas the resistivity of PuSb has a metallic character [11]. More recent calculations [12,13] do not yield a complete gap, but a pseudogap with a residual density of states at the Fermi level, $N(E_F)$. In the latter work it was shown that the lattice parameters of Pu chalcogenides can be accounted assuming the band character of the $5f$ states. The low $N(E_F)$ is, however, in contrast with appreciable values of the coefficient γ of the electronic specific heat (90 mJ/mol K^2 for PuSe [10]). Our aim is to perform photoemission experiments on both these materials to examine details of their electronic structure.

PuSb and PuSe layers were prepared by a dc sputtering technique from a stoichiometric target. The low pressure plasma discharge was stabilized by means of an additional W electrode, which is heated and kept at a negative potential. A special arrangement of targets and electrodes allows one to work with microtargets of the mass below 100 mg. The pressure of the high-purity (6 N) Ar gas can be varied within certain limits (2×10^{-3} to 3×10^{-2} mbar), affecting somewhat the stoichiometry of the deposited layers. Details of the preparation process will be published elsewhere. In this Letter we concentrate on properties of stoichiometric layers thicker than the active photoemission depth (>5 nm). We studied high-resolution ultraviolet photoelectron spectroscopy (UPS) spectra of the valence band for two photon energies $h\nu = 21.2$ and 40.8 eV (He I and He II lines), the latter having considerably larger photoexcitation cross section for the $5f$ states. The energy resolution (angle-integrated photoemission only) was ≈40 meV. Core-level spectra were studied using the Al-K_α radiation ($h\nu = 1486.6$ eV). The total energy resolution in this case is about 1.0 eV. A negligible surface contamination by oxygen can be deduced from

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the absence of any appreciable O-$2p$ line in He II spectra (see below), which is a very sensitive indicator to small traces of O and appears at 6 eV binding energy.

Figure 1 shows the $4f$ core-level spectra of PuSe and PuSb (the background was subtracted using the standard Shirley procedure) compared to data obtained on bulk α-Pu, consisting of a simple spin-orbit split doublet. All the spectra can be understood on the basis of a conventional two channel screening model [14]. For Pu, the positions of the $4f_{5/2}$ and $4f_{7/2}$ lines (at binding energies 435.1 and 422.2 eV, respectively) correspond to the final state with the $4f$ hole screened by the $5f$ electrons (so-called good screening), implying thus their itineracy. The satellites on the high binding energy sides of both lines (at 437.7 and 425.0 eV, respectively), which contain relatively small spectral weight, correspond to the final state with the poorly screened $4f$ hole by non-f conduction electron. In the case of the $5f$ localization, this is the only screening channel. Relatively weak poorly screened satellites in α-Pu reflect a situation found, for example, in most U intermetallic compounds with undoubtedly bandlike character of the $5f$ electronic states, and is for α-Pu fully corroborated by electronic structure calculations [15]. Therefore, the fact that we observe only poorly screened $4f$ peaks in PuSb (at binding energies 437.7 and 424.9 eV) can be unambiguously interpreted as due to the localization of the $5f$ states. Binding energies corresponding to the $4f$ peaks in PuSb are somewhat lower than those given by Baptist *et al.* (438.4 and 426.1 eV) [16]. For the purpose of fitting, the peaks were approximated using Pearson functions with variable width, shape, and asymmetry of the peaks. The asymmetry is important only for the well screened peaks; the poorly screened peaks are nearly symmetric.

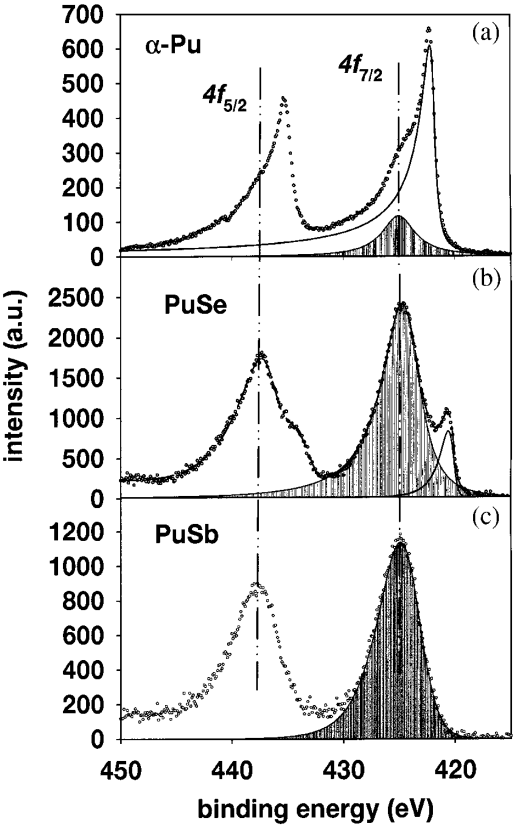

FIG. 1. $4f$ core-level spectra of bulk α-Pu (a), PuSe (b), and PuSb (c) thin layers. The spectra are displayed after the background subtraction. For the $4f_{7/2}$ peak the decomposition into a nearly symmetric poorly screened peak (shaded area) and an asymmetric well screened peak (full line) is demonstrated. The dash-dotted lines mark the energies of poorly screened $4f$ features.

In PuSe, we observe both types of screening channels, with dominating poorly screened $4f$ peaks at 437.6 and 424.7 eV. The well screened peak is better resolved at the $4f_{7/2}$ line, where it is located at 420.6 eV binding energy. For the $4f_{5/2}$ peak it manifests only as a shoulder, because the main peak (poorly screened) is broader. The different widths of the $4f_{5/2}$ and $4f_{7/2}$ poorly screened peaks can be understood considering that each peak contains manifold of final states of slightly different energy depending on the Coulomb interaction of the $4f$ hole with different states of the $5f$ multiplet in case of the localized $5f$ states. This Coulomb interaction can then be rather different for the $4f_{5/2}$ and $4f_{7/2}$ holes. This effect is particularly striking in PuSe. The shape of well screened peaks is asymmetric, with the tailing on the high binding energy side, which is traditionally ascribed to the creation of electron-hole pairs at E_F in the screening process [17].

Figure 2 shows the situation in the valence band of PuSb and PuSe compared with Am. As demonstrated in Ref. [2], valence-band spectra of pure actinide elements show a striking change of character between the Th-Pu series and Am, reflecting unambiguously the $5f$ localization between Pu and Am. Whereas the elements up to Pu display a more or less uniform picture of a broad triangular $5f$ spectrum with intensity increasing up to the Fermi level, Am exhibits a low Fermi level emission with the $5f$ spectral intensity concentrated into several partly resolved multiplet lines below E_F [Fig. 2(c)].

He II spectrum of PuSb [Fig. 2(a)] displays a maximum at 1.8 eV binding energy, a shoulder at 4 eV, and a small hump at 6 eV, which can be attributed to a very small O contamination (O-$2p$ line). The Fermi level is well resolved as expected for a metal, but the density of states at E_F is undoubtedly low. The comparison of the spectra taken with different photoexcitation energies shows that the emission from the $5f$ states must be located around the maximum, because the intensity in this range increases relatively comparing to other spectral features (those at 4 eV and at E_F) going from $h\nu = 21.2$ to 40.8 eV. The feature at 4 eV contains mainly the emission from the $5p$ states of Sb, and if we normalize the He I and He II spectra at the high binding energy side of this feature we also get nearly identical intensity at E_F. Therefore, we can conclude that the $5f$ states do not contribute to the emission at

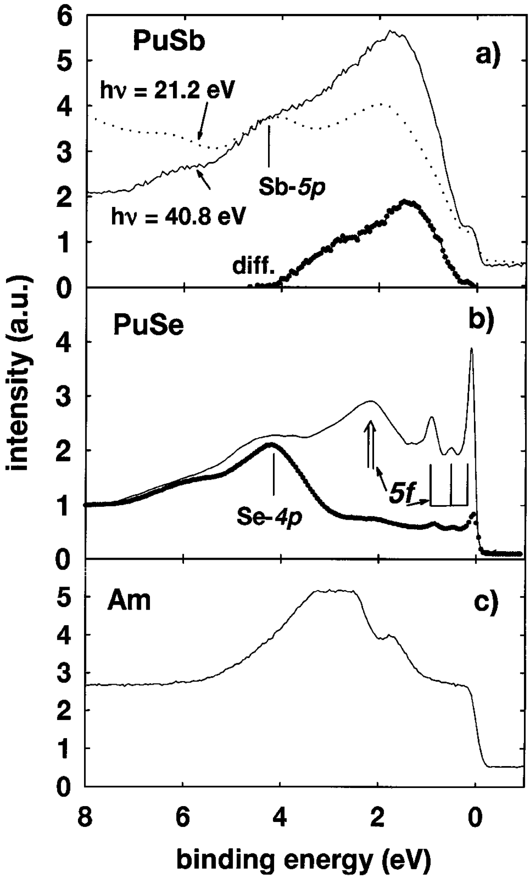

FIG. 2. UPS valence-band spectra. For PuSb (a), the full line represents the spectrum with $h\nu = 40.8$ eV, the dotted line the spectrum with $h\nu = 21.2$ eV; full circles represent the difference spectrum. For higher binding energies than 5 eV, the difference spectrum is negative due to the higher secondary-electron background for $h\nu = 21.2$ eV in this energy range. For PuSe (b) the spectrum taken with $h\nu = 40.8$ eV photon energy is represented by the full line, for $h\nu = 21.2$ eV by full circles. For Am (c), only the spectrum with $h\nu = 40.8$ eV is displayed (data taken from Ref. [2]).

E_F. Measurements at different temperatures from $T = 77$ to 477 K did not show any temperature dependence besides the Fermi level broadening due to Fermi-Dirac statistics.

In the case of PuSe we found that valence-band spectra [Fig. 2(b)] obtained on films synthesized at temperatures above the room temperature well reproduce the features observed on the bulk PuSe sample [18]. Besides the shoulder between 3 and 5 eV binding energy, which dominates for the 21.2 eV excitation energy and can be associated with the emission from the Se $4p$ states, we have observed four distinct features clearly related to the $5f$ emission. Most of the spectral intensity at 40.8 eV excitation energy is contained in a broad triangular peak centered at 2 eV binding energy. In addition, we observe two sharp (FWHM ≈ 0.15 eV) peaks, located at 0.85 and 0.50 eV, respectively, and a similarly sharp but more intense Fermi level emission. The intensity of the last three features depends strongly on the surface composition (monitored by intensities of the Se-$2p$ and Pu-$4f$ core-level lines). Depending on sputtering parameters (mainly the Ar gas pressure) we could go from a stoichiometric PuSe composition to a certain Pu excess, which led to a reduction of intensities of all three sharp lines compared to the intensity of the broad maximum at -2 eV. A similar tendency was found for bulk PuSe surfaces treated by sputtering with Ar, which leads to a Se-depleted surface, when compared to the stoichiometric surface prepared by scraping [18]. Moreover, all three lines are progressively suppressed with reduction of the substrate temperature from $T = 623$ K, and vanish for the deposition at $T = 77$ K (see Fig. 3), which does not affect the stoichiometry, but leads presumably to an amorphous state. All these phenomena point to a common origin of the three sharp peaks, which is different than the origin of the -2 eV maximum. In analogy with PuSb and Am, we assume that the 2 eV maximum corresponds to a multiplet of localized $5f$ states, which appears partly resolved for the Am $5f^6$ configuration, but for both Pu compounds remains unresolved.

The explanation for the three sharp peaks remains unclear. One possibility is to assume, in analogy to the two channel response approach used to interpret the $4f$ core-level spectra, that the three sharp peaks are related to the band structure of PuSe, in particular, to narrow features in the $5f$ band. In the case of high effective masses of $5f$ electrons, the full $5f$ screening probability of the $5f$ hole can be so small that the main response could correspond to a poorly (non-f) screened final state, which is represented by the maximum at -2 eV. Interpreting the sharp peaks as $5f$ band features would mean, though, a lack of dispersion, which is somewhat unusual. Trying to find a relation to results of band structure calculations, we see that both Refs. [12] and [13] indicate high density of $5f$ states at E_F and at about -1 eV, but low density in between. Moreover, the lack of any shift in energy of the sharp features at a change of stoichiometry, which changes only experimental intensities, seems to contradict the $5f$-band origin

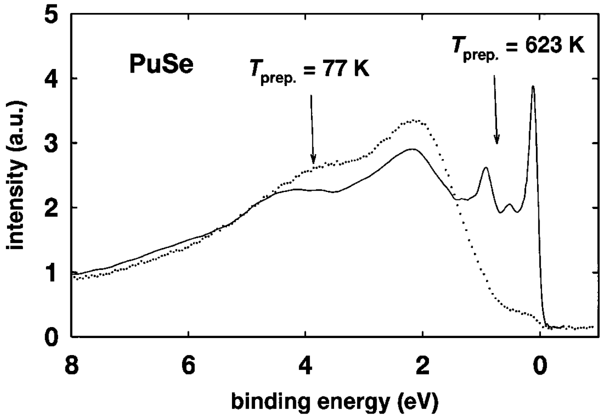

FIG. 3. UPS valence-band spectra (taken at $h\nu = 40.8$ eV photon energy) of PuSe layers deposited at $T = 623$ K (full line) and 77 K (dotted line).

of the features. Another variety of this approach (with the same drawbacks) is to assume, in analogy to calculations of δ-Pu [15], that the ground state corresponds to four $5f$ electrons in localized states and remaining electrons having an itinerant character.

Another type of explanation can be to relate the three sharp features to many-body states, analogous to Abrikosov-Suhl (Kondo) resonance [19]. One of the supporting arguments would be the relatively very high specific heat coefficient γ in PuSe. The analogy with Ce or Yb cannot be completely excluded. Although there is no explanation why we observe just three features related to a many-body state (detailed theory for $5f^5$ or $5f^6$ states is until now missing), spin-orbit coupling and crystal electric field splitting can lead to replicas of the Kondo resonance. One of the possibilities to confirm or reject this approach is to see whether these features exhibit an anomalous temperature dependence. Additional detailed experiments to check for are under way.

The last type of explanation we consider here is based on the possible analogy of PuSe with mixed-valent Sm compounds suggested in Ref. [20], in which one observes in valence-band spectra two multiplets corresponding to transitions from the two configurations involved ($4f^5 \longrightarrow 4f^4$, $4f^6 \longrightarrow 4f^5$) [21]. In this framework, the three sharp peaks in the valence-band spectra of PuSe would thus correspond to a multiplet arising from one of the transitions above (with one line accidentally crossing the Fermi energy); the other transition without any resolved multiplet structure would be represented by the broad peak at -2 eV. However, the much stronger spin-orbit interaction in Pu implies that the analogy with Sm has to be treated with caution. Alternatively we could also think about a surface valence change, assuming that the lower Pu coordination at the surface would drive the normally trivalent $5f^5$ system to a divalent $5f^6$ state. Such states should then be associated with the emission close to E_F, whereas the 2 eV emission should be, in analogy to PuSb, due to the $5f^5$ state. That would explain the observed sensitivity of the former features to the quality of the surface, or to any contamination. On the other hand, the $5f^6$ features should then be emphasized in the low-T prepared layers (presumably amorphous, with a high surface roughness). But the tendency is opposite and these features disappear.

In conclusion, we demonstrated using XPS and UPS techniques the localization of $5f$ states in PuSb. The spectra of PuSe, being of a different type than observed before for any other actinide material, show, besides a fingerprint of $5f$ localization, sharp features in the vicinity of the Fermi level, the origin of which remains still unclear.

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[1] See various articles in *The Actinides: Electronic Structure and Related Properties,* edited by A. J. Freeman and J. B. Darby, Jr. (Academic Press, New York, 1974), Vols. I and II.
[2] J. R. Naegele *et al.,* in *59/60 Structure and Bonding, Actinides-Chemistry and Physical Properties,* edited by L. Manes (Springer-Verlag, Berlin, 1985), pp. 197–262.
[3] B. R. Cooper *et al.,* Phys. Rev. Lett. **51**, 2418 (1983).
[4] G. H. Lander *et al.,* Phys. Rev. Lett. **53**, 2262 (1984).
[5] P. Burlet *et al.,* Phys. Rev. B **30**, 6660 (1984).
[6] G. H. Lander *et al.,* Physica (Amsterdam) **136B**, 409 (1986).
[7] G. J. Hua and B. R. Cooper, Phys. Rev. B **48**, 12 743 (1993).
[8] G. H. Lander *et al.,* Physica (Amsterdam) **146B**, 341 (1987).
[9] M. S. S. Brooks, J. Magn. Magn. Mater. **63–64**, 649 (1987).
[10] J. M. Fournier *et al.,* Physica (Amsterdam) **163B**, 493 (1990).
[11] A. Blaise *et al.,* Physica (Amsterdam) **130B**, 99 (1985).
[12] A. Hasegawa and H. Yamagami, J. Magn. Magn. Mater. **104–107**, 65 (1992).
[13] P. M. Oppeneer, T. Kraft, and M. S. S. Brooks, “Electronic Structure of Plutonium Monochalcogenides,” Phys. Rev. B (to be published).
[14] J. C. Fuggle *et al.,* Phys. Rev. Lett. **45**, 1597 (1980).
[15] For recent discussion of electronic structure of various Pu phases, see O. Eriksson *et al.,* J. Alloys Compd. **287**, 1 (1999).
[16] R. Baptist *et al.,* J. Phys. (Paris) **44**, 241 (1983).
[17] S. Doniach and M. Sunjic, J. Phys. C **3**, 285 (1970).
[18] J. Naegele (unpublished).
[19] See M. Garnier *et al.,* Phys. Rev. Lett. **78**, 4127 (1997), and references therein.
[20] P. Wachter *et al.,* Phys. Rev. B **43**, 11 136 (1991).
[21] J. M. Lawrence *et al.,* Rep. Prog. Phys. **44**, 1 (1981).