

Electronic Structure of Plutonium Chalcogenides

Alexander Shick¹, Ladislav Havela², Thomas Gouder³

¹ *Institute of Physics, Academy of Sciences, Prague 8, Czech Republic*

² *Department of Condensed Matter Physics, Charles University, CZ-12116, Prague 2, Czech Republic*

³ *European Commission, Joint Research Centre, Institute for Transuranium Elements, Postfach 2340, D-76125 Karlsruhe, Germany*

PuS as well as other plutonium chalcogenides PuSe and PuTe studied before [1,2] belong to NaCl structure type materials. They differ by their weakly paramagnetic behaviour from Pu pnictides and also from U and Np chalcogenides. Other exceptional feature is their semi-metallic behaviour. Here we concentrate on theoretical description, which would capture essential bulk properties as well as photoelectron spectra of PuS, and on implications for δ -Pu and other Pu systems.

Figure 1 shows valence-band spectra of PuS obtained with two photon energies. For the lower photon energy (21.22 eV), the $5f$ photoexcitation cross section is very low and the spectrum therefore captures non- f states. Those include the anion p -states forming the broad maximum around 5 eV binding energy (BE) for PuS, which shifts little more towards the Fermi level for PuSe and PuTe. The $5f$ states contribute to the spectra taken at higher photon energy (40.81 eV). The $5f$ emission can be associated with the triplet of sharp features within 1 eV below the Fermi level, the energies of which do not vary, and a broader emission around 2 eV BE, which shifts from PuS to PuTe opposite to the shift of the p -states.

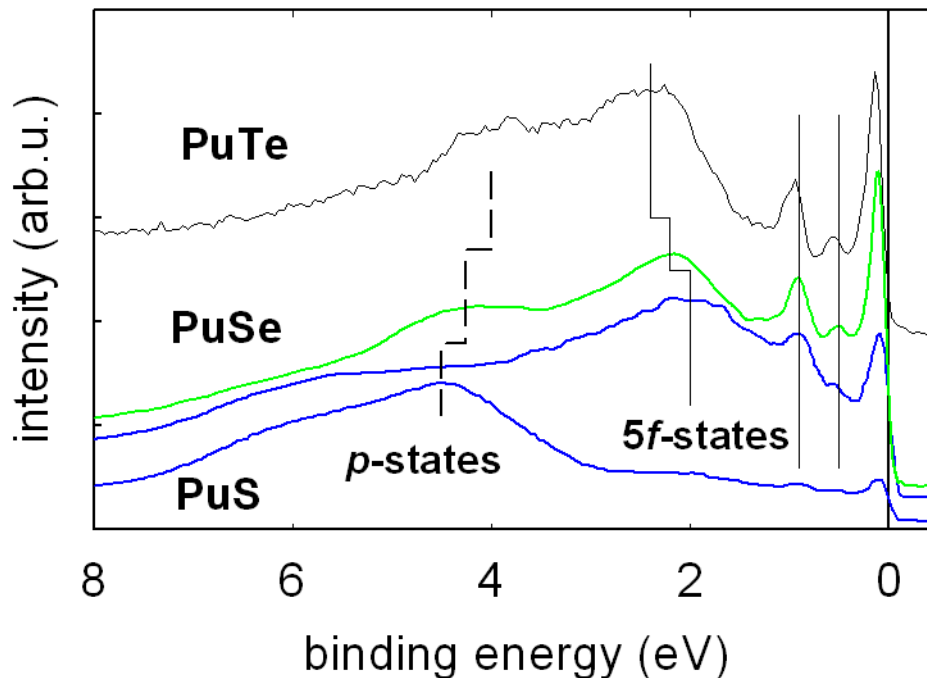


Fig. 1: Valence-band UPS spectra of PuS, PuSe [1], and PuTe [2] for $h\nu = 40.81$ eV and PuS for $h\nu = 21.22$ eV (at the bottom). They clearly demonstrate that the anion p -emission shifts gradually towards the Fermi level (each step 0.25 eV), whereas the $5f$ emission at about 2 eV binding energy shifts gradually from the Fermi level. The sharp spectral features of the $5f$ origin are at invariable energies 0.9 eV, 0.5 eV, and at the Fermi level, only their intensity increases in the sequence S, Se, Te.

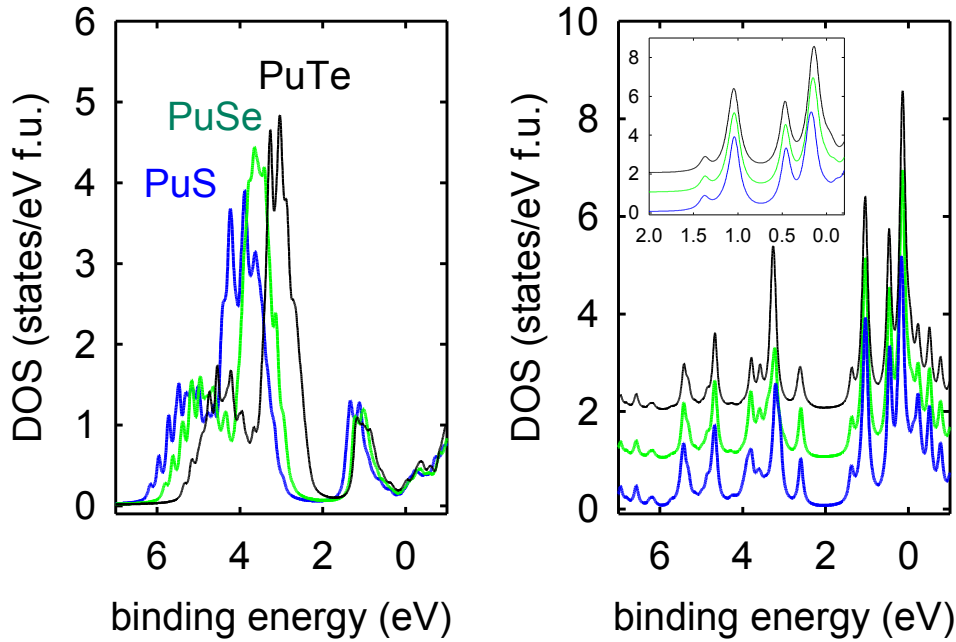


Fig. 2: Calculated densities of non- f states using the LDA+U around mean field method (left) and the $5f$ -based spectral density obtained from the LDA+HIA method (right). Here the spectral densities for PuSe and PuTe were shifted up for clarity. The inset shows in more detail the situation close to the Fermi level.

The f -state triplet is probably the most prominent characteristic feature of Pu-based systems. For its description, the intra-ionic Coulomb correlations and related excitations have to be treated as precisely as possible, for which the Hubbard I approximation (LDA+HIA) have been implemented [3]. While the non- f states are treated within the LDA approximation in both the LDA and around mean field LDA+U, their resulting position in the self-consistent LDA+U calculations agrees better with experimental spectra than in the LSDA calculations [4]. The $5f$ -spectral density contains features related to the $5f^5$ final state (reached from the $5f^6$ initial state) at lower BE, whereas the features from 2 eV down belong to the $5f^4$ final state. The prominence of the $5f^5$ multiplet is here a direct consequence of the large occupancy n_{5f} of the Pu $5f$ states, exceeding 5.6 and weakly increasing from PuS to PuTe. This can point to *the intermediate valence* in all three Pu chalcogenides.

Comparing with other calculations, which go beyond the conventional DFT methods, we see a better agreement with spectra than achieved by the calculations using the FLEX technique [5]. A certain problem is the description of the $5f$ emission at 2 eV BE, which is hard to associate with the $5f^4$ multiplet as obtained by us and Ref [5]. It was however successfully described for PuSe by another Hubbard I – based approach [6].

Acknowledgement. This work was supported by the ACTINET consortium under project No. JP 6-18, COST P16 (Project OC144), and Czech Grant Agency Project 202/07/0644.

References

- [1] T. Gouder, F. Wastin, J. Rebizant, L. Havela, Phys.Rev.Lett. 84 (2000) 3378.
- [2] T. Durakiewicz, J.J. Joyce, G.H. Lander, et al. Phys.Rev.B 70 (2004) 205103.
- [3] A. Shick, J. Kolorenc, L. Havela, V. Drchal, T. Gouder, EPL 77 (2007) 17003.
- [4] P.M. Oppeneer, T. Kraft, M.S.S. Brooks, Phys.Rev.B 61 (2000) 12825.
- [5] L.V. Pourovskii, M.I. Kastnelson, A.I. Lichtenstein, Phys.Rev. B 72 (2005) 115106.
- [6] A. Svane, Solid State Commun. 140 (2006) 364.