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Current understanding of photoelectron spectra in plutonium systems

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ABSTRACT

Analysis of available photoelectron spectra from Pu compounds indicates the presence of the $5f^5$ multiplet, which dominates the energy scale close to the Fermi level. As shown by the LDA+U+Hubbard I calculations, its intensity scales with the admixture of the $5f^6$ manifold in the $5f^5$ ground state, which can lead to an average occupancy substantially exceeding 5.0. This admixture also leads to the suppression of magnetic order and occurrence of heavy fermion behaviour.

1. Introduction

Agreement with photoelectron spectra is often taken as important criterion of truthfulness of electronic structure calculations. It is also the case of Pu metal for which different types of calculations were performed to specify the proper framework for description of the 5*f* states. The vague belief (undoubtedly correct) is that they are close to the verge of localization. This does not though give any particular detailed guidance, because of the complexity of many-body phenomena, which may give rise to various qualitatively different phenomena going beyond the one-electron picture and conventional electronic structure calculations.

A potential danger of using the ground state density of (occupied) states for direct comparison with the spectra is the fact that in the narrow-band regime or in the case of localization, the final state after the photoemission event can differ radically from the initial ground state. Not looking at that, calculations based on a Mixed Level Model, in which some 5*f* electrons occupy localized states, while a fraction still forms conventional bands, seemed to give a reasonable account of valence band spectra of δ-Pu [1]. The focus on pure Pu left behind the fact, that spectra of many other Pu-based compounds look strikingly similar, or at least exhibit some universal features close to the Fermi level (see Fig. 1), where the lifetime broadening allows for good energy resolution. The three sharp features, first recognized in PuSe [2], could be identified also in the spectra of Pu metal [3], although with much weaker intensity. Other compounds followed and the triplet can be observed for silicides [4], carbides [5], or nitrides [6]. It can be also traced in $PuCoGa_5$ [7,8]. The aim of this contribution is to discuss the origin of the features and consequences for understanding of electronic structure in Pu-based systems.

2. Photoelectron spectra and their understanding

For identification of the origin of the triplet spectral features, negative case may also give guidance. From all the cases studied, they definitely do not show up in PuSb as a representative of Pu pnictides, which has the 5*f* emission intensity at the Fermi level very low [2,9]. The reason can be in general twofold. One is the larger degree of the 5*f* localization, characteristic for PuSb, although there is no apparent reason why the triplet could arise due to a delocalization. Its invariant energy position in diverse systems excludes any relation to individual band structures. Another reason can be found in the specific 5*f* occupancy of PuSb, which proved to be 5.0 [10]. The dominance of the triplet in spectra of Pu chalcogenides such as PuSe [2], PuTe [9], or PuS [11] can be then related to the assumed significantly higher 5*f* occupancy [12]. This would mean that also in δ-Pu and other systems the 5*f* occupancy is higher than 5.0, although not necessarily reaching values over 5.5, obtained for the chalcogenides. Can this speculation have support in theory?

Unlike other type of calculations, the LDA+U around mean field method performed first for Pu metal and subsequently for Pu compounds started to yield resulting 5*f* occupancy, n_{5f}, significantly different from 5.0 and varying over a significant range. Their values are spread from $n_{5f} \approx 5.1$ in PuSb to 5.6–5.7 in Pu chalcogenides. The obtained densities of states were though very dissimilar to experimental spectra, mostly missing the 5*f* states at E_F. On the other hand, the triplet in the spectra was found reminiscent of the $5f^5$ final-state multiplet, obtained by calculations of excitation from a $5f^6$ free ion, if that was conveniently adjusted with respect to the Fermi energy of a solid [4]. The necessity to augment the

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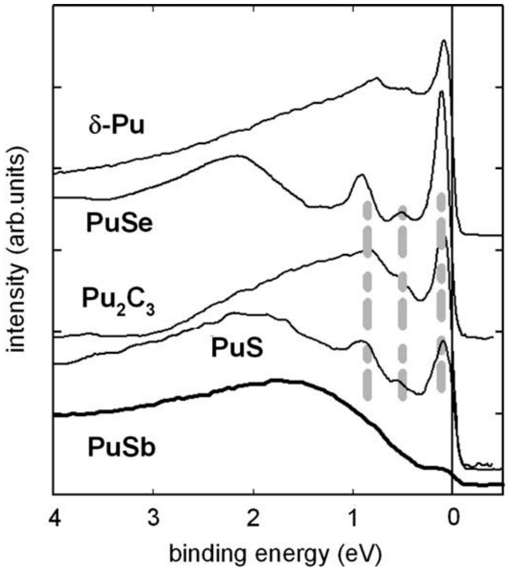

Fig. 1. Examples of photoelectron spectra taken with the photon energy ($h\nu = 40.81$ eV) with dominant emission of the 5*f* origin. The universal features discussed, belonging to the $5f^5$ final-state multiplet (absent for PuSb), are marked by the dashed lines.

LDA+U calculations to be able to describe the intra-atomic correlations giving rise to atomic multiplets led to calculations based on the Hubbard I approximation performed on top of LDA+U [12]. The multiplets belong to a standard inventory of spectra of regular rare earths with localized 4*f* states, but in the case of Pu the 5*f* states are still mostly forming a band of ≈1 eV width and hybridize with non-*f* states. The results of the Hubbard I calculations yield the (correct) position of the multiplet in the energy scale and finite width of individual features, so there are no adjustable parameters and the agreement with experimental spectra cannot be doubted. The intense $^7F_0 \rightarrow {}^6H_{5/2}$ excitation is practically touching the Fermi energy, which must also be affecting low-energy properties depending on excitations in the electron system, such as heat capacity, yielding a heavy fermion behaviour. The $5f^4$ multiplet, originating from excitations from the $5f^5$ initial state, is located at higher binding energies, and its details are not resolved in the photoelectron spectra (PES). Interestingly, the same $5f^5$ multiplet as in Pu also appears in spectra of Am metal, although at higher binding energies, again in full agreement with the given theoretical framework [12].

3. Occurrence of magnetism in Pu compounds

Although not related directly to photoelectron spectra, relevance of different theoretical approaches can be validated by reviewing the occurrence (or absence) of magnetic order, which is well established for majority of Pu compounds known. The number of magnetically ordered systems on the basis of Pu is significantly reduced when comparing to U or Np counterparts. To describe correctly the onset of magnetism is therefore a quite strict criterion of relevance of the particular approach. Furthermore, the size of magnetic moments or even its spin and orbital components (known unfortunately in a few cases only) can be used to test the theoretical results. The LDA+U around mean field method is in this respect successful. It reproduces the non-magnetic ground state of Pu chalcogenides, δ-Pu, Pu-Am *fcc* alloys, and of Pu_2C_3 from the carbides. On the other hand, PuSb and PuC come out correctly on the magnetic side. The important finding is that the magnetic state appears for those with n_{5f} below approx. 5.3, whereas higher 5*f* occupancy leads to a non-magnetic state. It is interesting that the superconductor $PuCoGa_5$ falls very close to the borderline (being on its non-magnetic side). It underlines a quite remarkable fact that one does not have to go as high as $n_{5f} = 6$ so as to suppress magnetism within the LDA+U around mean field, even without evoking quantum fluctuations. The non-magnetic ground state is, as a rule, found for anomalous rare earths with the valence fluctuating between one magnetic and one non-magnetic state. A deeper insight in the origin of non-magnetic behaviour could be perhaps based on the analysis in Ref. [13], deducing that a certain type of orbital polarization without breaking the time-reversal symmetry can develop in δ-Pu.

Currently there is a certain disagreement with the spectroscopy results described in Ref. [14]. To reconcile PES data suggesting, in agreement with LDA+U calculations, variable n_{5f} for Pu systems with the XAS and EELS data, more XAS and EELS experiments have to be done. Experiments on Pu chalcogenides, assumed as having the highest n_{5f}, would provide a suitable reference case.

The fact that the $5f^5$ final-state multiplet occurs in the PES spectra in case of higher 5*f* occupancy (stronger $5f^6$ admixture) leads to a correlation of the presence of magnetic order and the lack of the Fermi level peak (or its weak intensity). This correlation can also be seen in other case, in which calculations have not been performed yet, as PuSi [4] or PuH_3 [15].

4. Conclusions

Valence-band photoelectron spectra of Pu systems can be understood as being affected by the $5f^5$ final-state multiplet, which appears in the spectra when the LDA+U around mean field calculations yield the 5*f* occupancy higher than 5.0. The spectra can be captured calculating the spectral function using the Hubbard I method, which yields correct position and intensity of the respective spectral lines, with the most intense line touching the Fermi level. This theoretical framework also explains some fundamental properties, such as lack of magnetism for $n_{5f} > 5.3$ and concomitant heavy fermion behaviour.

These results suggest that a more complete theoretical description of the Pu metal and Pu compounds would have to capture the true many-body states $5f^5$ and $5f^6$ and fluctuations between them. The physics of Pu can be thus analogous to valence fluctuators known from the field of anomalous rare earths.

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References

[1] J.M. Wills, O. Eriksson, A. Delin, P.H. Anderson, J.J. Joyce, T. Durakiewicz, M.T. Butterfield, A.J. Arko, D.P. Moore, L.A. Morales, J. Electr. Spectr. Rel. Phenomena 135 (2004) 163.
[2] T. Gouder, F. Wastin, J. Rebizant, L. Havela, Phys. Rev. Lett. 84 (2000) 3378.
[3] L. Havela, T. Gouder, F. Wastin, J. Rebizant, Phys. Rev. B 65 (2002) 235118.
[4] T. Gouder, R. Eloirdi, J. Rebizant, P. Boulet, F. Huber, Phys. Rev. B 71 (2005) 165101.
[5] T. Gouder, L. Havela, A.B. Shick, F. Huber, F. Wastin, J. Rebizant, J. Phys.: Cond. Matter. 19 (2007) 476201.
[6] L. Havela, F. Wastin, J. Rebizant, T. Gouder, Phys. Rev. B 68 (2003) 085101.
[7] J.J. Joyce, J.M. Wills, T. Durakiewicz, et al., Phys. Rev. Lett. 91 (2003) 176401.
[8] R. Eloirdi, L. Havela, T. Gouder, J. Rebizant, F. Huber, R. Caciuffo, J. Nucl. Mater. 385 (2009) 8.
[9] T. Durakiewicz, J.J. Joyce, G.H. Lander, C.G. Olson, M.T. Butterfield, E. Guziewicz, A.J. Arko, L. Morales, J. Rebizant, K. Mattenberger, O. Vogt, Phys. Rev. B 70 (2004) 205103.

[10] G.H. Lander, A. Delapalme, P.J. Brown, J.C. Spirlet, J. Rebizant, O. Vogt, Phys. Rev. Lett. 53 (1984) 2262.
[11] A. Shick, L. Havela, T. Gouder, J. Rebizant, J. Nucl. Mater. 385 (2009) 21.
[12] A. Shick, J. Kolorenc, L. Havela, V. Drchal, T. Gouder, EPL 77 (2007) 17003.
[13] F. Chricchio, F. Bultmark, L. Nordström, Phys. Rev. B 78 (2008) 100404(R).
[14] J.G. Tobin, P.P. Söderlind, A. Landa, K.T. Moore, A.J. Schwartz, B.W. Chung, M.A. Wall, R.G. Haire, A.L. Kutepov, J. Phys.: Cond. Matter. 20 (2008) 125204.
[15] T. Gouder, A. Seibert, J. Rebizant, F. Huber, L. Havela, Mater. Res. Soc. Symp. Proc. 986 (2007). 0986-OO01-02.