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Electronic-structure theory of plutonium chalcogenides

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ABSTRACT

The correlated band theory methods, the around-mean-field LDA + U and dynamical LDA + HIA (Hubbard-I), are applied to investigate the electronic structure of Pu chalcogenides. The LDA + U calculations for PuX (X = S, Se, Te) provide non-magnetic ground state in agreement with the experimental data. Non-integer filling of 5*f*-manifold (from approx. 5.6 in PuS to 5.7 PuTe). indicates a mixed valence ground state which combines f^5 and f^6 multiplets. Making use of the dynamical LDA+HIA method the photoelectron spectra are calculated in good agreement with experimental data. The three-peak feature near E_F attributed to 5*f*-manifold is well reproduced by LDA + HIA, and follows from mixed valence character of the ground state.

1. Introduction

Plutonium chalcogenides PuS, PuSe and PuTe crystallize in the NaCl structure type. Their semi-metallic and weakly paramagnetic behaviour [1,2] is at variance with Pu pnictides and also with U and Np chalcogenides. Here we focus on theoretical studies of essential bulk properties as well as photoelectron spectra (PES) of Pu chalcogenides, and on implications for δ-Pu and other Pu systems.

During last few years, electronic structure calculations of Pu and Am based on the conventional band theoretical methods (the local density or generalized gradient expansion approximations –LDA/GGA– to the density functional theory) could not explain essential experimental data. While the LDA/GGA band structure calculations predict a local magnetic moment (ordered or disordered) to form at the Pu [3] and Am [4] atoms, none of them were seen in the experiment [5]. The same approaches attempted to evaluate the photoemission spectra and electronic specific heat in Pu and Am using single-particle LDA/GGA densities of states (DOS), incorrectly assuming weak electron correlation character of 5*f* systems at the borderline between the localized, nonbonding, behaviour and the bonding situation of electronic bands.

Here we apply a DMFT based computational scheme based on multi-orbital Hubbard-I approximation (HIA) [6,7] including the spin-orbit coupling (SOC), which explicitly accounts for the atomic-like multiplet-transition excitations in PuX (X = S, Se, Te) compounds [8]. Starting from the non-magnetic ground state calculated with the static mean-field AMF-LSDA + U approximation [9], we obtained excitation spectra of PuX in a reasonably good agreement with valence-band photoelectron spectra (PES), in support of the atomic-like origin of the electronic excitations in these materials.

2. Theoretical method

We start with the multi-band Hubbard Hamiltonian [6] $H = H^0 + H^{\text{int}}$, where

$$H^0 = \sum_{i,j,\alpha,\beta} H^0_{i,\alpha,j,\beta} c^\dagger_{i\alpha} c_{j\beta} = \sum_{\mathbf{k},\alpha,\beta} H^0_{\alpha,\beta}(\mathbf{k}) c^\dagger_{\alpha}(\mathbf{k}) c_{\beta}(\mathbf{k}) \qquad (1)$$

is the one-particle Hamiltonian found from ab initio electronic structure calculations for a periodic crystal. The indices *i*,*j* label the lattice sites, $\alpha = (\ell m \sigma)$ denote the spinorbitals, and $\mathbf{k}$ is the *k*-vector from the first Brillouin zone. It is assumed that the electron–electron correlations between *s*, *p*, and *d* electrons are well described within the density functional theory, while the correlations between the *f* electrons have to be considered separately by introducing the interaction Hamiltonian

$$H^{\text{int}} = \frac{1}{2} \sum_{i,m_1,m_2,m_3,m_4,\sigma,\sigma'} \langle m_1, m_2 | V^{ee}_i | m_3, m_4 \rangle c^\dagger_{im_1\sigma} c^\dagger_{im_2\sigma'} c_{im_4\sigma'} c_{im_3\sigma} \qquad (2)$$

The V^{ee} is an effective on-site Coulomb interaction [6] expressed in terms of the Slater integrals F_k and the spherical harmonic $|lm\rangle$. The corresponding one-particle Green function

$$G(\mathbf{k}, z) = (z + \mu - H^0(\mathbf{k}) - \sum(\mathbf{k}, z))^{-1} \qquad (3)$$

is expressed via H^0 and the one-particle selfenergy $\sum(\mathbf{k},z)$ which contains the electron–electron correlations, where *z* is a (complex)

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energy with respect to the chemical potential μ. The interactions (2) act only in the subspace of f-states. Consequently, the selfenergy $\sum(\mathbf{k},z)$ is non-zero only in the subspace of the f-states.

In what follows we use the local approximation for the selfenergy, i.e., we assume that it is site-diagonal and therefore independent of $\mathbf{k}$. Then we can employ the 'impurity' method of Ref. [6]. First, the self-consistent *around-mean-field*-L(S)DA + U calculations were performed, taking into account the presence of SOC as described in Ref. [8]. Next, we used LSDA + U eigenvalues and eigenfunctions calculated in the full-potential LAPW basis [9] to construct the local Green function (which is a matrix in $(m\sigma)$ spin-orbital space):

$$G_{+U}(z) = \frac{1}{V_{BZ}} \int_{BZ} d\mathbf{k}(z + \mu - H_0(\mathbf{k}) - V_{+U})^{-1}. \tag{4}$$

We evaluate the static 'bath' $G_0(z)$:

$$\begin{aligned}(z + \mu - \varepsilon_{+U} - \xi(\mathbf{l}\cdot\mathbf{s}) - \Delta(z))^{-1} &= G^0_{+U}(z)\\ &= (G^{-1}_{+U}(z) + V_{+U}(z))^{-1}.\end{aligned} \tag{5}$$

from Eq. (5) (right-hand part), and find the hybridization function $\Delta(z)$ together with $(\varepsilon_{+U} - \mu)$ which determines the energy of 'impurity' level with respect to the solid potential.

We construct the atomic Hamiltonian including the spin-orbit coupling (SOC):

$$\begin{aligned}H^{at} = &\sum_{m_1,m_2,\sigma,\sigma'} \zeta(\mathbf{l}\cdot\mathbf{s})^{\sigma\sigma'}_{m_1m_2} c^\dagger_{m_1\sigma} c_{m_2\sigma'} + \frac{1}{2}\\ &\times \sum_{m,\sigma} \langle m_1, m_2|V^{ee}_i|m_3, m_4\rangle c^\dagger_{im_1\sigma} c^\dagger_{im_2\sigma'} c_{im_4\sigma'} c_{im_3\sigma}\end{aligned} \tag{6}$$

and we can perform exact diagonalization of $H^{at}|\nu\rangle = E_\nu|\nu\rangle$ to obtain all possible eigenvalues E_ν and eigenvectors $|\nu\rangle$.

The atomic Green function is calculated as follows:

$$\begin{aligned}[G^{at}(z)]^{\sigma\sigma'}_{m_1m_2}(z) = \frac{1}{Z}\sum_{\nu,\mu} &\frac{\langle\mu|c_{m_1\sigma}|\nu\rangle\langle\nu|c^\dagger_{m_2\sigma'}|\mu\rangle}{z + (E_\mu - \mu_H N_\mu) - (E_\nu - \mu_H N_\nu)}\\ &\times \left[\exp(-\beta(E_\nu - \mu_H N_\nu))\right.\\ &\left.+ \exp(-\beta(E_\mu - \mu_H N_\mu))\right]\end{aligned} \tag{7}$$

and the atomic self-energy is evaluated as:

$$[\sum_H(z)]^{\sigma\sigma'}_{mm'} = z\delta_{m_1m_2}\delta_{\sigma\sigma'} - \xi(\mathbf{l}\cdot\mathbf{s})^{\sigma\sigma'}_{m_1m_2} - [(G^{at}(z))^{-1}]^{\sigma\sigma'}_{m_1m_2}. \tag{8}$$

Then we insert the HIA self-energy, calculated for the same number of correlated electrons as given by LDA + U, into static LDA+U 'bath' Eq. (5), and calculate the new Green function

$$G(z) = ([G^0_{+U}(z)]^{-1} + (\varepsilon_{+U} - \varepsilon_H) - \sum_H(z))^{-1}, \tag{9}$$

where $(\varepsilon_{+U} - \varepsilon_H)$ is chosen so as to ensure that $n = \pi^{-1}\mathrm{Im}\int^\mu dE\,\mathrm{Tr}[G(E)]$ is equal to a given number of correlated electrons.

3. Results and discussion

Valence-band PES spectra of PuS shown in Fig. 1 are obtained with two photon energies. For the lower photon energy, the 5f photoexcitation cross-section is very low and the spectrum captures non-f states only. 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 PES spectra (taken at higher photon energy) 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.

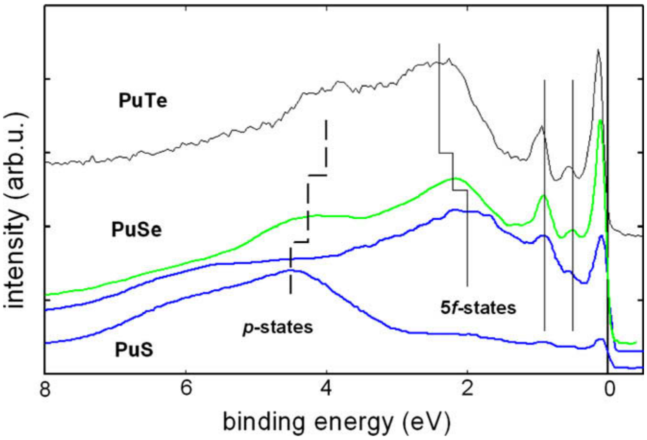

Fig. 1. Valence-band UPS spectra of PuS, PuSe [1], and PuTe [2] for hν = 40.81 eV and PuS for hν = 21.22 eV (at the bottom). They clearly demonstrate that the anion p-emission shifts gradually towards the Fermi level (each step 0.25 eV), whereas the 5f emission at about 2 eV binding energy shifts gradually 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.

The f-state triplet is probably the most prominent characteristic feature of Pu-based systems. The 5f-spectral densities of PuX (X = S, Se, Te), calculated by means of LDA + HIA, are shown in Fig. 2. While the non-f states are treated within the LDA in LDA + HIA calculations, their resulting position agrees better with experimental spectra than in the LSDA calculations [10]. The 5f-spectral density (shown in Fig. 2) contains the 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 [11]. 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. [11]. It was however successfully described for PuSe by another Hubbard I – based approach [12].

It is interesting to compare non-magnetic and semi-metallic PuTe with ferromagnetic metal PuSb. PuSb is a very well documented case of magnetic Pu compound with extended set of microscopic information. Photoelectron spectroscopy deduced the 5f states situated out of the Fermi level and concluded their localization [13]. Neutron diffraction identified a 5f^5 ground state with ordered magnetic moments 0.75 μ_B [14]. Applying LSDA + U with fully localized limit (FLL) double counting model, we obtain a ferromagnetic ground state with the magnetic moment of 0.87 μ_B/Pu and 5f-occupancy n_{5f} = 5.0, in accordance with the experimental data of Ref. [14]. The 5f-spectral density of PuSb calculated with help of LDA + HIA is shown in Fig. 2. When compared with PES the LDA + HIA spectral DOS is reproducing very well the essential features of the experimental spectrum. Importantly, we see virually zero f-contribution at Fermi edge, as in the experiment. It is different from PuTe where three peaks structure at the vicinity ofthe Fermi level is seen in both experimental PES (see Fig. 1) and theoretical DOS (see Fig. 2).

It allows us to suggest a direct link between lack of magnetism, f-manifold occupancy and photoemission spectra character: whenever the mixed-valence Pu ground state with non-integer filling of 5f-manifold is realized due to an admixture of f^5 and f^6 multiplets,

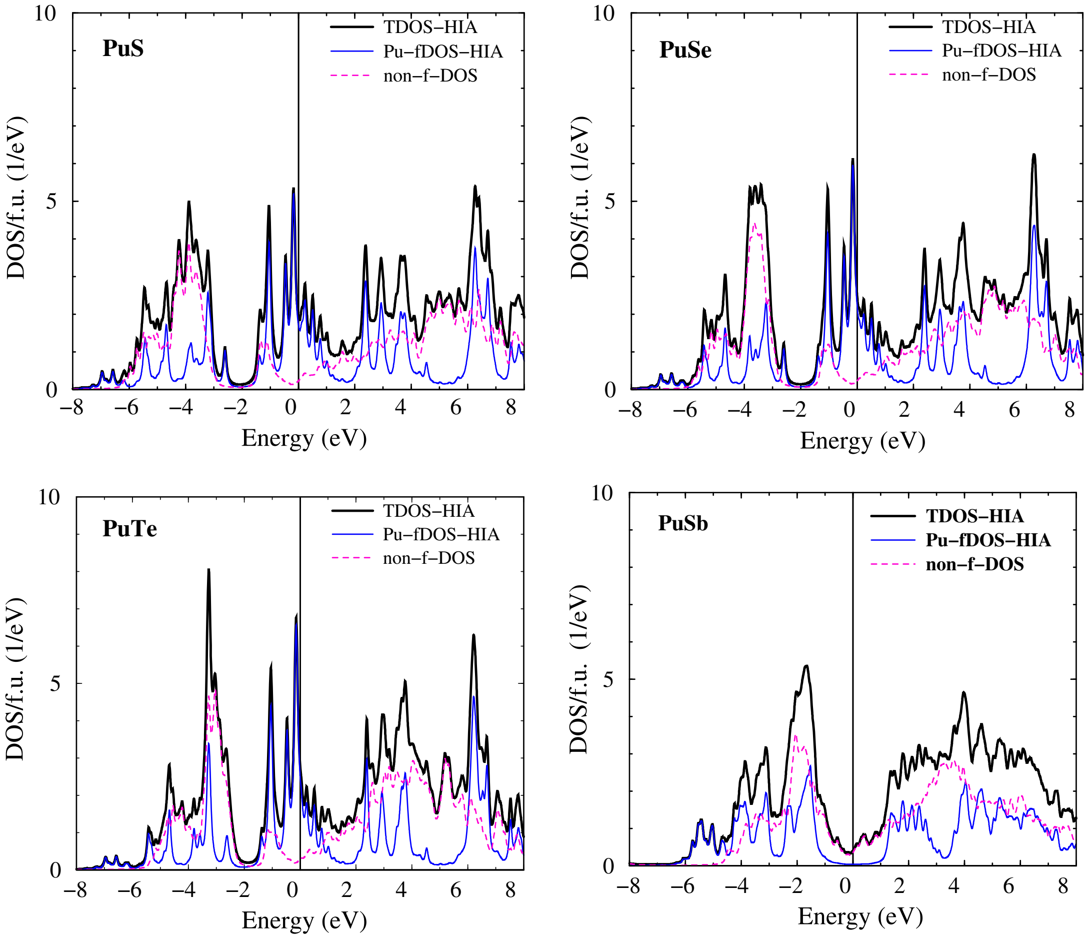

Fig. 2. Calculated densities of states of PuS, PuSe, and PuTe (non-*f*, 5*f*-, and total) obtained by means of LDA + HIA. Also density of state for PuSb (non-*f*, 5*f*-, and total) is shown.

it brings along the non-magnetic character and the high DOS at Fermi level.

The finding that FLL-LDA + U performs better for integer-f^5 magnetic PuSb and AMF-LDA + U for mixed-valent non-magnetic PuTe reflects a qualitative difference between the ground state of both compounds. The LDA + U as a static (Hartree–Fock) approach approximates the ground state in terms of single Slater determinant. When choosing the FLL double counting we are looking for an approximate ground state in a local atomic spin-orbital basis which is as close as possible to the configuration with integer (0 or 1) filling of the corresponding orbitals, and the resulting ground state is driven to the integer filling (f^5 in case of PuSb). On the other hand making use of AMF (which corresponds to the Hartree–Fock approximation for the single band Hubbard model) the ground state is given by a single Slater determinant in the Bloch state basis, and the spin-orbitals are not driven to an integer occupation, resulting in non-integer f-filling.

It is interesting to test the results of AMF-LSDA + U calculations for the equilibrium volume ($\boldsymbol{V}_{\mathrm{eq}}$) and bulk moduli ($\boldsymbol{B}$) of the Pu chalcogenides. Taking the PuTe case as an example, we made the total energy vs volume optimization and found $\boldsymbol{V}_{\mathrm{eq}}$ of 408 Bohr^3 and $\boldsymbol{B}$ of 255 kBar. The agreement with experiment [15] for $\boldsymbol{V}_{\mathrm{eq}}$ is within about 2% and is much improved over previous LDA calculations [10]. The value of bulk modulus is somewhat smaller than reported experimental value of 340-370 kBar [15]. We also checked $\boldsymbol{V}_{\mathrm{eq}}$ of AmTe which is experimentally practically the same as for PuTe and found $\boldsymbol{V}_{\mathrm{eq}}$ of 391 Bohr^3. Taking into account that the same value of Coulomb-$\boldsymbol{U}$ = 4 eV was used for PuTe and AmTe without any further adjustment, we conclude that AMF-LSDA + U reproduces correctly the experimental equilibrium lattice properies of Pu and Am tellurides.

4. Conclusions

The electronic structure of Pu chalcogenides has been investigated using LDA + U and dynamical LDA + HIA (Hubbard-I) methods and compared with PES experimental data. The LDA + U calculations provide correct non-magnetic ground state for PuX with a non-integer filling of the 5*f*-manifold. The 5*f* occupancy weakly increases from approx. 5.6 in PuS to 5.7 in PuTe. This can be taken as an indication of a mixed-valent ground state which is a combination of f^5 and f^6 many-body states. The theoretical analysis shows that: (i) atomic-like excitations can be observed even if the 5*f* states are not fully localized, and the atomic character fixes the characteristic energies; (ii) the mixed valence (and not a Kondo screening) is responsible for PuX (X = S, Se, Te) non-magnetic character.

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