Electronic and magnetic properties of UPdSn: the itinerant 5f electrons approach

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Abstract.   Density functional theory, modified to include spin–orbit coupling and an effective orbital field to simulate Hund's second rule, is applied to investigate the magnetic structure and electronic properties of the compound UPdSn. Our theoretical results are in overall good agreement with experiment. Thus both theory and experiment find the magnetic structure of UPdSn to be noncollinear, the calculated magnetic U-moments being in very good agreement with the measurements. Also, the calculated density of states is found to simulate closely the photoemission spectrum and the very low experimental value of 5 mJ mol^{-1} K^{-2} for the specific heat γ is reproduced reasonably well by the calculated value of 7.5 mJ mol^{-1} K^{-2}. Furthermore, the interconnection of the magnetic structure with the crystal structure is investigated. Here theory and experiment agree concerning the planar noncollinear antiferromagnetic configuration in the orthorhombic crystal structure and for the monoclinically distorted lattice we obtain deviations of the magnetic moments from the plane which, although qualitatively in agreement with the experimentally observed deviations, are smaller than the latter. We carry out a symmetry analysis and show that UPdSn belongs to the class of systems possessing a magnetic structure, the noncollinearity of which is predetermined by symmetry. Conclusions are drawn about the itinerant character of the U 5f electrons.

1. Introduction

In the last years UPdSn has been extensively studied experimentally revealing a number of interesting physical properties [1–7]. The main attention has focused on two magnetic phase transitions which were found to be accompanied by lattice distortions. Thus, the paramagnetic state has the GaGeLi hexagonal crystal lattice. Below 45 K UPdSn becomes magnetic with a noncollinear antiferromagnetic structure. In this phase (which we will refer to as structure I) all magnetic moments of the uranium atoms lie parallel to a plane and compensate one another completely. Simultaneously orthorhombic lattice distortions are detected. At 20 K a second phase transition is observed. Here the magnetic structure (structure II) is still noncollinear and compensated; however, the magnetic moments deviate from the plane, developing components perpendicular to it. Noncollinear magnetic structures have been observed in a number of different uranium compounds (see, e.g., [8–10]) and they seem to be quite common for this class of materials. Recently, we have therefore studied such structures in U$_3$P$_4$ [11, 12], U$_2$Pd$_2$Sn [11, 12], U$_3$As$_4$ and U$_3$Sb$_4$ [13] and found that two different types of noncollinearity must be distinguished. Simplifying somewhat, we may refer to them as *accidental noncollinearity* and *symmetry predetermined noncollinearity*. In the first case (e.g. U$_2$Pd$_2$Sn [11, 12]) there are a number of structures, both collinear and noncollinear, which are distinguished by additional symmetry, i.e. at least one symmetry

element will be lost with any deviation of the magnetic moments. This additional symmetry leads to a local extremum of the total energy for these structures, which in this sense are quasi-stable. Which of the magnetic structures possesses the lowest energy depends on a cumbersome competition of different interactions. In the second case (e.g. U_3X_4 compounds) the collinear structure is not distinguished by symmetry from the structures obtained from it by an infinitesimal rotation of magnetic moments, and therefore it does not possess an extremum of the total energy that is caused by the symmetry of the problem. In other words, the collinear magnetic structure has exactly the same symmetry properties as the canted noncollinear structures obtained by infinitesimal rotations of the atomic moments. Because the probability of the minimum of the total energy being assumed by the collinear structure is negligible, canting is the inevitable consequence. We have shown that in the formation of the second type of noncollinearity a crucial role is played by the relativistic spin–orbit coupling, which influences the symmetry properties of the physical system in an important way.

The complex antiferromagnetic noncollinear structures observed in UPdSn, as well as an interesting relation which exists between the magnetic structure and the lattice distortion, make this compound very attractive for the continuation of our studies of the magnetic ordering in U compounds.

Another interesting aspect of the physics of the UPdSn compound is the controversial nature of the 5f electrons. On the one hand, the very low specific heat γ value detected experimentally [2] can be treated as a sign of the highly localized nature of the 5f electrons in this compound [2, 7]. On the other hand, in photoemission experiments [4] the 5f states were observed to lie close to the Fermi level in apparent contradiction to the low γ value. The nature of the 5f electron states in UPdSn was discussed by Trygg *et al* [14] who, to our knowledge, reported the only band structure calculation of this compound. Their study was carried out for an assumed collinear ferromagnetic phase under two different kinds of assumptions. First, the 5f electrons were treated as itinerant valence electrons and, second, as localized core electrons. Accounting for the effective orbital field simulating Hund's second rule allowed these authors to obtain good agreement between the theoretical magnetic moment formed by the itinerant 5f electrons and the experimental uranium magnetic moment. However, the low γ value and the results of the photoemission experiment could not be satisfactorily explained in the itinerant picture for the 5f electrons. Although the treatment of the 5f electrons as localized resulted also in a number of discrepancies between calculation and experiment, Trygg *et al* concluded in favour of the localized nature of the U 5f electrons in UPdSn.

The essential difference between the noncollinear antiferromagnetic structures observed experimentally and the collinear ferromagnetic structure assumed by Trygg *et al* [14] demands further theoretical study of the UPdSn compound. In the present paper we report calculations of the antiferromagnetic noncollinear states in UPdSn.

In the following section we give a brief description of the Hamiltonian employed in the calculations discussing the crystal structure and calculational parameters. Next we report results for the magnetic structure calculated self-consistently in the undistorted crystal lattice of the paramagnetic state as well as for the lattices with orthorhombic and monoclinic distortions. We carry out a symmetry analysis and stress that we find in all three cases noncollinear magnetic structures that are predetermined by symmetry. We compare the calculated and experimental magnetic structures and discuss the electron density of states (DOS), comparing it with the experimental photoemission spectrum [4] and with the experimental estimate for the electronic heat capacity γ value [2]. In summarizing we draw our conclusions concerning the itinerant nature of the U 5f electrons in this compound.

2. Hamiltonian

The Hamiltonian of the problem employed in the present studies is identical to the Hamiltonian used in our previous investigations of U compounds possessing noncollinear magnetic structures [11–13]. It contains three terms: the scalar-relativistic Hamiltonian, the spin–orbit coupling (SOC) term and an effective orbital field term, the latter of which simulates the effect of Hund's second rule. To make the paper self-contained we describe briefly the Hamiltonian as well as the calculational scheme.

The scalar-relativistic Hamiltonian is given by

$$\hat{\mathbf{H}}_{sc}(\boldsymbol{a}_\nu, \boldsymbol{e}_\nu) = \sum_\nu \mathbf{U}^+(\theta_\nu, \phi_\nu) \begin{pmatrix} H_{sc}^{\nu\uparrow}(\boldsymbol{r}_\nu) & 0 \\ 0 & H_{sc}^{\nu\downarrow}(\boldsymbol{r}_\nu) \end{pmatrix} \mathbf{U}(\theta_\nu, \phi_\nu). \tag{1}$$

Here $\mathbf{U}(\theta_\nu, \phi_\nu)$ is the standard spin-$\frac{1}{2}$-rotation matrix which describes the transformation between a global and a local coordinate system of the νth atom whose spin orientation is given by the polar angles θ_ν and ϕ_ν with respect to the z-axis of the global system. $H_{sc}^{\nu\uparrow}(\boldsymbol{r}_\nu)$ and $H_{sc}^{\nu\downarrow}(\boldsymbol{r}_\nu)$ are the standard atomic scalar-relativistic Hamiltonians (spin up, spin down) [15] in the local frame of reference for the atom at site ν. They contain the mass velocity, the Darwin term and the effective one-particle potential which, as usual, is given by functional derivatives of the total energy and is spin-diagonal in the local frame of this atom.

The second term of the Hamiltonian

$$\hat{\mathbf{H}}_{so}(\boldsymbol{a}_\nu, \boldsymbol{e}_\nu) = \sum_\nu \mathbf{U}^+(\theta_\nu, \phi_\nu) \left\{ \sum_\alpha M_{\alpha\nu} \sigma_{\alpha\nu} \hat{l}_{\alpha\nu} \right\} \mathbf{U}(\theta_\nu, \phi_\nu) \tag{2}$$

accounts for the SOC; its inclusion renders the Hamiltonian fully relativistic. Here $\sigma_{\alpha\nu}$ and $\hat{l}_{\alpha\nu}$ are the Cartesian components of the Pauli spin matrices and the angular momentum operator, respectively, in the local system of the νth atom and the coefficients M can be found in [16]. Variables of the Hamiltonians are the positions of the atoms $\boldsymbol{a}_\nu$ and the directions of the atomic spin moments $\boldsymbol{e}_\nu$. The latter are obtained by recomputing and diagonalizing in each iteration step the two-dimensional spin-density matrix [17]; it is this quantity that must be diagonal in the local coordinate system thus giving self-consistent angles θ_ν and ϕ_ν, and a minimum of the total energy.

Not only the spin moment but also the orbital moment is treated as a three-dimensional vector. For the νth atom the latter is obtained directly as a sum over occupied electron states of expectation values of the angular momentum operator $\hat{l}_\alpha$:

$$L_\alpha^\nu = \sum_{kn,occ} \int_{\Omega_\nu} \psi_k^{n+}(\boldsymbol{r}) \hat{l}_\alpha \psi_k^n(\boldsymbol{r}) \, \mathrm{d}\boldsymbol{r} \qquad \alpha = x, y, z \tag{3}$$

where n is the band index and the integration is carried out over the νth atomic sphere. For the special case when the atomic moments are parallel to the global z-axis, an expression for the z-component of the orbital moment can easily be derived from equation (4) that agrees with that given in [18].

Following the work of Eriksson *et al* [19] we add the following term to the Hamiltonian of the problem

$$\hat{\mathbf{H}}_{orb} = I_{orb} L_z \hat{l}_{z\nu} \tag{4}$$

which takes into account interactions responsible for Hund's second rule. Here L_z is the projection of the atomic orbital moment onto the local atomic z-axis. The parameter I_{orb} was taken to equal 2.6 mRyd [19]. The actual numerical calculations are performed with the augmented spherical wave (ASW) method [20].

3. Crystal structure and calculational parameters

Paramagnetic UPdSn crystallizes in the hexagonal GaGeLi-type structure. The uranium atoms lie on a simple hexagonal lattice with two uranium layers per crystallographic unit cell. The coordinates of the atoms and the lattice parameters are collected in table 1.

Table 1. Crystal structure parameters of the orthorhombic UPdSn.

| Lattice constants	$a = 4.600$ Å	$b/a = 1.73205$	$c/a = 1.58464$
U(1)	0	0	$\frac{1}{4}$
U(2)	0	0	$\frac{3}{4}$
U(3)	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{4}$
U(4)	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{3}{4}$
Pd(1)	$\frac{1}{2}$	$\frac{1}{6}$	0.923
Pd(2)	0	$\frac{1}{3}$	0.423
Pd(3)	$\frac{1}{2}$	$\frac{5}{6}$	0.423
Pd(4)	0	$\frac{2}{3}$	0.923
Sn(1)	$\frac{1}{2}$	$\frac{1}{6}$	0.521
Sn(2)	0	$\frac{1}{3}$	0.021
Sn(3)	$\frac{1}{2}$	$\frac{5}{6}$	0.021
Sn(4)	0	$\frac{2}{3}$	0.521
Atomic radii	$R(\text{U}) = 1.895$ Å	$R(\text{Pd}) = 1.571$ Å	$R(\text{Sn}) = 1.740$ Å

A planar noncollinear antiferromagnetic structure (labelled I), see figures 1(a) and 1(b), observed below 45 K has an orthorhombic magnetic unit cell with $b = \sqrt{3}a$ [1]. The magnetic unit cell is two times larger than the crystallographic hexagonal unit cell. In a later experiment [5] an orthorhombic distortion of the crystal lattice accompanying the magnetic phase transition was observed, i.e. the value of b was found to deviate somewhat from $\sqrt{3}a$. In the magnetic structure (labelled II) observed below 20 K the magnetic moments rotate out of the yz-plane keeping, however, the structure compensated (figure 1(c)). This phase transition was found to be accompanied by monoclinic lattice distortions (see figure 1(c)).

Note that in a recent paper of Troc *et al* [7] on UPdSn these authors obtained results which are, in general, very similar to the results of previous investigations, but due to a different interpretation of the data they concluded that UPdSn possesses more complicated magnetic structures with a larger magnetic unit cell than the structures suggested in [1, 5]. Because Troc *et al* do not elaborate the magnetic structure any further, in the present paper we are guided by the experimental conclusions drawn in [1, 5].

4. Calculational results and discussion

4.1. Calculation of the magnetic structure

We start our calculations with the undistorted hexagonal lattice having initially all uranium magnetic moments directed along the z-axis and forming a collinear antiferromagnetic structure (see figure 1(a)) with an orthorhombic magnetic unit cell. Subsequently, allowing the moments to rotate, they deviated immediately from the z-axis keeping, however, their

(a) (b) (c)
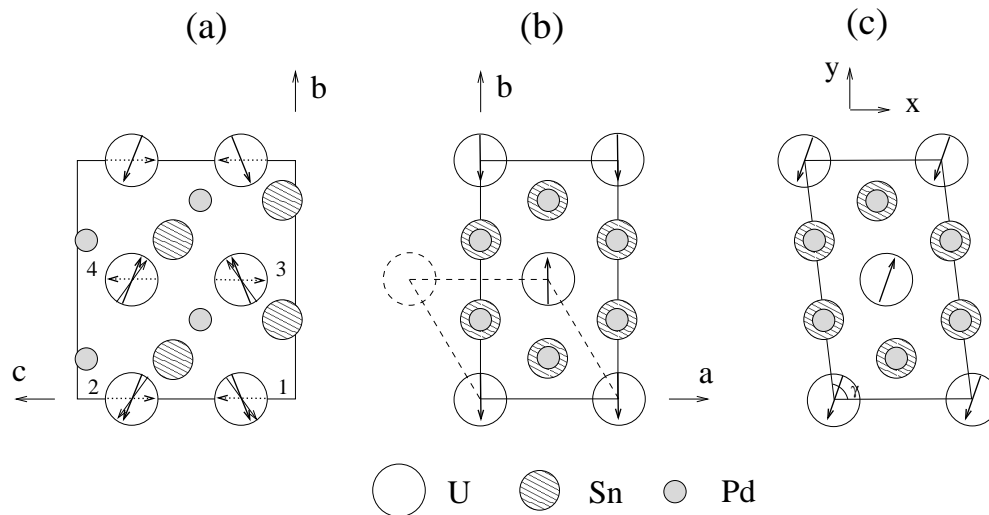
Figure 1. Projections of the crystal and magnetic structure onto the xy- and yz-planes. (a) Projection of the orthorhombic unit cell onto the yz-plane. Dotted arrows show the initial magnetic structure used to start the calculation, thick arrows show the resulting self-consistent directions of the magnetic moments. Thin arrows show the experimental magnetic structure [1]. (b) Projection of the orthorhombic unit cell onto the xy-plane. Both experimental and theoretical projections of the magnetic moments are parallel to the y-axis. (c) Projection of the monoclinic unit cell onto the xy-plane. Arrows show schematically the deviations of the magnetic moments from the yz-plane.

equivalence and the compensated character of the magnetic structure. The resulting self-consistent directions of the magnetic moments are shown in figure 1(a); they form a magnetic structure which is very similar to the experimental structure I. The following symmetry principle, formulated by us in previous studies of complex magnetic structures [13, 21, 22], helps us to expose the physical reasons for the instability of the initial collinear structure. *If a deviation of the magnetic moments from their initial directions destroys the invariance of the Kohn–Sham Hamiltonian with respect to at least one symmetry operation, this deviation cannot take place. Oppositely, if a deviation of the magnetic moments does not destroy any symmetry operation this deviation must take place*. In the latter case we deal with a noncollinearity of the magnetic structure that is predetermined by symmetry.

To apply the symmetry principle to our problem we begin with a symmetry analysis of the initial collinear antiferromagnetic structure. We will consider two types of symmetry transformations: unitary transformations which do not contain time reversal and anti-unitary transformations which are products of a unitary transformation with the time-reversal operation. The system at hand possesses four unitary symmetry transformations and four anti-unitary transformations which are collected in table 2. Note that the vector $\tau_2 = \frac{1}{2}(a, b, 0)$ is a lattice translation of the hexagonal chemical lattice, which in the magnetic case must be accompanied by time reversal to be a symmetry operator (operator 5 in table 2).

The following symmetry property of the initial collinear structure is important for us: all non-trivial unitary transformations, 2 to 4, and three of the four non-unitary transformations, 5, 6 and 8, do not leave the atomic positions unchanged and transfer every atom into the position of another atom. Simultaneously, the moment of the atom is transformed to assume a direction corresponding to the new atomic position. Therefore, these operations do not

Table 2. Symmetry properties of the orthorhombic UPdSn. $\varepsilon = \begin{pmatrix} 1 & & \\ & 1 & \\ & & 1 \end{pmatrix}$; $C_{2z} = \begin{pmatrix} -1 & & \\ & -1 & \\ & & 1 \end{pmatrix}$; $\sigma_x = \begin{pmatrix} -1 & & \\ & 1 & \\ & & 1 \end{pmatrix}$; $\sigma_y = \begin{pmatrix} 1 & & \\ & -1 & \\ & & 1 \end{pmatrix}$. $\tau_1 = \frac{1}{2}(a, b, c)$; $\tau_2 = \frac{1}{2}(a, b, 0)$; $\tau_3 = \frac{1}{2}(0, 0, c)$. R represents the time reversal operation.

	Operation	Transposition of U atoms	Restriction on U moments
1	$\{\varepsilon\|0\}$	No	No
2	$\{C_{2z}\|\tau_1\}$	$1 \leftrightarrow 4; 2 \leftrightarrow 3$	$\begin{pmatrix} m_x \\ m_y \\ m_z \end{pmatrix}_i = \begin{pmatrix} -m_x \\ -m_y \\ m_z \end{pmatrix}_j$; $i \leftrightarrow j$
3	$\{\sigma_x\|\tau_2\}$	$1 \leftrightarrow 3; 2 \leftrightarrow 4$	$\begin{pmatrix} m_x \\ m_y \\ m_z \end{pmatrix}_i = \begin{pmatrix} m_x \\ -m_y \\ -m_z \end{pmatrix}_j$; $i \leftrightarrow j$
4	$\{\sigma_y\|\tau_3\}$	$1 \leftrightarrow 4; 2 \leftrightarrow 3$	$\begin{pmatrix} m_x \\ m_y \\ m_z \end{pmatrix}_i = \begin{pmatrix} -m_x \\ m_y \\ -m_z \end{pmatrix}_j$; $i \leftrightarrow j$
5	$\{\varepsilon\|\tau_2\}R$	$1 \leftrightarrow 3; 2 \leftrightarrow 4$	$m_i = -m_j$; $\quad i \leftrightarrow j$
6	$\{C_{2z}\|\tau_3\}R$	$1 \leftrightarrow 2; 3 \leftrightarrow 4$	$\begin{pmatrix} m_x \\ m_y \\ m_z \end{pmatrix}_i = \begin{pmatrix} m_x \\ m_y \\ -m_z \end{pmatrix}_j$; $i \leftrightarrow j$
7	$\{\sigma_x\|0\}R$	No	$m_x = 0$; $\quad$ all i
8	$\{\sigma_y\|\tau_1\}R$	$1 \leftrightarrow 4; 2 \leftrightarrow 3$	$\begin{pmatrix} m_x \\ m_y \\ m_z \end{pmatrix}_i = \begin{pmatrix} m_x \\ -m_y \\ m_z \end{pmatrix}_j$; $i \leftrightarrow j$

impose any restrictions on the directions of particular atomic moments but only on their relative directions. These restricting relations are collected in the last column of table 2.

The only non-trivial symmetry operation which keeps atoms in their initial positions is the anti-unitary transformation 7. This symmetry operation requires the condition $m_x^i = 0$ for each atom i. Because of this the restrictions on the relative directions of the atomic moments resulting from the other symmetry operations take the following form: $m_y^1 = m_y^2 = -m_y^3 = -m_y^4$ and $m_z^1 = -m_z^2 = m_z^3 = -m_z^4$. This means that the initial collinear structure has the same symmetry as the noncollinear structures satisfying these relations. The noncollinear magnetic structure detected experimentally belongs to this type of structures. Thus, according to the symmetry principle, the realization of an extremum of the total energy by the collinear structure is improbable and hence the moments will deviate from collinearity. The details of this deviation can only be ascertained by self-consistent calculations which establish the minimum of the total energy. To further expose the origin of the noncollinearity we must uncover which physical interactions determine the decisive symmetry property. One of these interactions is the SOC. As was shown earlier [21, 22], in absence of the SOC any collinear magnetic structure is quasi-stable. The reason for this is that the symmetry of the non-relativistic Hamiltonian must be treated on the basis of the generalized spin-space groups which are essentially different from the usual space groups used in the relativistic case.

Another important feature which contributes decisively to the formation of the noncollinearity is the influence of the Pd and Sn atoms. Numerical experiments with only

the U atoms taken into consideration have shown that the initial collinear structure becomes stable in this case. Again this property is easy to understand if one notices that the U atoms form a simple hexagonal lattice which has a higher symmetry than the GaGeLi structure. As a result, the collinear antiferromagnetic structure possesses a symmetry operation C_{2z} (see table 2) without any accompanying non-primitive translation. This symmetry operation demands that $m_x^i = 0$ and $m_y^i = 0$ for any atom i. To preserve this symmetry the collinear structure must be kept unchanged. Thus, in the presence of SOC it is the influence of the Pd and Sn atoms that forces the U moments to become noncollinear.

Next we study the influence of lattice distortions on the magnetic structure. We start with the orthorhombic distortions which were observed to accompany the magnetic structure I. Following the experiment [5], we introduce a small variation of the lattice parameters a and b such that the relation $b = \sqrt{3}a$ valid for the ideal hexagonal lattice is no longer satisfied. This distortion does not affect the symmetry of the system because the magnetic structure has already lowered the symmetry of the crystal from hexagonal to orthorhombic. As a result no qualitative changes of the magnetic structure were observed due to the orthorhombic lattice distortion and quantitative changes also appeared to be very small. The magnetic structure is very close to the structure shown in figure 1(a) and is still in good agreement with the experimental structure I.

A basically different response was obtained to the monoclinic distortions. In agreement with experiment the b-side of the basal rectangle (figure 1) was rotated by 0.4° about the c-axis. We start the calculations with the magnetic structure I. Already after the first iteration all uranium magnetic moments deviated from the yz-plane, staying, however, mutually equivalent and compensating the magnetic structure.

Again, a symmetry analysis helps us to understand this process. The monoclinic distortion decreases the symmetry of the system, such that from the eight operations of the orthorhombic structure only four are left over in this case. These are the operations numbered in table 2 as 1, 2, 5 and 6. Operation 5 demands equivalence of atom 1 to atom 3 and atom 2 to atom 4. Simultaneously, the moments of the equivalent atoms must be antiparallel: $m_1 = -m_3$ and $m_2 = -m_4$. Operation 2 is responsible for the equivalence of atoms 1 and 4 and the following relation between the components of the magnetic moments: $m_x^1 = -m_x^4$, $m_y^1 = -m_y^4$, $m_z^1 = m_z^4$. Further symmetry operations do not lead to additional restrictions. Thus we see the important difference between the orthorhombic and the monoclinic structures of UPdSn: in the monoclinic structure there is no symmetry operation demanding that the x-component of the magnetic moments are zero. This means that a deviation of the magnetic moments from the yz-plane does not change the symmetry of the system and therefore such a deviation will take place according to our symmetry principle. Thus the result of the calculation for the monoclinically distorted lattice and the corresponding symmetry analysis are in qualitative agreement with the experimental data. However, quantitatively there is a large difference between the calculated and experimental parameters of the magnetic configuration. Moreover, experimentally the m_x component of the atomic moments is found to be close to the value of the m_y components, i.e. the rotation of the magnetic moments out of the yz-plane is about 45°. Our calculation gives a much smaller rotation value of 1.3° for the experimental lattice distortion. To study the sensitivity of the out-of-plane rotation to the value of the monoclinic distortion, we carried out a numerical experiment and calculated the magnetic structure for a number of distortions, with distortion angle up to 2°. We found the value of the deviation of the moments out of the yz-plane to be practically proportional to the monoclinic distortion. At present we have no explanation for the difference between the experimental and theoretical estimates of the value of the out-of-plane rotation of the U moments. This difference could perhaps be

related to the assumption of Troc *et al* [7] that a larger magnetic unit cell must be taken into account. However, at present there is no information on which kind of magnetic structure it could be and how this hypothetical structure will react to monoclinic distortions.

Note that, in qualitative agreement with experiment, we obtained a high stability of the polar angle θ. For both, orthorhombic and monoclinic, experimental lattice distortions the change in the angle did not exceed $0.05°$, in comparison with $1.3°$ for the variation of the angle ϕ in the monoclinically distorted lattice.

Summarizing our study of the magnetic structures, we conclude that the two types of lattice distortions observed experimentally have very different properties. On the one hand, the orthorhombic distortion does not lower the symmetry of the undistorted magnetic crystal. This distortion can be treated as an inevitable adjustment of the lattice to the magnetic structure. Orthorhombic relaxation of the lattice brings the symmetry of the atomic positions into agreement with the symmetry of the system as a whole. Our calculation shows that this distortion is not important for establishing the magnetic structure: only small variations of the lengths and angles of the moments are obtained due to this distortion.

On the other hand, the second type of distortion having monoclinic symmetry decreases the symmetry of the crystal. The same decrease of the symmetry is connected with the deviation of the atomic moments from the yz-plane and the appearance of the m_x component. Appearance of one of these effects immediately enforces the other.

This connection makes the question a difficult one concerning the primary agent: is the symmetry decrease due to the lattice or the magnetism? To answer this question at least partially we carried out the following numerical experiment: we started a calculation assuming the noncollinear magnetic structure II, however, without the monoclinic distortion. The result was that the magnetic structure relaxes to the planar structure I, i.e. in our calculations the structure II appeared to be unstable in the absence of the monoclinic distortions. In principle, density functional theory allows us to estimate the energy change related to a lattice distortion, a calculation that should be done next. However, to be reliable such a calculation must be full potential, i.e. no approximation to the form of the potential can be used. Our present calculations are based on the atomic sphere approximation (ASA) [20] which does not permit a sufficiently reliable estimate of the energy change due to atomic displacements.

Up until now only the directions of the magnetic moments have been discussed. Turning, therefore, next to the discussion of the magnitude of the moments, we note that in the case of U there are two contributions: the spin and orbital moments. For collinear magnetic structures both atomic moments are antiparallel [23, 24]. Recent investigations [13, 21, 25, 26] have shown, however, that in general the spin and orbital moments of the same atom are noncollinear. For instance, for any noncollinear magnetic structure where the noncollinearity is predetermined by symmetry, the spin and orbital moments of individual atoms must also be noncollinear. Symmetry arguments supporting this statement have been given in [13]. The intra-atomic noncollinearity of the orbital and spin moments is a result of the different influence of the crystal environment on both moments.

It is therefore not surprising that also in the case of UPdSn we find the spin and orbital moments to be noncollinear. However, because of the strong intra-atomic SOC tending to direct both moments antiparallel, the noncollinearity of the spin and orbital moments of the U atom in this compound is very weak and assumes in both magnetic structures, I and II, a value of about $1°$. So, qualitatively, the two atomic moments can be thought of as being antiparallel.

The values of the moments do not change noticeably upon introduction of the lattice distortions. In all cases studied by us the length of the spin moment amounts to $2.23\mu_B$,

the length of the orbital moment to $4.24\mu_B$ and the length of the summed atomic moment is $2.01\mu_B$. This value is in very good agreement with the experimental estimate of $2.05\mu_B$ [1].

It is of interest to comment briefly on the magnetic moments induced on the Pd and Sn atoms, even though they are small. First, in all cases studied the atoms of the same kind stayed equivalent. Second, similar to the U atoms the moments of Pd and Sn formed noncollinear compensated magnetic configurations, which were planar for structure I and with a finite m_x component of atomic moments for structure II. Because the Pd and Sn atoms are influenced by various U atoms with different directions of magnetic moments, the directions of the induced moments of these atoms differ from the directions of the U moments. For example, the angles between the Sn and the U moments reach a value of several tens of degrees. The magnitudes of the induced moments amount to $0.04\mu_B$ for Pd and to $0.02\mu_B$ for Sn. Again, the induced spin and orbital moments of Pd and Sn are noncollinear, the angles between the two atomic moments reaching in this case values of up to several tens of degrees.

4.2. Density of states

We show in figure 2 the total and partial density of states calculated for the magnetic structure I in the undistorted hexagonal crystal lattice. Both orthorhombic and monoclinic distortions result in only minute changes in the DOS. The general structure of the DOS can be described as follows. The large peak at the bottom of the valence band in the energy interval from about -0.35 to about -0.15 Ryd is formed by predominantly the Pd 4d states, and the next large group of peaks from -0.15 up to 0.15 Ryd by the U 5f states. Simultaneously, a noticeable hybridization of the U 5f, U 6d, Pd 4d and Sn 5p is observed. This hybridization is reflected in the common fine structure of the different partial DOS.

A remarkable feature of the DOS is a local minimum at the Fermi energy. Numerical experiments show that this minimum is a result of the combined influence of the magnetism, SOC, effective orbital field and hybridization of different states. Exclusion of at least one of these components results in a sharp increase of the DOS at the Fermi energy. Obtaining the specific heat γ value from the calculated DOS at the Fermi energy, we estimate a low value of 7.5 mJ mol^{-1} K^{-2} which is of the same order as the experimental estimate of 5 mJ mol^{-1} K^{-2}.

In figure 3 we compare the theoretical DOS with an experimental photoemission curve [4]. Both curves are in rather good agreement concerning the positions of two maxima at about -3.5 and 0.5 eV and the minimum at about 2.0 eV. From an analysis of the partial contributions to the DOS, it can be unambiguously established that the lower peak is formed mainly by the Pd 5d states and the higher peak by the U 5f states.

Thus our calculations allow us to explain the apparent contradiction between a low specific heat γ value and a large number of U 5f states close to the Fermi level observed in the photoemission experiment: because of the rather low resolution of the photoemission experiment the narrow minimum of the DOS at the Fermi energy, which determines the small value of the specific heat γ, cannot be observed with this experiment.

We note that our calculation supplies a DOS which is in better agreement with the photoemission experiment than the DOS of Trygg *et al* [14] which was also obtained in the itinerant-electron picture for the 5f electrons. Here we believe the following features of the calculations are important. First, Trygg *et al* performed their calculation for an assumed collinear ferromagnetic structure which differs considerably from the experimental noncollinear antiferromagnetic structure. Second, the DOS used in [14] for comparison with
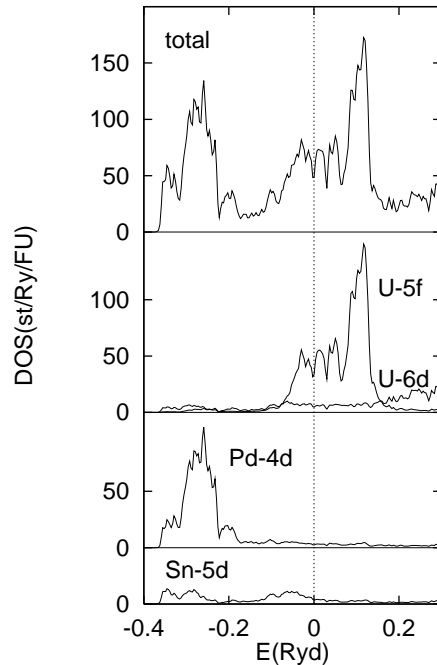
Figure 2. Total and partial densities of states of UPdSn.

experiment was calculated without the effective orbital field, although the corresponding term was used by the authors to improve the agreement with the experimental value of the atomic moment. Our calculation shows that changes in the DOS caused by this term can be important.

5. Conclusions

Summarizing, we applied the local density approximation to density functional theory to investigate the magnetic structure and electronic properties of the compound UPdSn. Our calculation technique is modified to include the SOC and effective orbital field which simulates Hund's second rule. In general, the agreement is good between the theoretical picture and the experimental results: first, the calculated magnitude of the U magnetic moment is very close to the experimental value; second, theory and experiment are in agreement concerning the directions of the magnetic moments in the orthorhombic structure I; third, for the monoclinic structure II both our calculations and experiment reveal a direct connection between the monoclinic lattice distortions and the out-of-plane rotation of the U magnetic moments, although the theoretical value of the rotation is much smaller than the experimental estimate; fourth, the theoretical DOS is in good agreement with the experimental photoemission spectrum; fifth, both theory and experiment result in a small value of the specific heat γ.

We have shown that the magnetic structure of UPdSn belongs to the class of magnetic crystals with noncollinearity of magnetic moments which is predetermined by the symmetry of the problem. In other words, the magnetic structure of this compound must be noncollinear. We suggest an explanation for the apparent contradiction between the low
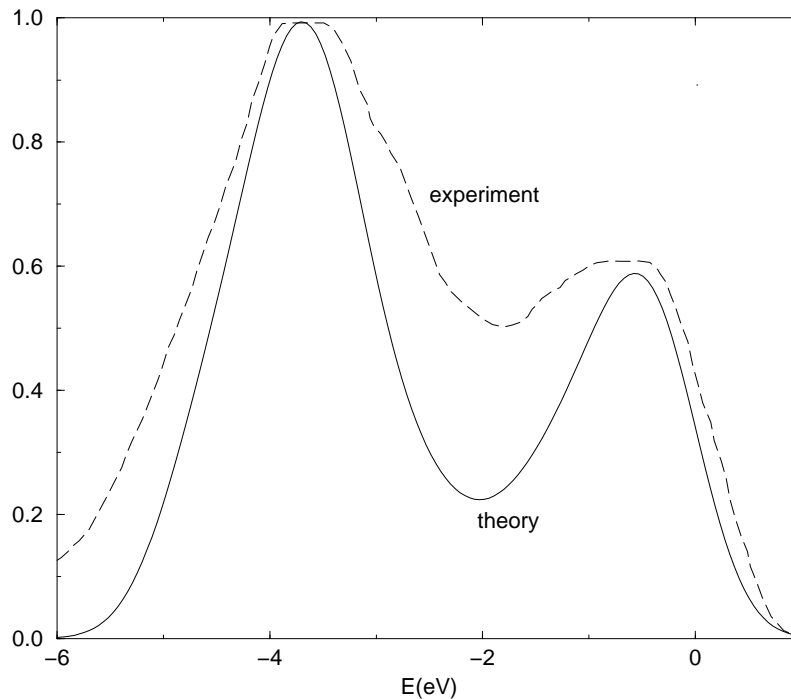
Figure 3. Comparison of the experimental photoemission spectrum [4] with the calculated DOS. The theoretical curve is smoothed by 0.4 eV to take into account limited instrumental resolution and finite lifetime effects.

specific heat γ value and the large number of the U 5f states close to the Fermi level observed in the photoemission experiment.

On the basis of the good agreement between theory and experiment we conclude that the 5f electrons in UPdSn are itinerant.

Acknowledgments

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