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Density functional prediction of a magnetic ground state of UFeSi

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Abstract

Density functional (DF) electronic structure calculations for UFeX (X=Si, Ge) compounds were performed using fully relativistic optimized linear combination of atomic orbitals (OLCAO), relativistic general potential linear augmented plane wave (LAPW) and scalar relativistic augmented sphere wave (ASW) methods. The 5f-states of uranium were assumed itinerant and treated as band states. We confirm the experimental observation that UFeGe is a paramagnet. On the other hand, our extensive DF calculations including the fixed-spin-moment method predict an instability of the paramagnetic state of UFeSi in the orthorhombic TiNiSi structure. Since both UFeSi and UFeGe are isoelectronic with respect to the number of valence electrons the actual ground states result from a subtle interplay between the band filling of the free electron background (s-, p-, and U-d electrons) and the iron bonding bands on one side and the covalency (hybridization) between bonding predominantly 3d states of iron and antibonding predominantly 5f-states of uranium on the other side. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Actinide intermetallic compounds; Density functional calculations; Itinerant magnetism; Magnetocrystalline anisotropy

1. Introduction

The magnetism of actinide intermetallic compounds is mostly determined by the partially occupied 5f-electron states. Being comparably easy to access and to handle, uranium and its compounds have been addressed by the majority of experimental investigations within this class of systems. A rich variety of physical, in particular magnetic properties have been revealed by various experimental techniques during recent decades [1]. So far, however, no general theory exists that allows a quantitative description and understanding of this variety. A partial description at the parameter-free level can be obtained from the application of density functional theory (DFT) where the numerical calculations are usually performed using the local spin density approximation (LSDA) or adequate extensions [2].

The uranium ternary intermetallics UFeSi and UFeGe crystallize in the orthorhombic structure of TiNiSi type. Recently it was found that UFeGe undergoes a structural phase transition at $T=475$ K with a monoclinic distortion present below this temperature, but no such distortion was reported for UFeSi [3]. The UFeSi compound was classified as a paramagnet. For the other compound a maximum observed in the temperature dependence of the electrical resistivity led to a speculation about magnetic ordering below 80 K [3]. Since this result would be rather unexpected, Havela et al. [4] investigated basic magnetic and transport properties and performed preliminary electronic structure calculations by means of the fully relativistic optimized linear combination of atomic orbitals (OLCAO) method. In that investigation it was concluded that the behaviour of UFeGe is compatible with the generally observed decay of 5f magnetism in U–T (T=transition metal) compounds with decreasing filling of the T-3d (4d, 5d) band, which can be attributed to a stronger 5f–d covalency (hybridization) and the position of the Fermi level inside the hybridization pseudogap. Such nonmagnetic behaviour is frequently observed for uranium–iron-based intermetallics by experiment [1]. Several other U–Fe compounds were also theoretically investigated, e.g. U_2Fe_2Sn [5,6], UFeAl [7] and UFe_2Si_2 [8]. In this work we continue the theoretical studies of ground state magnetic properties of UFeGe and present new calculations for the UFeSi compound.

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2. Electronic structure calculations

The UFeSi compound crystallizes in the orthorhombic TiNiSi-type structure (space group *Pnma*, No. 62) shown in Fig. 1. The uranium, iron and silicon atoms occupy the 4*c* positions with free structural parameters *x* and *z* and the unit cell contains four formula units. Also UFeGe crystallizes in this structure, however, for temperatures $T > 475$ K [3]. In our calculations the literature values for the lattice parameters of UFeSi and the corresponding six structural parameters of UFeSi [3] were used. In the case of UFeGe we also used the literature values for the lattice parameters [3] and the corresponding six structural parameters of UCoGe [3] were used. The monoclinic distortion of UFeGe was not taken into account. The nearest distance between U ions is $d_{\mathrm{U-U}} \approx 0.318$ nm and $d_{\mathrm{U-U}} \approx 0.346$ nm for UFeSi and UFeGe, respectively. These distances are smaller than Hill's limit $d_{\mathrm{Hill}} \approx 0.35$ nm. The distances between U ions and nearest neighbour ligands are $d_{\mathrm{U-Fe}} \approx 0.283$ nm ($d_{\mathrm{U-Fe}} \approx 0.284$ nm) and $d_{\mathrm{U-Si}} \approx 0.289$ nm ($d_{\mathrm{U-Ge}} \approx 0.296$ nm) for the case of UFeSi (UFeGe). Therefore, both the direct overlap between 5f wave functions and the hybridization between 5f and other electrons from ligands are expected to influence the electronic structure and related properties.

In the present study we used three different computational methods, namely (i) fully relativistic optimized linear combination of atomic orbitals (OLCAO) [9], (ii) general potential linearized augmented plane wave (LAPW) [10] with spin–orbit coupling (SOC) [11,12], and (iii) scalar relativistic augmented spherical wave (ASW) [13]. The Kohn–Sham equations were solved using LSDA but in a few calculations we also tested the influence of the generalized gradient approximation (GGA) [14].

The OLCAO method was used to solve the Kohn–Sham–Dirac equations [9]. The valence basis set involved the 7s, 6p, 6d, and 5f optimized orbitals on the uranium sites, 4s, 4p, and 3d-orbitals on the iron sites and 3s (4s) and 3p-orbitals (4p-orbitals) on the silicon (germanium) sites. Such a basis set was extensively tested in a comparison with the results of full potential LMTO calculations for the case of URh_3 [15] and later on successfully used in the OLCAO calculations for uranium [5] and neptunium [16] intermetallic compounds. The valence states were orthogonalized to the core states. Core states were recalculated in the atomic site potential within each

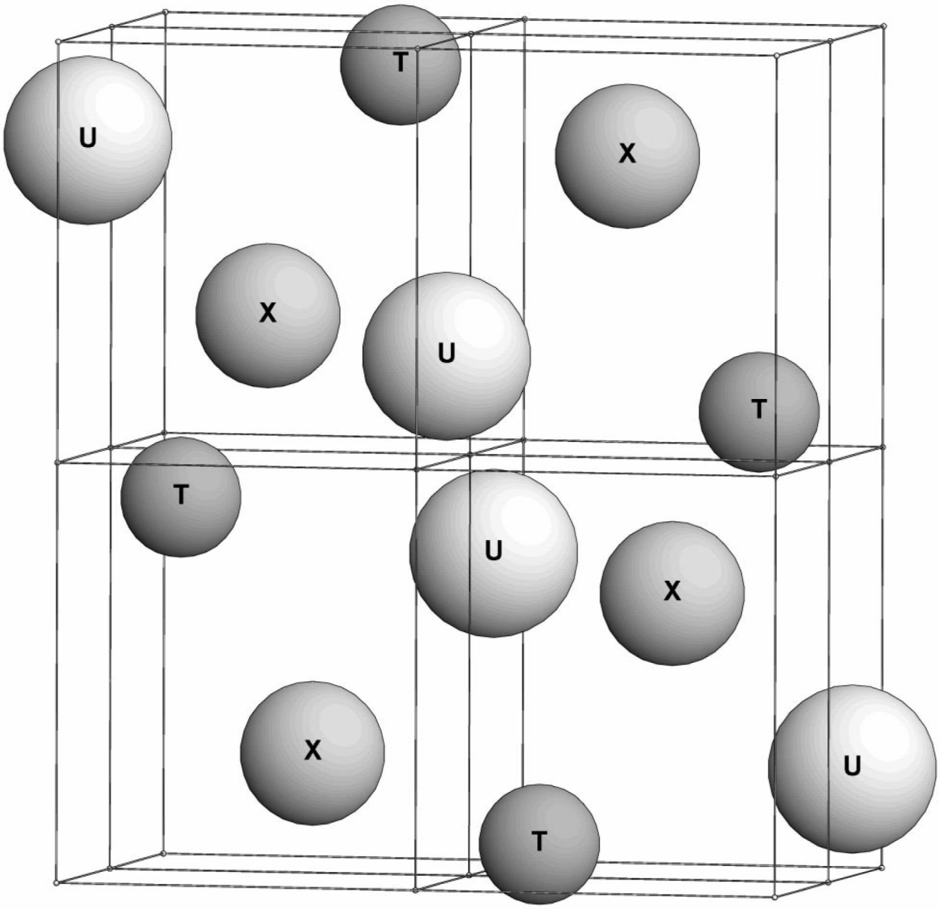

Fig. 1. The orthorhombic TiNiSi crystal structure of UTX compounds.

step of the self-consistency cycle. The density of states and electron charge distribution were calculated using the linear tetrahedron method [9]. We have used 100 k-points in the irreducible wedge (IW) of the Brillouin zone (BZ) to construct the charge density in each self-consistency step. Finally, we have used the orbital polarization (OP) correction [17] within the fully relativistic spin-polarized calculations. Different orientations of the magnetic moments with respect to the crystal axes provide different Kohn–Sham eigenvalues in the presence of spin–orbit coupling. The magnetocrystalline anisotropy energy (MAE) is approximated as the difference between the related eigenvalue sums of the occupied valence states (‘Force Theorem’) [18].

Total energy calculations were performed with the LAPW method using the WIEN97 code [10]. Atomic sphere (AS) radii of 2.8, 2.2 and 2.1 (2.1) Bohr radii were chosen for U, Fe and Si (Ge), respectively. We used about 1200 plane wave basis functions (more than 100 per atom) in the interstitial region and a maximum $l=12$ in the expansion of the radial wave functions inside the AS to represent the valence states. Both the potential and the charge density were expanded inside the spheres into crystal harmonics up to $L=6$ and in the interstitial region into a Fourier series with about 4000 K stars. For the BZ integration a modified tetrahedron method [10] with 45 special k-points in the IW was used. We have carefully checked that with these parameters the calculations are converged as described for similar LAPW calculations for isostructural URhSi and URhGe compounds [19]. The relativistic effects were treated in the scalar relativistic approximation [11] and spin–orbit coupling (SOC) was self-consistently added via the second variational step scheme [11,12]. Local orbitals were used to treat the U-6s and 6p, Fe-3p, and Ge-3d states with the valence states in a single energy window. The advantage of this treatment is that the 6p-states are orthogonal to the valence states. On the other hand, the second variational step scheme yields a spin–orbit splitting of the uranium 6p-states of only ~0.28 Ry in comparison with the value of 0.54 Ry obtained from our fully relativistic OLCAO calculations. Such a large deviation is, however, only present in the 6p-semicore states, while a comparison of the DOS provided by the two methods shows no visible influence of the approximations on the spin–orbit splitting of the 5f and 6d states that are mainly responsible for magnetic moments and magnetocrystalline anisotropy.

In the present study we were mainly interested to search for a possible ground state magnetic ordering in UFeX compounds. For this purpose, the total energy fixed-spin-moment (FSM) method is a very valuable tool [20]. In order to be able to perform fast total energy FSM calculations we employed the augmented spherical wave (ASW) method in the scalar relativistic version [13]. Our ASW calculations in the atomic sphere approximation (ASA) were performed on a uniform k-mesh with at least 125 k-points in the IW. The calculation of the total energy as a function of the overlapping ASA sphere radii allows us to find the optimum radii of the spheres, which minimize the total energy at the experimental volume. We have found the optimum radius $R_U=3.4$ Bohr radii and the ratio $R_U/R_{Fe}=R_U/R_X=1.2$ for UFeX. These values were kept constant for all present ASW calculations. Tests with a larger number of k-points in the IW (maximum 1750) were performed to check the stability of our numerical results. To ensure good convergence in the total energy, the self-consistency-cycle was carried out until the stability of interband charge transfer was better than 10^{-6} electrons.

3. Results and discussion

The results of the fully relativistic non-spin-polarized OLCAO calculations are consistent with a nonmagnetic ground state for both, UFeGe and UFeSi. The obtained DOS (see Figs. 2 and 3) is characterized by a nearly free electron background of s-, p- and U-6d electrons, which extends down to about 0.8 Ry below Fermi level (E_F). The dominant features of the DOS consist of bonding states

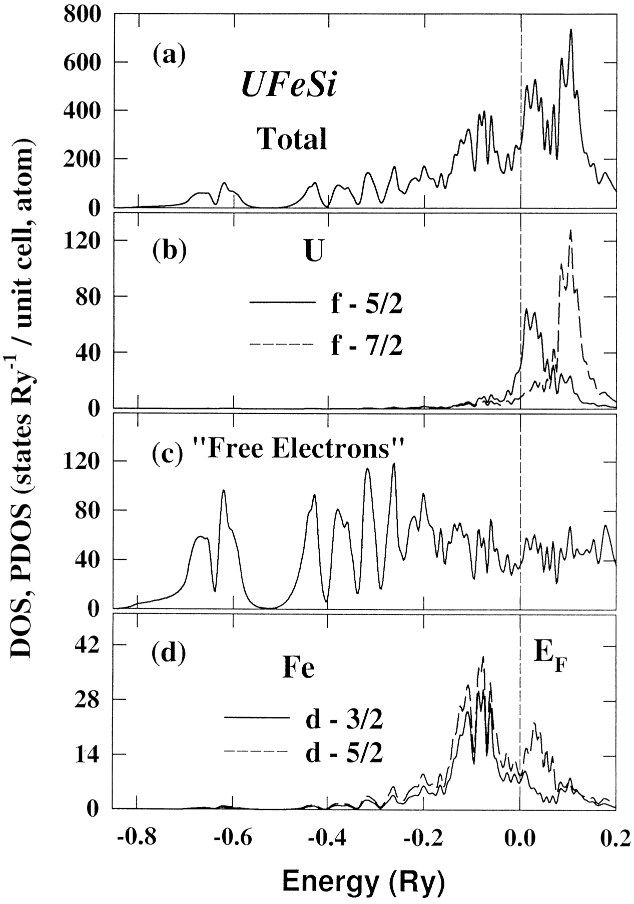

Fig. 2. Total (a) and partial (b, c, d) DOS of UFeSi. The ‘free electron’ DOS (c) represents the sum of s, p and uranium d partial DOS.

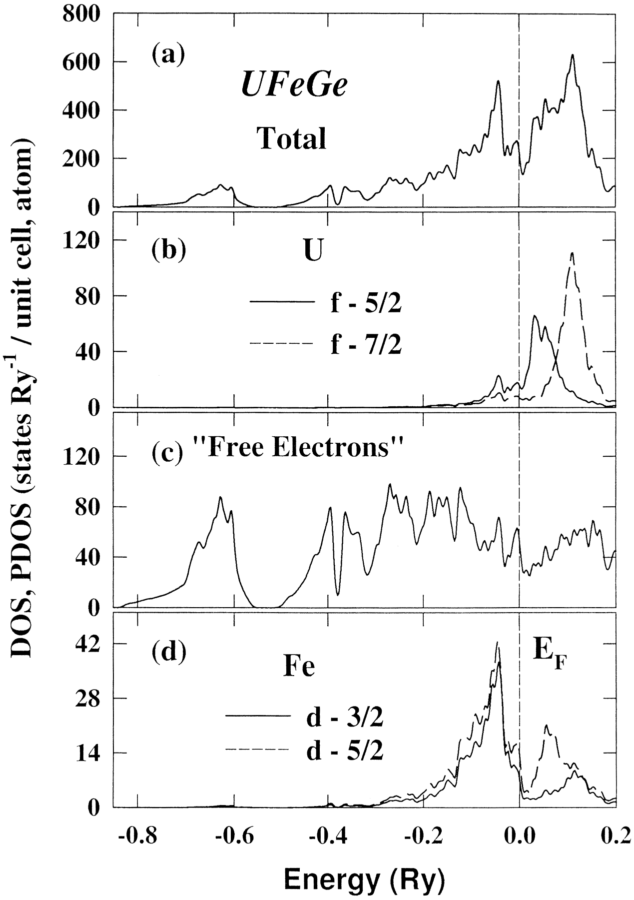

Fig. 3. The same as Fig. 2 for UFeGe.

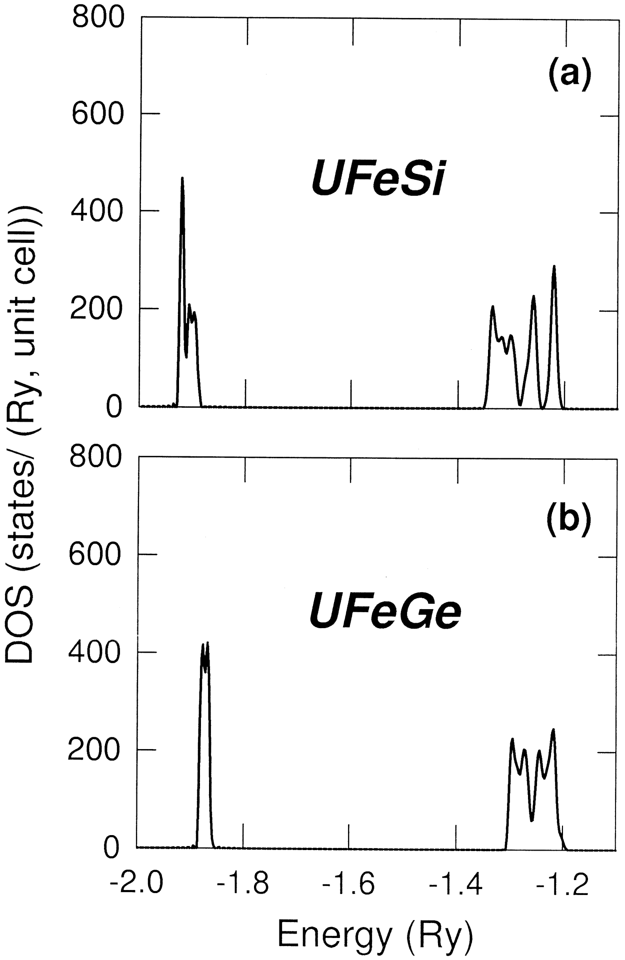

Fig. 4. Total DOS of UFeSi (a) and UFeGe (b) in the energy region of the uranium 6p states.

(mainly Fe-3d) spread from -0.15 Ry up to E_F and antibonding states (mainly U-5f) from E_F to 0.15 Ry (see Figs. 2 and 3). The U-6p states (see Fig. 4) are situated around -1.9 Ry ($6p_{1/2}$) and -1.2 Ry ($6p_{3/2}$) below the Fermi level. It should be noted that especially the U-$6p_{3/2}$ electronic states have some overlap with nearest neighbour uranium $6p_{3/2}$ states and moreover hybridize with true valence states. They therefore contribute to the cohesive properties. There is a substantial amount of covalency, as the U-5f states strongly hybridize with the Fe-3d states and therefore participate in the metallic bonding. The orbital and total angular momentum j projected DOS shows remarkable relativistic effects even within the Fe-d states, which originates from the large hybridization of the Fe-3d states ($j = 5/2$) with the U-f states ($j = 5/2$) and a rather small hybridization of the related $j = 3/2$ states of iron with the uranium 5f-states. There are also significant differences between both compounds studied in the position of E_F inside this valence band complex. The Fermi level is located at the bottom and top of the hybridization pseudogap between the Fe-3d and U-5f states in the case of UFeGe and UFeSi, respectively. This difference is presumably caused by the somewhat larger electronegativity of Ge in comparison to Si (see Table 1). The Fe-3d occupation in UFeGe is therefore by ≈0.3 electrons smaller than in UFeSi (see Table 1), bringing the bonding 3d band closer to E_F in the former compound.

To investigate the tendency with respect to a ferromagnetic instability, we have derived the Stoner product $IN(E_F)$ from calculated densities of state at E_F where I is the Stoner parameter for a multiband system [21,22]. We have found that the Stoner product $IN(E_F)$ equals 0.4 and 0.6 for UFeGe and UFeSi, respectively. While the total values are rather similar, the former originates mainly from Fe-3d states and the latter mainly from the U-5f states.

Next, we performed total energy calculations (LAPW method including SOC) varying the volume of the orthorhombic unit cell for both compounds studied (see Fig. 5).

Table 1
Calculated partial gross charges for UFeX compounds. Q_{FE} means the sum of uranium s, p, d and iron s, p charges

Charges	Q_{FE}	Q_f(U)	Q_d(Fe)	Q_{sp}(X)
UFeSi	11.172	2.245	7.221	3.362
UFeGe	10.667	2.301	6.966	4.057

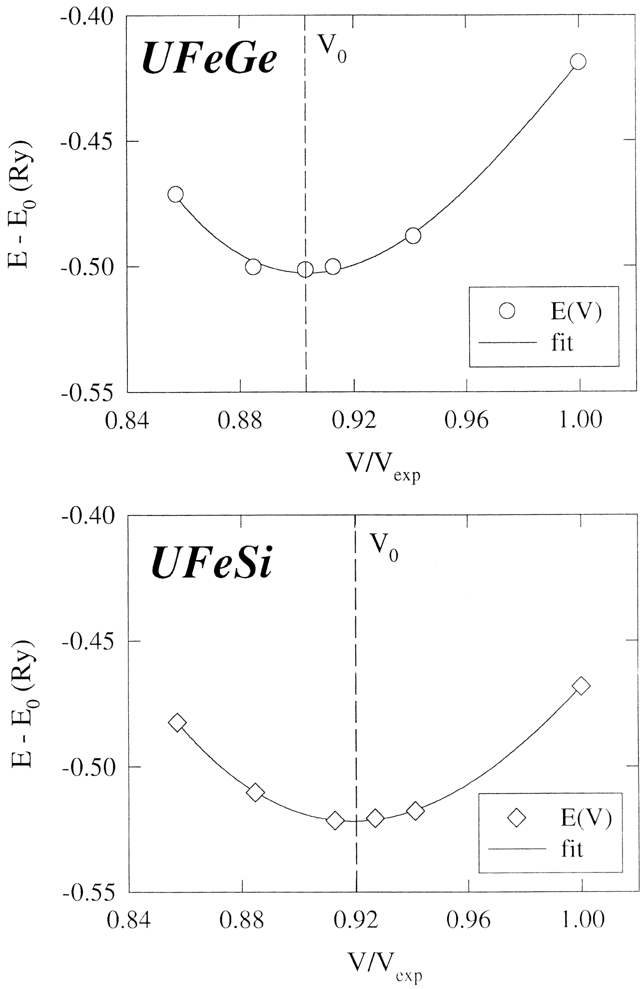

Fig. 5. The total energy per unit cell of UFeSi and UFeGe as a function of the volume. The calculations were done using LAPW including SOC and assuming a nonmagnetic state. The constant E_0 equals −237022 Ry for UFeSi and −251479 Ry for UFeGe.

We have found a reasonably good agreement between the experimental volumes and ground state equilibrium volumes calculated in the framework of LDA. The agreement is somewhat better for UFeSi ($V_{th}/V_{exp} = 0.92$) than for UFeGe ($V_{th}/V_{exp} = 0.90$). This difference could be related to the experimental observation that a monoclinic distortion, not taken into account in the calculation, is occurring for UFeGe but not for UFeSi. The data were fitted to the Murnaghan equation of state from which the equilibrium volume and the bulk modulus B were obtained by analytic differentiation. Values of $B = 190$ and 231 GPa were found for UFeSi and UFeGe, respectively. We note that we did not minimize the remaining structural parameters (a/b, a/c, x_i, z_i, $i = 1, 2, 3$), but we have found that the atomic forces calculated at the experimental positions [1] were quite small and thus the positions are presumably not much influenced by the volume change.

Further, total energy calculations were performed using the scalar relativistic fixed-spin-moment method (ASW). These calculations showed that the paramagnetic ground state is stable with respect to ferromagnetic spin polarization for UFeGe (see Fig. 6a). We do not expect that the observed monoclinic distortion may change this finding, since reductions of the lattice symmetry reduce the tendency to magnetic ordering in most cases by removing band degeneracies. However, in the case of UFeSi a peculiar ferrimagnetic state was found (see Fig. 6b), which has a total energy lower than the paramagnetic state. In this state the uranium spin moments are coupled antiparallel to the iron spin moments. We have repeated a part of the FSM calculations using the LAPW method and we have found qualitatively the same results as using the numerically more efficient and faster ASW method. It is interesting to see the dependence of the APW sphere projected spin moments as a function of the total FSM of the unit cell. We have found that the relative direction of the uranium and iron spin moments (see Fig. 7) depends on the value of the total FSM. The mutual cancellation is most pronounced near the value of FSM~2 μ_B/unit cell close to the minimum of the total energy ($E_{para} - E_{ferri} = 6.4$ mRy/unit cell). For larger values of FSM the total energy, AS projected U-moment and interstitial moment further in-

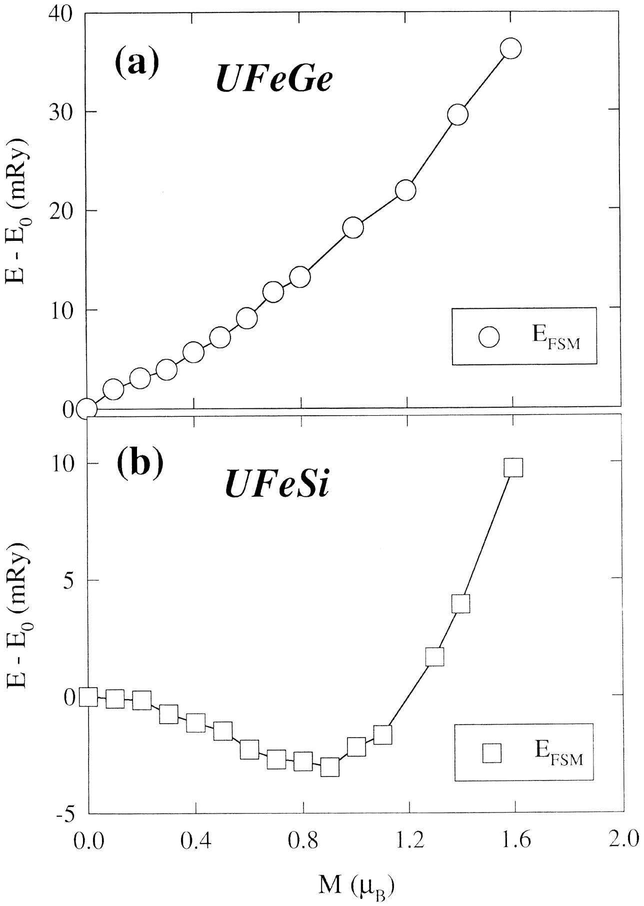

Fig. 6. The total energy per unit cell of UFeGe (a) and UFeSi (b) as a function of the fixed-spin-moment inside the ASW atomic sphere of uranium. The energy of the nonmagnetic state is shifted to zero.

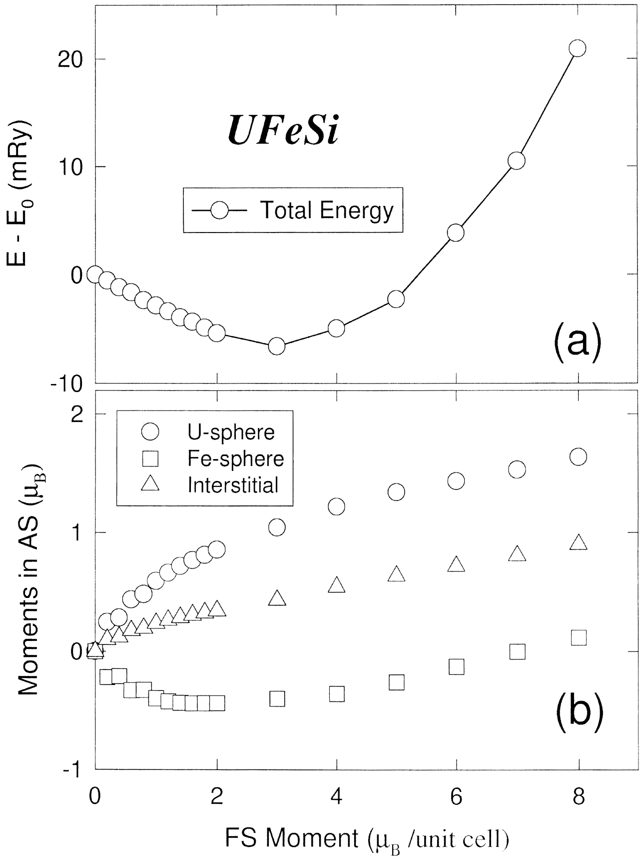

Fig. 7. The total energy per unit cell (a) and projected spin moments (b) of UFeSi as a function of the fixed-spin-moment inside the unit cell (LAPW method). The energy of the nonmagnetic state is shifted to zero. The interstitial moment is given per unit cell.

crease but the AS projected Fe-moment begins to decrease and for FSM~8 μ_B/unit cell even changes the sign (see Fig. 7).

The FSM calculations did not included spin–orbit coupling. Therefore, we checked the stability of the ferromagnetic state of UFeSi using the LAPW method including SOC in the second variational step. A stable magnetic solution is found with almost complete cancellation of U spin and orbital moments, $M_S = 0.93$ μ_B, $M_L = -0.92$ μ_B, inside the uranium AS. The AS projected iron moments ($M_S = -0.36$ μ_B, $M_L = -0.04$ μ_B) are reasonably close to the related OLCAO results ($M_S = -0.59$ μ_B, $M_L = -0.04$ μ_B) considering that the OLCAO and LAPW methods employ entirely different basis sets during the self-consistent solution of the Kohn–Sham equations. This involves also a different site projection of magnetization. In particular there are by construction no interstitial contributions present in the OLCAO scheme. The interstitial spin magnetic moment represented by spin polarized plane waves in the region between the LAPW atomic spheres is rather low ($M_S = 0.41$ μ_B). The stabilization energy estimated from the difference between total energies of spin-polarized and non-spin-polarized calculations with SOC accounted for is equal to 1.6 mRy/unit cell. We have also found that the GGA increases the value of the spin and orbital uranium moments but leaves the total moment almost the same as in the LSDA calculations. The GGA does not influence the iron moments substantially for the case of UFeSi. To provide a prediction for Mõssbauer studies of UFeSi we have calculated the values of the electric field gradient EFG $= -2.7 \times 10^{21}$ V/m^2 and of the asymmetry parameter $\eta = 0.89$ at the iron site using LSDA. The self-consistent values of the spin densities at the iron nucleus allow us to derive the hyperfine field of 1.55 T, which results from a strong cancellation between a core contribution of -2.58 T and a valence electron contribution of 4.13 T.

The importance of OP corrections for the description of orbital polarization and magnetic anisotropies of 5f band magnets is well documented [2]. In the particular case of UFeSi, including the OP correction in the relativistic OLCAO calculations preserves the strong cancellation of uranium spin and orbital moments but gives a small overweight to the latter ($M_S = 0.34$ μ_B, $M_L = -0.50$ μ_B). The values of the silicon magnetic moments induced by the covalency are negligibly small (< 0.01 μ_B).

In order to study the magnetocrystalline anisotropy for UFeSi, we have rotated the magnetic moment from the *c*-direction (001) to *a*-direction (100) or *b*-direction (010), respectively, and calculated the related band energies (eigenvalue sum over occupied states) using the fully relativistic OLCAO method including OP corrections. We have determined the difference in energy $\Delta E_{100} = E_{100} - E_{001} = -0.94$ meV/f.u. and $\Delta E_{010} = E_{010} - E_{001} = 20.8$ meV/f.u. To see how sensitive ΔE is to details of the band structure, we also calculated ΔE for noninteger fillings close to band filling $n = 96$ using the band structure calculated self-consistently for $n = 96$ corresponding to the correct Fermi level for UFeSi (see Fig. 8a). There is a minimum in ΔE_{100} at $n = 93$ electrons and ΔE_{100} changes in sign just around the filling corresponding to E_F. On the other hand ΔE_{010} exhibits only a smooth dependence on the band filling from $n = 78$ to 96 electrons and starts to increase above E_F. A similar situation is observed in the calculated anisotropy of the orbital moment that is mainly connected with the uranium site (see Fig. 8b). We assume the band energy difference to be a good approximation for the magnetic anisotropy energy. From our calculations it follows that the MAE in the *a*–*c* plane is relatively small. This might give rise to the idea that the actual magnetic ground state of UFeSi could be quite complicated. For example, it could involve a noncollinear magnetic ordering of uranium moments in the *a*–*c* plane.

4. Summary

Density functional calculations for UFeGe and UFeSi intermetallic compounds were performed. The electronic

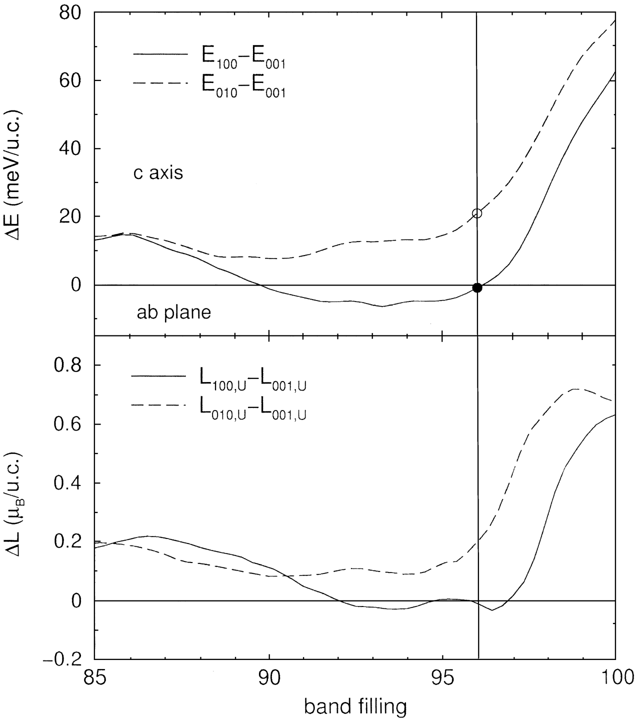

Fig. 8. Magnetocrystalline anisotropy energies $E_{100}-E_{001}$ and $E_{010}-E_{001}$ and corresponding uranium orbital moment anisotropies $L_{100}-L_{001}$ and $L_{010}-L_{001}$ of UFeSi in dependence on band filling, calculated using OLCAO method including SOC and OP. The Fermi energy of UFeSi corresponds to a band filling of 96 valence electrons indicated by the vertical line.

structure and related properties (equilibrium volume, bulk modulus, magnetic moments) were investigated. We predict an instability of the paramagnetic state of UFeSi in the orthorhombic TiNiSi structure with the literature values for the lattice parameters of UFeSi and the corresponding six structural parameters [3] assuming the LSDA form for the effective exchange correlation potential.

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