Electronic structure and magnetic behavior of UMn$_2$ and UFe$_2$

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The electronic structure of UMn$_2$ and UFe$_2$ has been determined using the first-principles self-consistent spin-polarized scalar-relativistic linear muffin-tin-orbital method. The calculations were performed at several lattice spacings for these materials in the $C15$ (cubic Laves phase) crystal structure. In agreement with experimental data it is found that UMn$_2$ is almost nonmagnetic (small moments on the sites) whereas in UFe$_2$ both U and Fe sites have appreciable moments. Furthermore, the magnetism in these systems is determined by exchange splitting and not by charge-transfer effects. The calculated moments in UFe$_2$ are larger at the U sites than those seen experimentally. The total moment in UFe$_2$ is somewhat insensitive to changes in lattice spacing (over the limited range determined) while the moments on individual sites are very sensitive to this variation.

INTRODUCTION

Among the transition-metal elements the late $3d$ metals have generated many studies because of their itinerant magnetism. There is presently a great deal of ongoing work attempting to understand the magnetism of Fe, Co, and Ni. The local-spin-density (LSD) formalism of the electronic structure of these materials has given a correct picture of the bonding and magnetism of the ground state (lattice constants, crystal structure, cohesion, and average magnetic moments).[1] However, many of the details of the high-temperature behavior have yet to be worked out.[2] Qualitatively, the origins of the $3d$ magnetism can be understood in terms of the electronic configurations of these atoms. Starting with Mn, which has five unpaired spins in the d shell, one progressively adds nonbonding electrons of opposite spin in going from Fe to Ni. This indicates that bonding and magnetism should be a maximum at Mn and a minimum at Ni. For Fe through Ni this is the trend. For Mn, however, the competition between bonding and magnetism may lead to the lattice distortions (e.g., α-Mn with 58 atoms per unit cell) which make the crystallography and metallurgy of the element so complicated. In addition the exchange-splitting causes larger lattice constants than those given by paramagnetic calculations.[1] Elemental uranium (U) also shows complex crystallography and metallurgy, and although it is nonmagnetic it forms a range of intermetallic compounds with magnetic ordering. One such series is UMn$_2$, UFe$_2$, UCo$_2$, and UNi$_2$. In this series UMn$_2$ and UCo$_2$ are paramagnetic while UFe$_2$ and UNi$_2$ are ferromagnetic.[3] Also in this series UMn$_2$, UFe$_2$, and UCo$_2$ form in the $C15$ crystal structure at room temperatures whereas UNi$_2$ forms in the $C14$ (hexagonal form of $C15$) crystal structure. At low

temperatures UMn$_2$ distorts and becomes orthorhombic.[4] Also in UFe$_2$ the onset of ferromagnetism at 165 K is accompanied by a rhombohedral distortion which indicates a large magnetoelastic interaction in this system.[3] The magnetic properties of these materials are connected to the electronic structure, and although there have been no self-consistent field calculations performed on these compounds, there have been arguments that relate the magnetism to the electronic structure.[3] It has been argued that the experimental data indicate charge transfer from the U $5f/6d$ states into the $3d$ band. It has been suggested that the magnetic moment in UNi$_2$ is on the U sites ($5f$ electrons) where in UFe$_2$ the magnetic moment is on the Fe sites. In UCo$_2$ it has been speculated that the U $5f$ band is empty and the Co $3d$ band is full leading to no moment. Also in UMn$_2$ an almost-empty U $5f$ band (due to charge transfer) has been given as the reason for the small moment in this system.[3]

Because of the success of the local-density approximation (LDA) calculations for the ground state properties of the $3d$ magnetic elements it seems reasonable to attempt to explain the magnetic properties of these materials using such a technique. In this paper we have calculated the electronic structure and magnetic moments of cubic UMn$_2$ and UFe$_2$ (UCo$_2$ and UNi$_2$ are left for a future study as are the distorted phases of UMn$_2$ and UFe$_2$). In the next section the details of the calculation are given.

CALCULATIONAL DETAILS

One difficulty in calculating the electronic structure of actinide compounds is that both spin-polarization and spin-orbit coupling are important. While methods for performing spin-polarized Dirac calculations are being developed, they have not become standard techniques for electronic structure calculations of materials.[5] To include

TABLE I. Lattice constants a (a.u.), sphere radii R (a.u.), and atomic positions in the $C15$ structure used in these calculations.

		UMn$_2$	UFe$_2$	
a		13.528	13.310	
R_u		3.529	3.469	
R_{3d}		2.470	2.428	

	Atom	Position (in units of a)		
1	U	0.125	0.125	0.125
2	U	−0.125	−0.125	−0.125
3	Mn or Fe	0.500	0.500	0.500
4	Mn or Fe	0.500	0.250	0.250
5	Mn or Fe	0.250	0.500	0.500
6	Mn or Fe	0.250	0.250	0.500

exchange splitting important for the late $3d$ atoms and minimal relativistic effects for the actinide component one must perform a spin-polarized scalar relativistic calculation. In performing such calculations spin-orbit coupling is neglected, and only by comparing the results with experimental data one can assess this neglect. The calculations were peformed using the linear muffin-tin-orbitals (LMTO) method within the local-density approximation.[6,7] The Barth-Hedin exchange-correlation potential was used.[8] The calculations were performed for the cubic Laves phase ($C15$) crystal structure with six atoms per primitive unit cell and at several lattice spacings near the experimental values. Because this is a somewhat open structure and because we have previously discovered the spin-polarized calculations to be sensitive to the combined correction term in the LMTO scheme these calculations include this correction. For the $C15$ crystal structure, the band structure was converged for 95 **k** points in the irreducible wedge of the Brillouin zone. The tetrahedron method was used to obtain the density of states functions.[9] The core states were taken from atomic Dirac calculations and were held fixed throughout the self-consistent-field cycles for the valence electrons. For compounds and for electronic structure calculations that spherically average potential, one is always faced with the problem of the choice of sphere radii for the different components. In line with our earlier calculations on $C15$ compounds we have arbitrarily chosen the $3d$ metal sphere to be 0.70 times that of the uranium sphere. In Table I we give the lattice constants, sphere radii and atomic positions for the calculations reported in this paper. For each compound the calculations were performed at two other lattice constants on either side of those given in Table I. Those calculations were performed to obtain the change in the magnetic moments with a change in volume.

RESULTS AND DISCUSSION

Presented first are the electronic structure results of UMn$_2$, then that of UFe$_2$, and finally the calculated magnetic properties of the two materials are compared with each other and with the experimental data.

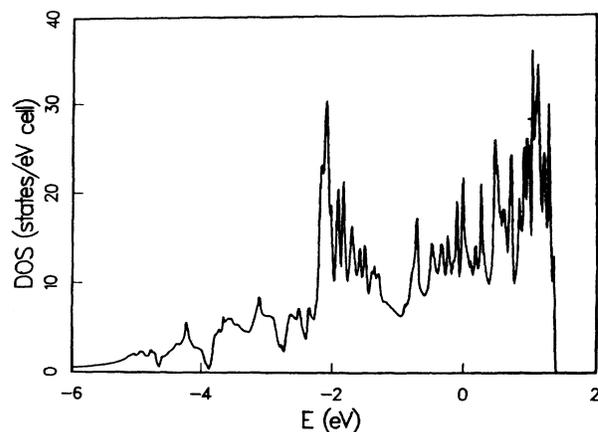In Fig. 1 the UMn$_2$ total density of states (DOS) is

FIG. 1. Total density of states (DOS) of UMn$_2$. The Fermi energy E_F is at 0.

given and in Figs. 2–4 the spin-up and spin-down partial DOS functions for U f, U d, and Mn d states are presented. As can be seen from Fig. 1 the occupied valence band states are about 4.5 eV wide (with a small tail extending to 6.5 eV below E_F) and have a lot of structure. From Figs. 2–4 it is seen that most of the structure below E_F is due to Mn $3d$ and U $6d$ states as the U $5f$ states give rise to rather flat DOS functions below E_F. Of course the most obvious feature of these figures is that there is almost no spin-polarization in these states. This is also seen in the charge analysis given in Table II. This charge analysis does not indicate any large charge transfer from U to Mn or Fe. The results actually indicate an increase in charge on the U site (relative to the atom), but the exact numbers are a function of the relative sphere sizes. The fact that the U atom contains about 2.5 $6d$-like and 3.0 $5f$-like electrons indicates to us that charge transfer is not an important feature of the electronic structure of these materials.
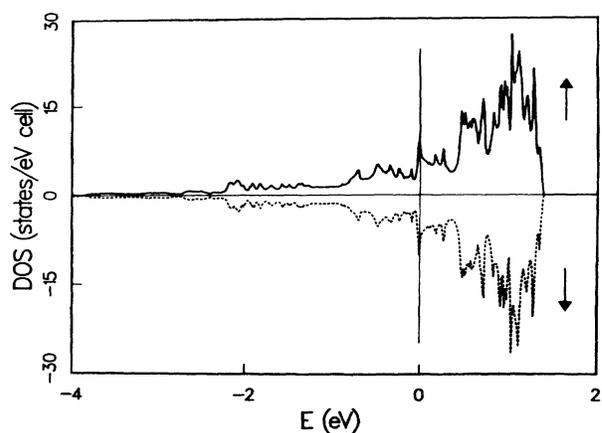

FIG. 2. Spin-up and spin-down partial DOS functions for $l = 3$ around the U site. E_F is at 0.

TABLE II. Charge- and spin-density analysis for UMn_2 and UFe_2.

Atom	U				Mn			
l component	s	p	d	f	s	p	d	f
				UMn_2				
Spin up	0.33	0.27	1.26	1.46	0.29	0.30	2.75	0.025
Spin down	0.33	0.27	1.27	1.47	0.29	0.29	2.71	0.025
Total	0.66	0.54	2.53	2.93	0.58	0.59	5.46	0.05

Atom	U				Fe			
l component	s	p	d	f	s	p	d	f
				UFe_2				
Spin up	0.31	0.26	1.25	1.66	0.29	0.30	2.98	0.025
Spin down	0.30	0.25	1.18	1.29	0.29	0.30	3.54	0.025
Total	0.61	0.51	2.43	2.95	0.58	0.60	6.52	0.05

In Fig. 5 the UFe_2 total DOS is given and in Figs. 6–8 the spin up and spin down partial DOS functions for U f, U d, and Fe d states are shown. As can be seen the total DOS function for UFe_2 is very different from that of UMn_2 (Fig. 1). This difference is reflected in the large spin polarization seen in Figs. 6–8. As can also be seen, the major exchange splitting occurs in the Fe $3d$ states (Fig. 8). An inspection of Figs. 6–8 shows that spin polarization on the U sites is opposite that on the Fe sites. The charge analysis of Table II gives the details of this large exchange splitting. Again there is very little charge transfer in this system.

Comparing the two systems we see that the spin polarization in UFe_2 leads to a very different total DOS function than that of paramagnetic UMn_2. We believe this difference could be seen in x-ray photoemission spectroscopy (XPS) data on these two systems. Because the XPS intensities are a product of a cross-section times the initial DOS functions these intensities would not exactly reflect our calculated DOS functions. However, because the same cross sections will dominate in both systems and are

probably similar, differences in the DOS functions should still show up in the XPS data. Because the charge distribution is rather similar in these two systems, differences in resistivities should be due to the exchange splitting in UFe_2 (with both materials in the $C15$ structure).

In Table III the calculated moments for both components are given. For both systems the first two lattice constants are experimental values and the third is for a slightly contracted lattice. One of the most interesting features of both systems is that the total moment (given per formula unit) is nearly independent of lattice constant over this range. It was also found that the total moment stabilized early in the self-consistent-field procedure (after about 10 iterations) whereas the moments on each site took many more iterations (about 20 more) to stabilize.

For UMn_2 it looks like there is a small moment on the U sites (coming from the $5f$ and $6d$ states) and small $3d$ moments on the Mn sites. There had been speculations that both U sites and Mn sites have a small moment in the compound. From the charge density analysis (Table II) it is seen that there is very little difference in the
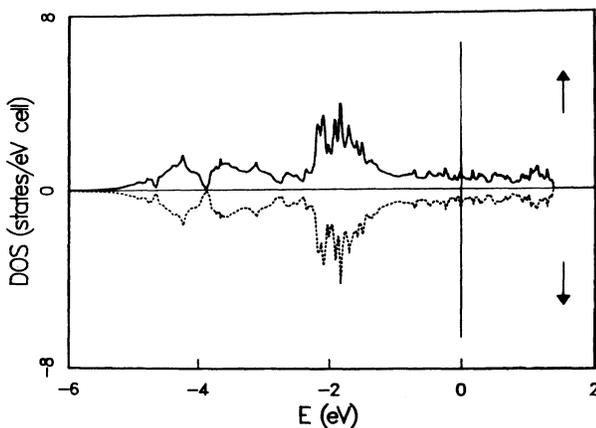

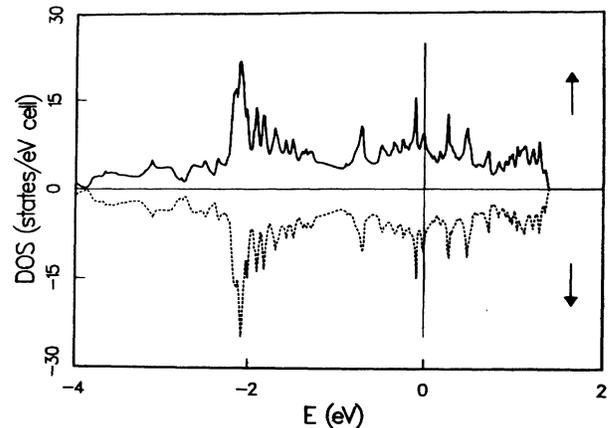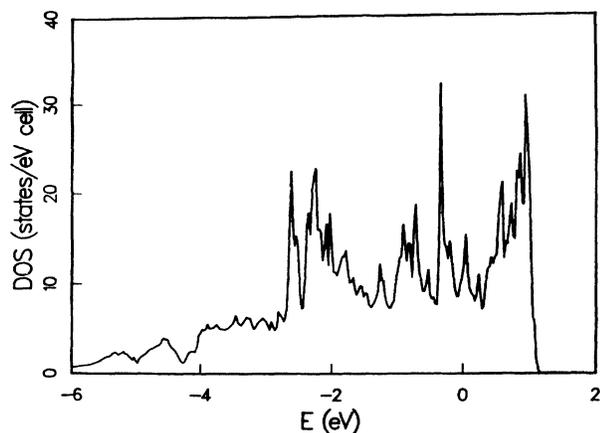FIG. 3. Spin-up and spin-down partial DOS functions for $l = 2$ around the U site. E_F is at 0.
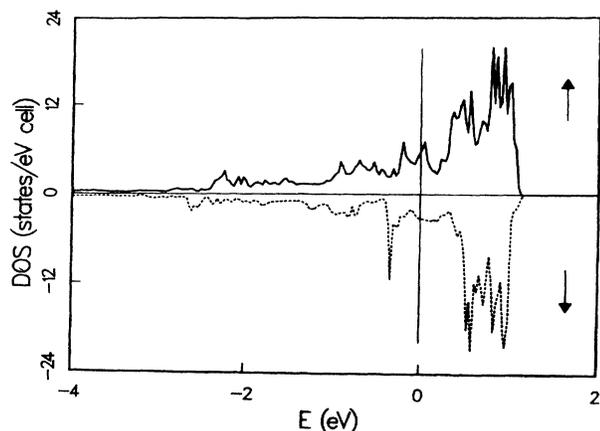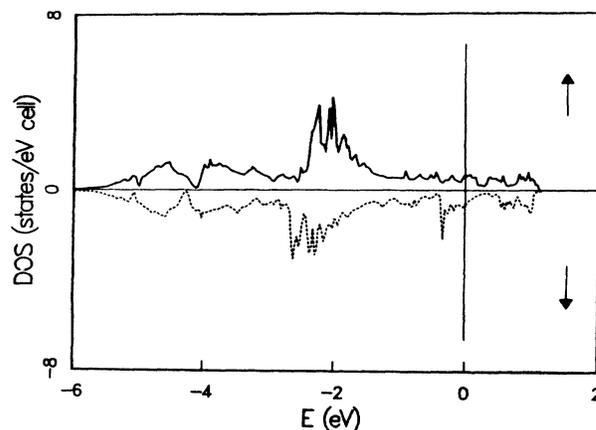

FIG. 4. Spin-up and spin-down partial DOS functions for $l = 2$ around the Mn site. E_F is at 0.

FIG. 5. Total DOS function of UFe_2. E_F is at 0.

charge distribution between UMn_2 and UFe_2, but that UMn_2 simply does not spin polarize.

In UFe_2 it is seen that the calculated moments are large on both sites. It is also seen that the site moments change dramatically upon reducing the spacings from the experimental lattice constants. The moments on the Fe sites are in good agreement with those obtained from neutron data ($\mu_{Fe}=0.44$), while the calculated moments on the U sites are much larger than those seen experimentally ($\mu_U=0.034$). Because we obtain large moments on the U sites that are opposing the Fe moments, we get a smaller total moment than seen experimentally (from $1.02\mu_B$ to $1.36\mu_B$). There are several reasons why the calculated U-site moments are larger. First, we have not allowed for core polarization. The main reason for not doing this is that the spin orbit is so large and it was felt that this feature of the core states should be maintained, and since we cannot yet include both spin orbit and spin polarization on equal footing, we opted for spin-orbit coupling in the core states. Another factor, also tied to this problem, is that of an orbital contribution to the moment from the itinerant states. These difficulties will eventually be overcome, but, for the

FIG. 7. Spin-up and spin-down partial DOS functions for $l=2$ around the U site. E_F is at 0.

present, the calculations of this paper are state of the art and do give a better understanding of these materials than we have had.

Note added in proof. After this paper was written we received a copy of an article by M. S. S. Brooks *et al.*[12] of their spin-polarized band calculation of UFe_2 prior to publication. They performed their calculations in the atomic sphere approximation (ASA) and with a lattice constant of 13.246 a.u. They obtained moments of $-0.6\mu_B$ at the U site, $+0.7\mu_B$ at the Fe site, and an overall moment of $+0.8$ per formula unit (f.u.). If we interpolate from our results of Table III we get values of -0.42 at the U site, 0.48 at the Fe site, and $+0.61$ for the total moment per formula unit (f.u.) at a lattice constant of 13.246 a.u. This indicates a difference of between 30% and 45% in the moments calculated in the ASA method compared to the calculation including the combined-correction terms.

FIG. 6. Spin-up and spin-down partial DOS functions for $l=3$ around the U site. E_F is at 0.

TABLE III. Magnetic moments in UMn_2 and UFe_2 at three different lattice constants.

	UMn₂ Moments (in μ_B)		
Lattice constant a	U site	Mn site	Total/f.u.
13.539[a]	−0.02	+0.05	+0.08
13.528[b]	−0.02	+0.05	+0.08
13.495	−0.02	+0.04	+0.06
	UFe₂ Moments (in μ_B)		
Lattice constant a	U site	Fe site	Total/f.u.
13.337[c]	−0.62	+0.64	+0.66
13.310[c]	−0.46	+0.52	+0.65
13.046	−0.29	+0.38	+0.48

[a]Experimental value, Ref. 10.
[b]Experimental value, Ref. 4.
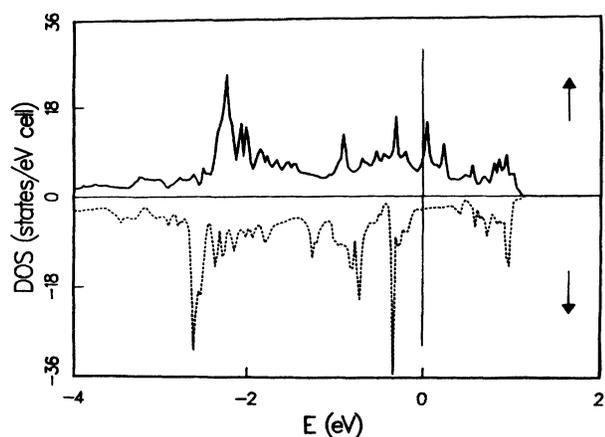[c]Experimental value, Ref. 11.

FIG. 8. Spin-up and spin-down partial DOS functions for $l = 2$ around the Fe site. E_F is at 0.

CONCLUSIONS

We have presented the detailed electronic structure of UMn_2 and UFe_2 by performing self-consistent-field cal-culations that include spin-polarization effects. We have shown that while the charge distribution is rather similar in these two systems, the spin polarization is very different and accounts for their different magnetic behavior. We have no simple explanation for why UMn_2 does not polarize. For the strongly polarized UFe_2 we find that polarization on the U site is the opposite of that of the Fe site. It would be nice to argue that the spin polarization of the $3d$ metal drives the system, i.e., Fe polarization induces a strong polarization at the U site, whereas—because Mn does not polarize—it induces no polarization at the U site; however, the situation may not be that simple. In a general way, these calculations are in good agreement with experimental data, which also indicate very small (if any) moments in UMn_2 and sizable moments in UFe_2. That the calculated moments in UFe_2 are larger than those seen experimentally is reasonable in light of the effects not included in the cal-culations (core polarization and orbital contributions to the moments). These calculations lend strong support to an itinerant picture of magnetism in these systems. The complications of the low-temperature crystal distortions in these systems were not addressed.

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