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Ground-state properties of ternary uranium compounds: I. Hybridization effects

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Abstract. We report self-consistent LMTO energy band calculations for the compounds U(T)Al with the ZrNiAl structure where T is a group 6–8 transition metal. The role of hybridization between transition metal d states and uranium f states is examined by analysis of the structure and modelling of the results of the self-consistent energy-band-structure calculations. It is found that these compounds belong to a class of strongly hybridizing materials where the bonding between the uranium f states and transition metal d states dominates.

1. Introduction

Although they lie towards the end of the chemical periodic table, the actinides are in a pivotal position as regards electronic structure, with their properties straddling those of the transition metals and the rare earths. Their wide range of physical properties is due to the presence of resonant 5f states which are involved in both chemical bonding and magnetism. Consequently much actinide research is devoted to the nature of actinide magnetism. However, since the actinides are heavy elements, relativistic effects are also abnormally large and the magnetic properties are influenced both by chemical bonding and large spin–orbit interaction. The large spin–orbit interaction in the actinides leads to broken-symmetry effects, for example, strong orbital itinerant magnetism and associated magneto-crystalline anisotropy and magneto-optical effects [1–4]. The nature of the magnetic moments in these compounds is not straightforward; therefore in this paper we will restrict our considerations to the basic electronic structure and its influence upon chemical bonding for paramagnetic ground states.

Ideally, one would follow the onset and nature of magnetism across the elemental 5f series, just as for V, Cr, Mn, Fe, Co, Ni, across the 3d series. Unfortunately, the light actinide metals do not order magnetically and the heavy actinide metals, although magnetic, have localized 5f states and anyway only exist in very small quantities. Magnetism in Np has been shown to be suppressed by spin–orbit interaction [5] and an attempt to induce magnetism by increasing the lattice constant might lead to localization of the 5f states. Given that one cannot follow any such trend across the series, one is then forced to study compounds. By judicious choice of alloyed element the dependence of moment formation upon composition may be followed. One appropriate such system is the ZrNiAl-type structure, formed from actinides, transition metals (Fe–Ni and 4d, 5d equivalents), and group 3–4 atoms (Al, Ga, In, Ge, Sn). These compounds then provide a wide range of possibilities as properties are changed by the variation of any one of the three atom types forming the compounds. Furthermore, there is now a large collection of experimental data from which conclusions may be drawn [6, 7, 8].

We have studied the compounds UTAl, where T is Fe, Co, Ni, Ru, Rh, Ir, Pt and followed the trends in electronic structure across this series. In section 2 we discuss the fully self-consistent energy band calculations and in section 3 we examine a simplified model for the electronic structure, in order to explain these trends clearly.

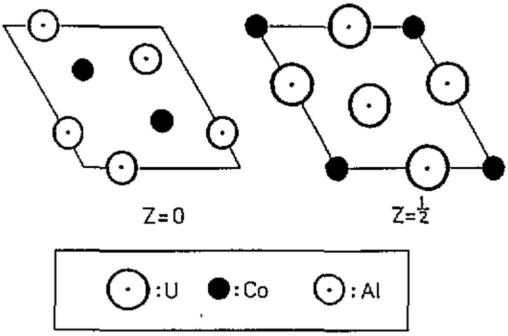

Figure 1. ZrNiAl structure, after Wulff *et al* [7].

Table 1. Lattice constants [6, 7] and self-consistently calculated occupation numbers.

	a (Å)	c (Å)	n_{5f}	n_{Td}
UFeAl	6.672	3.981	2.63	6.56
UCoAl	6.686	3.966	2.65	7.52
UNiAl	6.733	4.035	2.66	8.60
URuAl	6.895	4.029	2.70	6.55
URhAl	6.965	4.019	2.73	7.55
UIrAl	6.968	4.030	2.66	7.51
UPtAl	7.012	4.127	2.69	8.30

Table 2. Lattice positions in terms of the lattice constants a and c as given in table 1.

	Number per crystallographic cell	a_0/a	b_0/a	z_0/c
T(1)	1	0.000	0.000	0.5
T(2)	2	0.333	0.667	0.0
		0.667	0.333	0.0
Al	3	0.256	0.000	0.0
		0.000	0.256	0.0
		−0.256	−0.256	0.0
U	3	0.594	0.000	0.5
		0.000	0.594	0.5
		−0.594	−0.594	0.5

The ZrNiAl crystal structure (a modified form of the hexagonal Fe_2P structure) is shown in figure 1 and the lattice constants are given in table 1. Table 2 shows the atomic positions for this structure; the values for Al and U are those given for URhAl [9] but are essentially constant across the series. With three different types of atom in the unit cell, this is essentially a layered structure since the uranium atoms lie in the central plane in figure 1. The uranium atoms lie in the x–y-plane, with a spacing of between 3.5 Å and 3.6 Å. This is around or above the Hill limit [10], 3.5 Å, and much less than the z–z separation of 4.0 Å. The nearest neighbour to any uranium (A) atom is a transition metal (T) atom. Since uranium f–f and uranium–transition metal f–d bonding depends strongly upon spacing, the fact that the A atoms have T nearest neighbours suggests that f–d bonding will be important in these compounds. The transition metal atoms lie in all three planes of the figure but are isolated from each other by Al and A atoms, resulting in a spacing of 3.9 Å in the x–y-plane and 4.4 Å between the z-planes. The T atoms have A or Al nearest neighbours, reducing direct d–d bonding and increasing the relative importance of d–f bonding. The electronic structure of the Al atoms consists of (to a first approximation) broad s–p bands, and one would expect the Al atoms to act as no more than spacers between the T atoms.

2. Self-consistent energy band calculations

2.1. Method

The calculations reported here were performed using the self-consistent linear muffin-tin orbital (LMTO) method in the atomic-sphere approximation (ASA) [11] with the von Barth and Hedin [12] exchange–correlation term in the local spin-density approximation [13] to density functional theory. In this paper, where we are primarily concerned with chemical bonding, we have used calculations where the spin–orbit interaction is set to zero for the conduction bands and have solved the Pauli equation [11]. For a more detailed description of the magnetism this approximation is not acceptable and it will be removed in the following paper. The charge densities were spherically averaged at each iteration. The basis was composed of s, p and d states at the Al and T sites and s, p, d and f states at the U sites. The resulting LMTO Hamiltonian and overlap matrices were of dimension 102×102 and the irreducible Brillouin zone was sampled at 75 points. The two T sites were treated as inequivalent although the resulting partial densities of states at the two sites turned out to be very similar.

2.2. Localized f electrons

An initial calculation was performed on UFeAl with the f electrons treated as localized, or semi-core states, i.e. they were not allowed to hybridize with conduction states. The equation of state of compounds may be computed from the total energy as a function of lattice constant or, more elegantly, from the electronic pressure formula [14]. With the f states treated as semi-core states and therefore making no contribution to chemical bonding, the calculated electronic pressure at the measured lattice constants was given by $3PV = 6.64$ Ryd (unit cell volume) corresponding to a pressure $P = 32$ GPa. The calculated lattice constant would therefore be far too large. Thus the removal of f-electron bonding leads to serious errors in the calculated cohesive properties and itinerant f-electron states are essential to the description of the ground-state bulk properties.

2.3. Delocalized f electrons

Calculations were performed for all seven compounds with the f states in the band structure. The total densities of states are shown in figure 2 for UFeAl, UCoAl and UNiAl. The densities of states for the 4d and 5d compounds appear similar to their 3d counterparts, but with broader T d bands, as shown in figures 4 and 5. The essential physics of f–d bonding in these compounds is contained in figure 2 and table 3.

Table 3. Calculated band parameters: bandwidth parameter Δ in Ryd and C also in Ryd.

	Δ_{Td}	C_{Td}	Δ_{Ud}	C_{Ud}	Δ_{Uf}	C_{Uf}	E_{Fermi} (Ryd)
UFeAl	8.0	−0.075	79.0	0.250	10.0	0.012	−0.0380
UCoAl	6.5	−0.125	79.9	0.250	9.6	0.017	−0.0132
UNiAl	5.4	−0.197	77.4	0.230	9.3	0.011	−0.0195
URuAl	16.2	−0.138	71.3	0.218	8.0	−0.015	−0.0525
URhAl	13.6	−0.228	68.9	0.215	7.7	−0.019	−0.0390
UIrAl	17.8	−0.227	69.2	0.211	7.7	−0.021	−0.0407
UPtAl	14.5	−0.346	65.6	0.199	7.3	−0.018	−0.0347

It is useful to imagine that pure d and f bands are formed initially and that hybridization between the two sets of bands leads to bands of mixed character. Before hybridization is introduced the pure d bands will lie below, and the pure f bands above, the Fermi energy. Upon introduction of hybridization the pure bands acquire mixed character and are referred to as d-derived or f-derived bands depending upon their original character. In UFeAl the d-derived bands are filled with the Fermi energy lying in the hybridization gap between the states derived from the Fe d bands and the U f bands. However, the d and f occupation numbers are (table 1) 6.5 and 2.7, respectively. Thus, although the d-derived bands are full the d occupation is far less than ten electrons per atom. That this is possible is due to the strong hybridization that mixes the d and f states, allowing the d-derived bands to sink completely below the Fermi energy with 3d character corresponding to 6.5 electrons and f character being responsible for the remainder. Similarly, the f-derived bands are above the Fermi energy but f occupation is maintained due to the f character of the d-derived bands.

In UCoAl compared to UFeAl there is one added electron, which increases the d character of the d-derived bands by one. Hybridization between d and f states is reduced by the decreased d bandwidth and by the increased distance between the d- and f-band centres, reducing the f character due to hybridization. But as there is one more electron than in UFeAl the Fermi energy rises to the beginning of the f-derived bands—maintaining the total f occupation. Since the d-derived bands contain one more d electron they contain one less f electron; therefore the f-derived bands must contain one more f electron. The pattern is repeated in UNiAl, with the Fermi energy rising up into the f-derived bands and the d-derived bands sinking further.

The d occupation number remains approximately the same as in the elemental metal: 6.5 for Fe, 7.5 for Co and 8.5 for Ni, even through the d-derived bands lie completely below the Fermi energy. This is shown in table 1, which also shows that the U 5f occupation is relatively constant—a result of the huge energy cost in changing the d or f occupation number [15] which results in metals maintaining an almost constant occupation number. The transition metal d band is very narrow—as small as 2 eV for UNiAl, compared with 5 eV in elemental Ni—in agreement with experiment [16].

As one would expect, the d bands of the compounds containing 4d transition metals are broader than those of the compounds containing 3d transition metals. Furthermore,

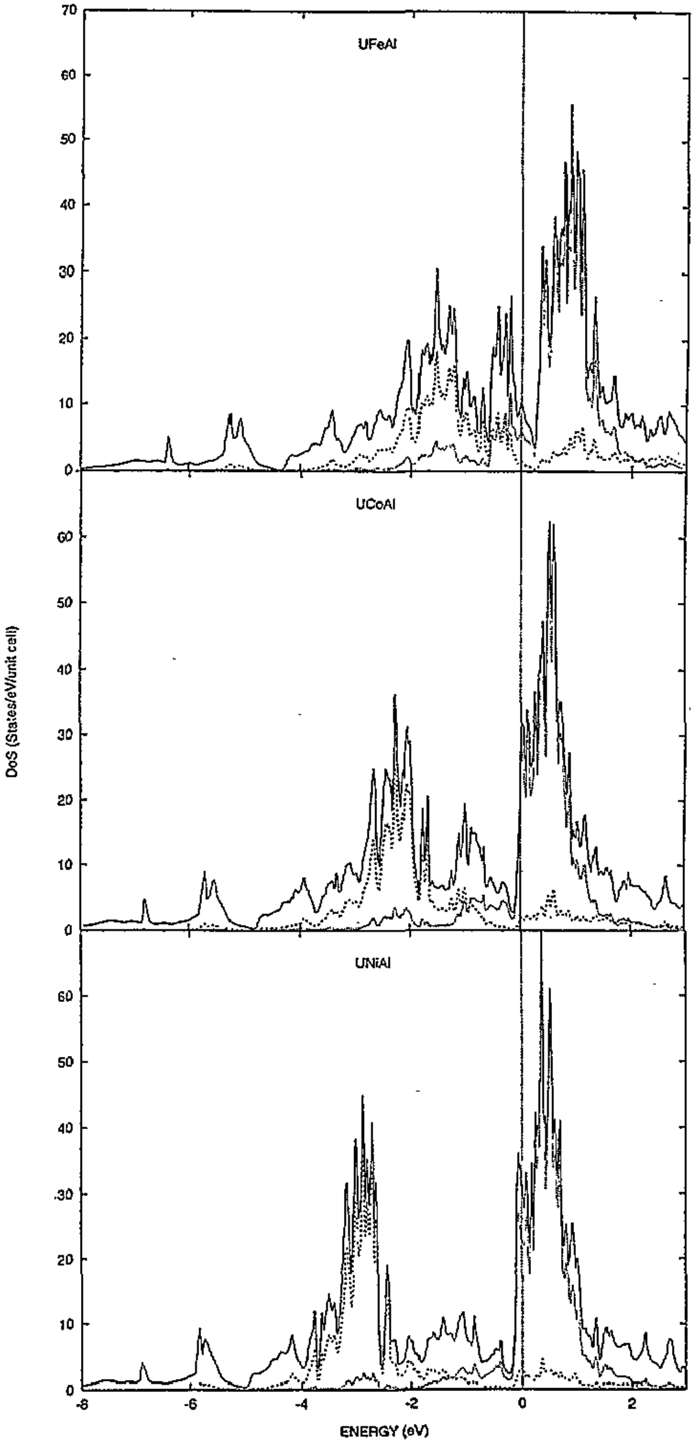

Figure 2. The calculated density of states for U(Fe–Ni)Al. The total DOS (full line), uranium f (dotted) and transition metal d (broken line) partial densities of states are shown. At low energy, the d density is greater than the f density. At, and above, the Fermi level, the f density is greater than the d density. The Fermi level is at zero.

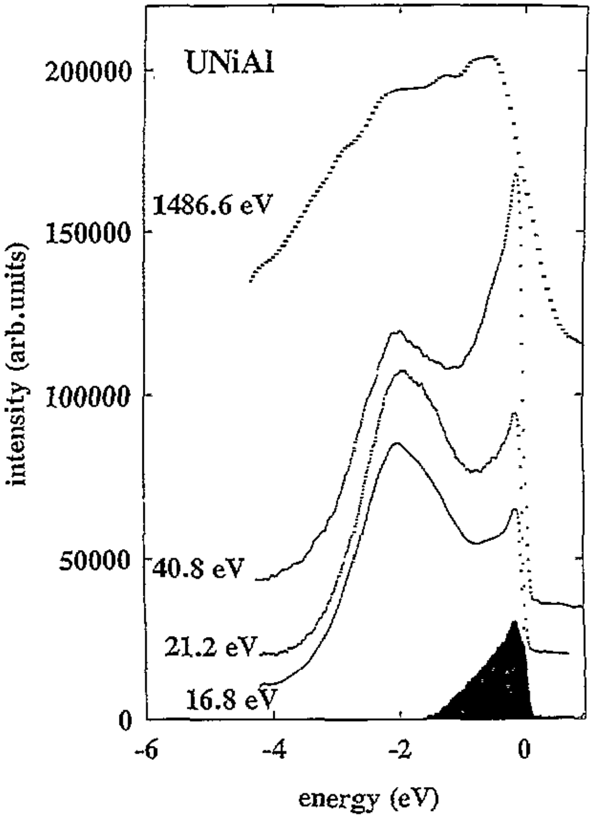

Figure 3. Photoemission spectra for UNiAl with varying photon energy. The f density of states is deduced from the variation of the cross-section with photon energy and is shown as the shaded area. From Havela *et al* [16].

relative to the 5f bands, the 4d bands are lower than the 3d bands for a given column of the periodic table and the 4d–5f hybridization and 3d–5f gap in URhAl are more similar to those in UNiAl than to those in UCoAl. Similarly, apart from the width of the 4d bands, the densities of states of URuAl and UCoAl are similar. The d bands of the 5d transition metals are again slightly broader than those of the 4d transition metals but, for a given column of the periodic table, they lie at about the same energy. Therefore the density of states of UIrAl is similar to those of URhAl, UNiAl and UPtAl, and has an even larger gap between the 5d and 5f states than UNiAl.

In each of these cases two factors determine the placing and width of the d bands: firstly the natural centre of the d bands in the elemental metal; secondly the hybridization between d and f bands. We shall show in section 3 how reasonable approximations to the ASA may be used to separate these two effects and discuss trends across the series of ternaries. Finally, a glance at the position of the Fermi energy in the densities of states indicates how moment formation arises in these compounds. For transition metals towards the left of the periodic table the Fermi energy falls in the hybridization gap between the f and d bands. Therefore UFeAl and URuAl are Pauli paramagnets. In the next row the Fermi energy is at the bottom of the 5f bands. The Stoner criterion is not fulfilled in UCoAl, but UCoAl has been shown to be a metamagnet [17]. URhAl and UIrAl are similar to to UNiAl where the Stoner criterion is fulfilled, as it is in UPtAl. Thus, in the latter cases,

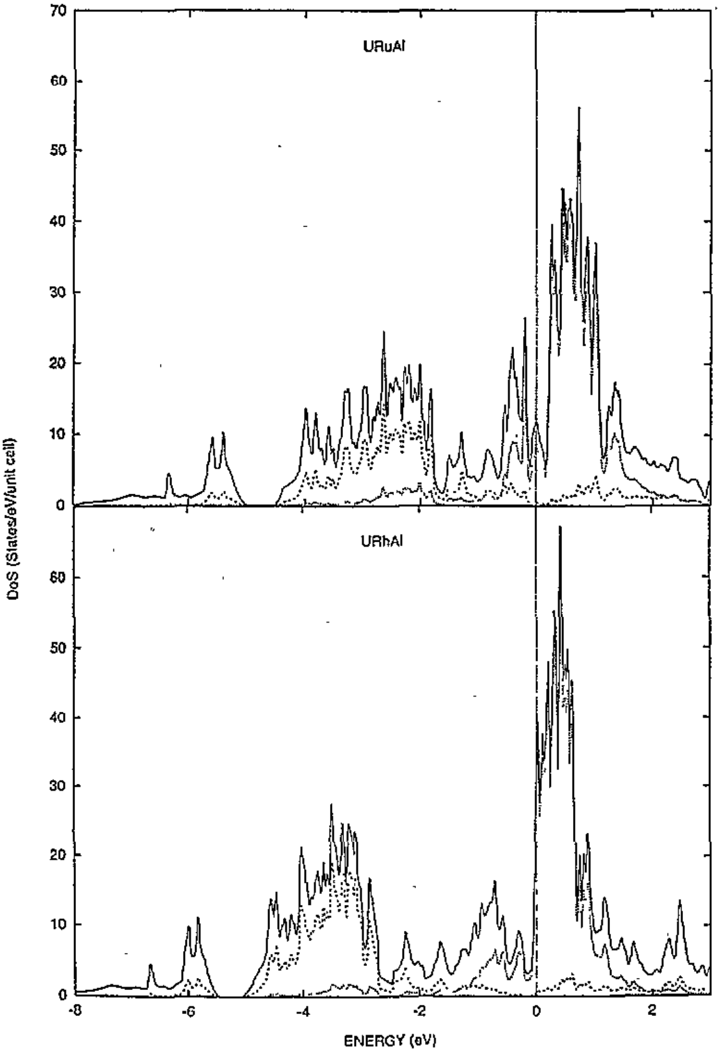

Figure 4. The calculated density of states for U(Ru–Rh)Al. See figure 2 for details.

we expect magnetic ordering. In general, the presence of a hybridization gap between 3d and 5f states tends to lead to densities of states with peaks both above and below the Fermi energy, which is a necessary condition for metamagnetism [18]. One would therefore expect to find metamagnetism relatively frequently in compounds composed of actinide and transition metals although the required applied fields are often larger than can be obtained in the laboratory.

2.4. *Comparison with experiment*

The only photoemission data on these compounds are for UNiAl [16]. Measurements show that the transition metal d band is very narrow, only 2 eV, and that the d-band centre lies 2 eV below the Fermi energy. Calculations are therefore in agreement with experiment [16]. By considering the photoemission spectra for different incident photon energies and the variation of the cross-section with photon energy, Havela *et al* [16] were able to derive the occupied f character; see figure 3. Our results reproduce this behaviour and predict that such measurements on UCoAl and UFeAl would find decreasing f intensity and that the f occupation would lie more within the d density peak.

3. Model band structure

3.1. Band model

Although the self-consistent energy band calculations that we have described provide the ground-state charge densities and densities of states required for comparison with experiment, a better understanding of the electronic structure and the influence of f–d hybridization may be obtained by modelling of the band structure in a simpler manner. The simplest approximation to the densities of states is to assume that the partial densities of states are rectangular—that is to fit them up to their second moment. Secondly, since the physics of interest is due to f–d hybridization it is reasonable to consider just the f and d bands and the hybridization between them. The remaining states give rise to a free-electron background. To get a feel for the role of hybridization it is instructive to first consider the unhybridized bands and then follow the effect of hybridization on these 'pure' bands.

This method is developed from the formalism of Andersen *et al* [19] and has been used, for example, for the uranium pnictides and chalcogenides [20] and $CeCo_5$ [21]. We may write the bandwidth as

$$W_T = \left[\frac{12S_{TT}^2}{(2l+1)N_t}\right]^{1/2} \Delta_T \tag{1}$$

where N_t is the number of atoms of type t in the unit cell, T = (t, l), and S_{TT}^2 is the second moment of the structure constants. These two quantities are structure dependent but independent of potential. The bandwidth parameter, $\Delta_T = (1/\mu_T S_t^2)[S_t/S]^{(2l+1)}$, where S and S_t are the average and atomic Wigner–Seitz radii, scales as the inverse band mass, which is potential dependent and therefore dependent upon the specific compound. The problem may therefore be analysed in terms of a structure-dependent part and a compound-dependent part. The other principal potential parameter is C_T—the centre of the unhybridized, or pure, T band. Since the structure is constant for the entire series, table 3, which contains the potential parameters, may be used to discuss trends in a transparent manner. For example, UNiAl has a narrower 3d bandwidth than UFeAl, an effect due to the contraction of the 3d wavefunctions as the series is traversed. Similarly, the centres of the d bands fall across any of the d series and the 3d bandwidth of UNiAl is less than that of UFeAl table 3 quantifies these effects.

Table 4. Second moments of the structure constants.

S_{Td-Td}^2	S_{6d-6d}^2	S_{5f-5f}^2	S_{Uf-Td}^2	S_{Ud-Td}^2
19	39	39	510	376

Calculated values for S_{TT}^2 for the ZiNiAl structure are listed in table 4. This crystal structure has two non-equivalent transition metal (T) sites. However, to ease the analysis we have treated them as equivalent in this section—an approximation justified by the fully self-consistent calculations. The second moment of the 3d–3d structure constants is small, a result of the large separation between the transition metal atoms in this structure and the fact that for d and f states it is the nearest neighbours that yield the greatest contribution to the structure constants, as may be seen from the form of S^2_{TT} which is given by

$$S^2_{TT'} = \sum_R \frac{(4(2l+1)(2l'+1))[(2l+2l')!]}{(2l)!(2l')!} \left[\frac{S_{WS}}{R}\right]^{(2(l+l'+1))} \tag{2}$$

where the sum is over R from all atoms of type t to all atoms of type t′ with angular momentum l and l' respectively, and S_{WS} is the average Wigner–Seitz radius. In an elemental fcc transition metal, for example, S^2_{3d3d} is 229 whereas it is reduced to 19 in the ZrNiAl structure. In addition, the transition metal Wigner–Seitz radius is less than the average Wigner–Seitz radius of the compound containing larger uranium atoms and the d-bandwidth parameter is therefore smaller than the d bandwidth in the elemental metal. Therefore, whereas pure Ni d bands have a width of about 5 eV, the width of the pure d bands in UNiAl is only 0.29 eV. In UFeAl, the Fe-band mass is a little smaller and the pure 3d bandwidth is 0.4 eV. The uranium atoms are more closely coordinated in this structure and their Wigner–Seitz radii are larger than the average Wigner–Seitz radius of the compound. The result is that although the second moment of the f–f structure constants is only 39 compared with 542 in an fcc metal, the unhybridized bandwidth is about 0.6 eV in both UFeAl and UNiAl compared with about 2–3 eV in elemental fcc uranium. Therefore, in these ternary compounds, a most unusual situation—due to the special coordination of the actinide and transition metal atoms—arises: the pure 5f bands are actually broader than the pure transition metal 3d bands. The bandwidth parameters of the 4d and 5d transition metals are far larger than for Ni, and the pure 4d bandwidths become larger than the pure 5f bandwidths, but remain far smaller than in the elemental metals. Both the 5f and d bands are broadened by d–f hybridization, the second moment of the d–f structure constants is 510, and f–d hybridization is in fact more important than either direct d–d or f–f overlap. In this sense these compounds really belong to a class of strongly hybridized d–f metals.

3.2. *Hybridization*

Hybridization between the d and f states has three effects: it pushes the bands apart, mixes their character and broadens them. The equations that describe hybridization in second-order perturbation theory [20] are of the form similar to equation (1), except that they include a factor $1/(C_T - C_{T'})$ where C_T is the band centre of band T. Thus, the further apart the bands are, the less they hybridize. The shift in the average position of the bands of type T is given by

$$\Delta E_T = \frac{1}{N_t(2l+1)} M^2_{TT'} \frac{\Delta_T \Delta_{T'}}{(C_T - C_{T'})} \tag{3}$$

and the charge transfer into or out of the entire set of bands of type T is given by

$$\Delta Q_T = 2M^2_{TT'} \frac{\Delta_T \Delta_{T'}}{(C_T - C_{T'})^2}. \tag{4}$$

The calculated band centres for U(Fe–Ni)Al are plotted in figure 6. The Fermi energy and the f-band centre remain nearly constant but the 3d-band centre sinks as the 3d atomic number increases, increasing the energy gap to the 5f band. When hybridization is introduced the Ni-derived 3d bands contain admixtures of other angular momentum character according to equation (4). We consider first UFeAl and assume that there are approximately six Fe d and three uranium f electrons per formula unit available to occupy the d and f bands, as in the elements. These numbers are in agreement with the self-consistently calculated occupation numbers shown in table 1. In the absence of f–d hybridization the d bands would be filled, with the Fermi energy falling between the d and f bands. Therefore, when hybridization is introduced, charge transfer is entirely from the d to the f bands and, according to equation (4) and table 3, is equal to about three electrons per formula unit. Therefore the occupation numbers for the d and f bands are six and three, respectively—as in the elements but *the entire 5f occupation is due to hybridization with the d bands.* The d–f hybridization opens up a gap between the d and f bands in which the Fermi energy falls (see figure 2) and UFeAl is a paramagnet.

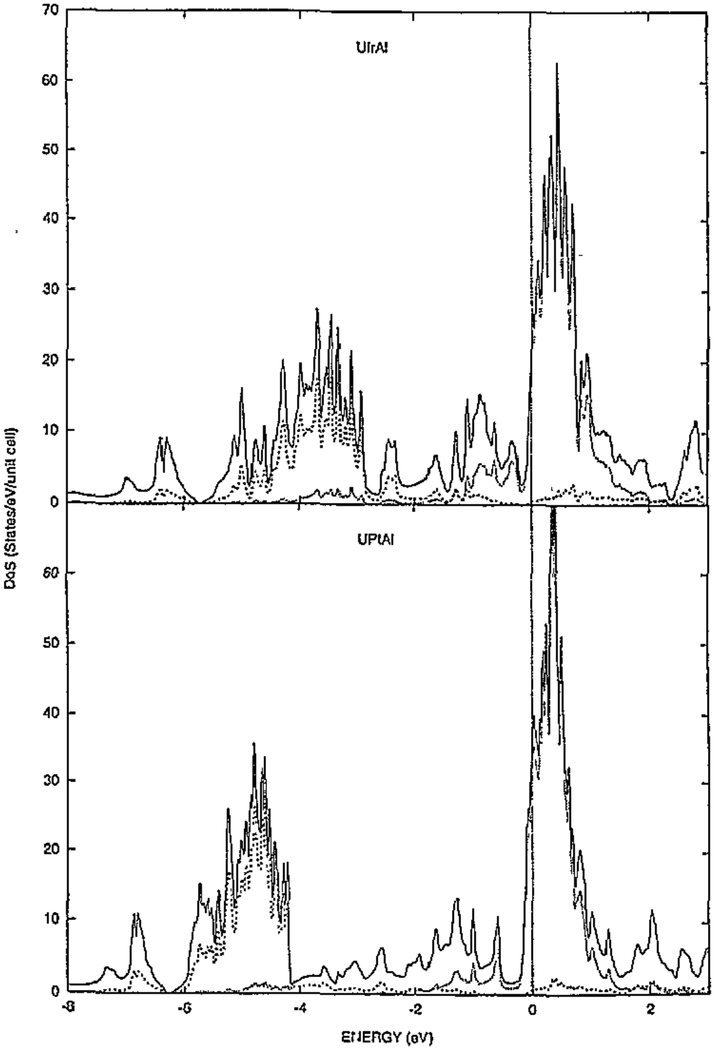

Figure 5. The calculated density of states for U(Ir–Pt)Al. See figure 2 for details.

In UCoAl there is one additional valence electron, bringing the total f and d population per formula unit to ten. The Fermi energy lies at the bottom of the unhybridized f bands, the unhybridized d bands are essentially filled and there is a small occupation, less than one electron, of the unhybridized f bands. The transition metal d-band centre is a little lower than for UFeAl. As the U f and T d bands are now more separate, f–d hybridization,

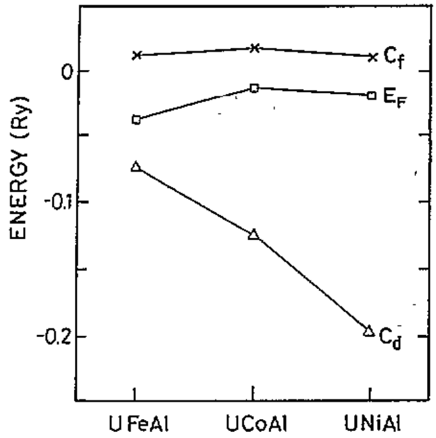

Figure 6. The calculated band centre and Fermi energy for U(Fe–Ni)Al

according to equation (4), is decreased. The charge transfer from the whole of the d bands is decreased a little but this is compensated for by the fact that there is an additional electron before hybridization and the 5f occupation—again almost entirely due to hybridization with the d bands—remains at about three electrons per formula unit. Finally, the d band is narrower since the unhybridized bandwidth is less, and broadening due to f–d hybridization is decreased.

In UNiAl an additional electron per formula unit ensures that the Fermi energy lies in the unhybridized f bands. When hybridization is introduced it is far weaker than in the other two compounds, due to the increase in the denominator in equation (4) and the narrower unhybridized d bandwidth. The reduced charge transfer is compensated for by the fact that the f bands are occupied before hybridization with the d bands and the final f occupation number remains about the same as in the other two compounds, the final d occupation number being increased by about one electron per formula unit. Although the gap between the Ni d bands and the uranium f bands is larger than in UFeAl, this is not entirely due to hybridization. The unhybridized Ni d bands have dropped in energy before hybridization with the 5f bands relative to the d-band position in the other compounds (see figure 6). Nevertheless, it is hybridization with the 5f bands that allows the d-derived bands to be below the Fermi energy whilst maintaining a d population of less than ten, as observed in photoemission experiments [16].

4. Conclusion

We have considered the system U(T)Al where T is Fe, Co, Ni, Ru, Rh, Ir or Pt. A model of hybridization was used to derive the general features of the band structure. Specifically, we have emphasized the role of hybridization in electron transfer from the f to the d blocks of states. Fully self-consistent band-structure calculations confirm the model and provide accurate results for the densities of states. Finally, although hybridization plays a fundamental role in the electronic structure, f and d occupation remains relatively constant for the series.

Agreement with experiment for UNiAl, the only compound where photoemission data are available, is good, as regards both the Ni d bandwidth and position. Since four of the seven compounds are magnetic the transition to magnetism and its nature are treated in the following paper [22].

Acknowledgments

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