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1995 J. Phys.: Condens. Matter 7 9511

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Ground-state properties of ternary uranium compounds: II. Magnetic properties

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Received 28 March 1995, in final form 2 October 1995

Abstract. We examine the compounds U(T)Al forming in the ZrNiAl structure where T is a group 6–8 transition metal. From first-principles calculations we find, in agreement with experiment, the transition from paramagnetism to magnetism across the series. The inclusion of spin–orbit coupling and orbital polarization yields fair agreement with measurements for the calculated magnetic moments. Two magnetic states are found for URhAl.

1. Introduction

The transition metals, rare earths and actinides are responsible for contrasting types of magnetism. The first type is Stoner magnetism, where the itinerant electron states break spin symmetry around the Fermi energy. This costs kinetic energy, but if the density of states at the Fermi energy is sufficiently high, the gain in exchange energy is greater and the system polarizes [1]. The other extreme is localized magnetism, where the 4f states of most of the rare earths do not participate in chemical bonding. The 4f states are localized and satisfy bound-state boundary conditions in which case there is no change in their kinetic energy when a 4f moment forms. Such 4f states are therefore nearly always magnetic, the only cases of zero ground-state moments occurring being when their crystal-field ground state is non-magnetic or when $J = |L - S| = 0$ as for Eu^{3+} and Sm^{2+} . Physically, the actinides lie between these two extremes and one of the most important areas of actinide research has been that of actinide magnetism. It is now believed that the early actinides have itinerant 5f electrons and that the heavier actinides (americium and onwards) have localized f electrons.

Due to the large spin–orbit coupling of the actinides, itinerant magnetism holds the promise of broken-symmetry effects such as magneto-crystalline anisotropy and magneto-optical effects. Judicious choice of the elements in compounds allows moment formation to be followed with the change in composition. A well studied system of compounds with the ZrNiAl-type structure [2, 3, 4] is formed from actinides, transition metals (Fe–Ni and 4d, 5d equivalents), and group 3–4 atoms (Al, Ga, Ge, Sn). These compounds provide wide possibilities for study via the variation of any one of the three atom types. The compounds forming with atoms to the left of the transition metal series (Fe, Co, and Ru) are paramagnetic—although UCoAl is metamagnetic [5]—while URhAl, UIrAl and UPtAl are ferromagnetic and UNiAl is antiferromagnetic.

We have previously [6] reported a study of the theory of chemical bonding in these compounds and followed the trends in bonding across this series (to be referred to as I). In the present paper we report a theoretical study of the magnetic properties of these compounds.

2. Itinerant and localized magnetism

Itinerant magnetism arises from the competition of two contributions to the energy for states around the Fermi energy. If the spin-up and spin-down densities of states are split by a small amount, Δ , the kinetic energy is increased by $\frac{1}{4}\Delta^2N(E_F)$ where $N(E_F)$ is the density of states per spin at the Fermi energy. The magnetic moment corresponding to this splitting is $M = \Delta N(E_F) \mu_B$ and the corresponding gain in exchange energy is $-\frac{1}{4}IM^2$ where I is the exchange interaction. Thus if $IN(E_F) > 1$ the net energy shift is negative and it is energetically favourable for the system to spin polarize. This may be expressed more generally by writing the enhanced susceptibility χ as

$$\chi = \frac{\chi_0}{1 - IN(E_F)}. \quad (1)$$

When the Stoner criterion is fulfilled, the system is unstable to moment formation. In intermetallic compounds, this criterion is often fulfilled at a particular atomic site. Then that atom spin polarizes first and induces a moment on the other sites via hybridization. In the case of localized magnetism, the moment arises from the localized, non-bonding f electrons. In this latter case, the density of states at the Fermi energy is irrelevant; the localized electrons induce a conduction electron moment at the same atomic site via local exchange splitting. The conduction electron states transmit the exchange splitting to other sites by hybridization—as has been examined in detail for the case of some rare-earth intermetallics [7].

In paper I we considered the case of UFeAl where the f states were treated as localized. Our conclusion was that it was necessary to include the f electrons as itinerant to allow their contribution to the bonding. Magnetic properties provide even stronger evidence of this. When the f electrons are treated as localized, the calculated Stoner product for UFeAl is greater than 2 at the Fe site and a large Fe moment would develop if allowed. The fact that UFeAl is paramagnetic then argues against this model. Interestingly, this is an example of f electrons quenching magnetism—a phenomenon which can also occur in some cerium compounds.

3. Crystal and band structure

The ZrNiAl crystal structure has been analysed in paper I. Basically, it consists of close-packed transition metal and uranium atoms, interspaced with aluminium atoms. However, the uranium atoms have transition metal (T) nearest neighbours and vice versa, so both uranium and T atoms are well separated from atoms of the same type. There are two sites for the T atoms which are quite well spaced within the structure and the densities of states for the two T types were found to be very similar. The T d band lies below the uranium f band. Hybridization leads to mixing of these two bands and the d band retains its atomic occupation number (6.5 3d electrons in Fe, 7.5 in UCoAl etc) even though it sinks down below the Fermi energy. In UFeAl the f band is unoccupied before hybridization, the 5f occupancy is provided by hybridization with the d band, and the Fermi energy lies in the hybridization gap between the 3d- and 5f-derived bands. In UCoAl the Fermi energy has

risen into the f band and the density of states at the Fermi energy rises as a result. For UNiAl the Fermi energy lies at a peak in the U 5f density of states. Referring to the condition $IN > 1$ for itinerant magnetism, we see that N increases with increasing d occupation and that moment formation should therefore occur as the series is traversed towards the right. Given that the Fermi level falls mainly on the uranium f partial density of states the magnetic moment should form initially at the uranium site.

4. Results of full calculations

4.1. Method of calculation

These calculations were performed using the linear muffin-tin orbital (LMTO) method in the atomic-sphere approximation (ASA) [8] with the von Barth and Hedin parametrization [9] of the exchange-correlation term in the local spin-density approximation [10]. s, p and d basis states were used for the Al and T sites and s, p, d, f basis states were used for the U site. This resulted in a LMTO Hamiltonian matrix of dimension 102×102 and the Brillouin zone was sampled at 75 points. The Stoner integral, I , was calculated [11] and, when the Stoner product was found to be greater than 1, the system was allowed to spin polarize. UNiAl was treated as ferromagnetic to ease the calculations and to facilitate comparison with the other compounds.

4.2. Spin-polarization results

In table 1 the experimental ground states and calculated Stoner products are given. The transition to magnetism is clearly reproduced. In agreement with Eriksson *et al* [20] we find UCoAl to have a stable paramagnetic ground state. By performing fixed spin moment calculations Eriksson *et al* [20] found UCoAl to be metamagnetic.

Table 1. Experimental data and calculated Stoner products.

| | a (Å) | c (Å) | Magnetism | $ID(E_F)$ |
|-------|---------|---------|--------------------|-----------|
| UFeAl | 6.672 | 3.981 | Paramagnetism | 0.57 |
| UCoAl | 6.686 | 3.966 | Metamagnetism | 0.81 |
| UNiAl | 6.733 | 4.035 | Antiferromagnetism | 1.52 |
| URuAl | 6.895 | 4.029 | Paramagnetism | 0.35 |
| URhAl | 6.965 | 4.019 | Ferromagnetism | 1.23 |
| UIrAl | 6.968 | 4.030 | Ferromagnetism | 1.46 |
| UPtAl | 7.012 | 4.127 | Ferromagnetism | 1.94 |

The model given in section 3 argues that the onset of magnetism stems from the rise of the Fermi level into the 5f density of states. This is confirmed by writing the multiband Stoner parameter [12] as

$$ID = D \sum_{qll'} \left(\frac{D_{ql}}{D} I_{qll'} \frac{D_{ql'}}{D} \right) \quad (2)$$

where we sum over atom types q with angular momentum l and l' and D_{ql} is the partial density of states. As $I_{ll'}$ is an atomic-like property we find $I_{U,5f5f}$ to be an almost constant 28.7 mRyd and $I_{T,dd}$ to be 62, 71, 81 mRyd for Fe, Co and Ni, respectively. Thus the Stoner product depends, essentially, upon the site-resolved density of states at the Fermi

energy. This is shown in table 2, where the effect of the rise in the Fermi energy into the 5f band is clearly seen as an increase in D . Results for the 4d and 5d compounds follow a similar pattern. Applying the above model, we argue that UMnAl, if it existed in this structure, would be magnetic with the moment originating at the Mn site, with a low partial Stoner product on the uranium site. This is analogous to the case of $U(T_2)Si_2$ where the Mn compound has a moment at the Mn site, the Fe compound is paramagnetic and the Ni compound has a moment at the U site. Similarly, we can compare UFeAl with UFe_2 . In the former, uranium can provide 3.5 d and f states to fill the Fe d band, allowing it to sink below the Fermi energy. In UFe_2 this is not the case as U does not possess enough electrons to fill the doubled number of d bands. The result is that these d bands are pinned to the Fermi energy and UFe_2 is magnetic with the driving contribution to the Stoner product coming from Fe [13].

Table 2. Site-resolved paramagnetic densities of states (states Ryd⁻¹/unit cell).

| | U f | U d | T(1) d | T(2) d | sp states | Total |
|-------|--------|------|--------|--------|-----------|--------|
| UFeAl | 27.23 | 3.79 | 2.73 | 9.10 | 6.66 | 49.51 |
| UCoAl | 61.11 | 3.21 | 5.27 | 3.53 | 8.16 | 98.20 |
| UNiAl | 101.43 | 7.86 | 29.29 | 6.00 | 22.01 | 166.59 |

Table 3. Magnetic properties: calculated spin moments and experimental magnetizations (μ_B /formula unit).

| | U f | T(1) d | T(2) d | Total | Measured |
|-------|------|--------|--------|-------|---------------------------------------|
| UNiAl | 1.59 | -0.027 | -0.017 | 1.54 | 0.5 ^a |
| URhAl | 0.57 | -0.029 | -0.047 | 0.51 | 1.05 ^b / 0.15 ^c |
| UIrAl | 0.46 | -0.024 | -0.040 | 0.38 | 0.4 ^c |
| UPtAl | 1.38 | -0.013 | -0.053 | 1.31 | 0.8 ^c |

^aAntiferromagnetic—extrapolated from high-field measurements [2].

^bNeutron scattering on a single crystal [21].

^cPowder measurement [3].

In table 3 we present the calculated spin moments and compare them with experiment. What one notices is that the uranium and transition metal moments are antiparallel. This can be explained by analysis of the hybridization between these two atom types. The reasoning is similar to that used for $LuFe_2$ [14] and builds upon the fact that the Stoner criterion is fulfilled mainly due to the contribution from the uranium site. We begin with paramagnetic UNiAl, and then spin split the U 5f band; at this stage the Ni d band is not spin split. The spin-up uranium 5f bands are closer to the d bands than are the uranium spin-down bands (figure 1(a)). The greater the energy gap between two hybridizing states, the smaller the hybridization strength (as is explained in greater detail in paper I); therefore there is a stronger hybridization between the spin-up bands than between the spin-down bands. This induces a larger admixture of spin-up than spin-down d bands into the (nearly empty) 5f bands, depleting the spin-up d bands more than the spin-down d bands. Similarly, more spin-up f states are admixed into the spin-up d bands than are spin-down states. However, the amount of admixture in this case is less as the initial occupation of the 5f bands is far smaller than that of the d bands. The net result is that the d band has more spin-down 3d electrons than spin-up ones, and therefore the transition metal and uranium spin moments

are antiparallel. This is clear from table 3, where the calculated spin moments are listed. While the transition metal moments are antiparallel to the uranium moments, they are much smaller since they are induced by hybridization.

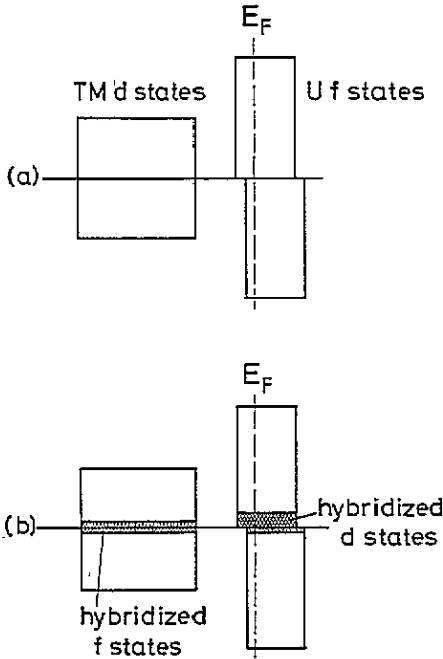


Figure 1. The model density of states for UNiAl. The situations before hybridization (a) and after hybridization, where a moment is induced by hybridization on the Ni site (b), are shown.

Considering the four theoretical values, we see that the moments for UNiAl and UPtAl, on the one hand, and for URhAl and UIrAl, on the other, are similar. These similarities may be explained by referring to section 3. As UNiAl and UPtAl are isoelectronic, we would expect that the Fermi level lies in (approximately) the same place in the f density of states, giving rise to a similar splitting of the two densities of states and, hence, a similar spin moment. This argument can then be repeated for the case of URhAl and UIrAl, which are also isoelectronic. Based on the fact that the (paramagnetic) Fermi level falls at the beginning of the f density of states for these two compounds, we would expect a lesser moment than for UNiAl and UPtAl. Thus, these spin-only calculations reproduce the experimental non-magnetic-magnetic transition across the series and the trend in the calculated magnetic moment is explained by reference to band-filling arguments. However, the experimental values are not reproduced: we deal with this discrepancy in the following two sections.

4.3. Spin-orbit interaction and orbital polarization

The magnetism of itinerant 5f-electron systems contains contributions from both spin and orbital magnetism [15, 5]. In order to describe orbital magnetism it is necessary to include spin-orbit coupling in the calculations. Inclusion of spin-orbit coupling in the band-structure problem doubles the size of the Hamiltonian matrix to 204×204 . The results of such calculations are shown in table 4. One effect of spin-orbit coupling is that the bands broaden due to the spin-flip contribution. For the narrow bands of the U sites this is noticeable as the spin-orbit splitting of 0.8 eV is of the order of the bandwidth of 2 eV. Normally, spin-orbit coupling has no large effect on transition metals, but the narrowness

of the T metal bands in this structure emphasizes this effect. Unfortunately, these d bands are below the Fermi energy and thus no appreciable orbital moment can form. Otherwise, an anomalously large moment would be expected, similar to that in the case of CeCo_5 [12], for example.

Table 4. Magnetic properties: calculated orbital moments with spin-orbit coupling (so) and orbital polarization (op) (μ_B /formula unit)

| | | U f moment | | T d moment | | Total moment |
|-------|----|------------|---------|------------|---------|--------------|
| | | Spin | Orbital | Spin | Orbital | |
| UNiAl | so | 0.79 | -0.25 | -0.03 | -0.002 | 0.51 |
| UNiAl | op | 0.86 | -0.85 | -0.03 | -0.003 | -0.04 |
| URhAl | so | 0.26 | -0.10 | -0.02 | -0.003 | 0.13 |
| URhAl | op | 0.29 | -0.29 | -0.02 | -0.003 | -0.02 |
| UIrAl | so | 0.24 | -0.09 | -0.02 | -0.004 | 0.13 |
| UIrAl | op | 0.26 | -0.19 | -0.02 | -0.005 | 0.05 |
| UPtAl | so | 0.88 | -0.33 | -0.05 | -0.005 | 0.49 |
| UPtAl | op | 1.02 | -0.93 | -0.05 | -0.005 | 0.04 |

An improvement to the LDA of including orbital correlation has been suggested [16, 17, 18]. Here we have implemented the commonest scheme, a shift in the energies of $-E^3 L m_l$ where E^3 is the Racah parameter and L the total atomic orbital moment per spin channel. The Racah parameter is found to be 3.2 mRyd, almost the same as in other calculations for uranium compounds [17] which is not surprising given its atomic nature for 5f electrons. Inclusion of orbital polarization has the effect of increasing both spin and orbital moments, as is clear from table 4. In previous calculations, it has been found that orbital polarization gives higher calculated spin and orbital moments [17] than experiment. This problem has been previously examined for UNi_2 [13] where it was found that fixing the spin moment to that found experimentally led to a very accurate value for the orbital moment. This is, however, not a general solution as it fails for UFe_2 [19].

As is always found, the calculated uranium orbital moment is antiparallel to the uranium spin moment—which is similar to the finding that the transition metal orbital moments are parallel to the spin moments. This is in agreement with Hund's second rule in both cases. Finally, the uranium and transition metal *spin* moments continue to be *antiparallel*.

We are now in a position to compare our results with experiment. From table 3 we see that the calculated total moments are much lower than the measured values. We first consider the measured values: that for UNiAl is the high-moment extrapolated value. UNiAl itself is antiferromagnetic and the high anisotropy of these compounds makes accurate measurements difficult to obtain. The data for UIrAl and UPtAl are old measurements that were performed on powder, and again the high anisotropy of these compounds could have affected the results. As evidence of this we refer to URhAl, where the powder measurement yields $0.15\mu_B$ [3] and the single-crystal measurement yields $1\mu_B$ [2]. Thus, for UIrAl and UPtAl, we suspect that the magnitude of the measured moments may be unreliable and measurements on a single crystal may yield better values.

While we can explain the discrepancy between theory and experiment for UNiAl, UIrAl and UPtAl, the problem for URhAl remains: our calculated moment is much lower than the reliable neutron data. With this problem in mind, we shall return to general consideration of this structure type.

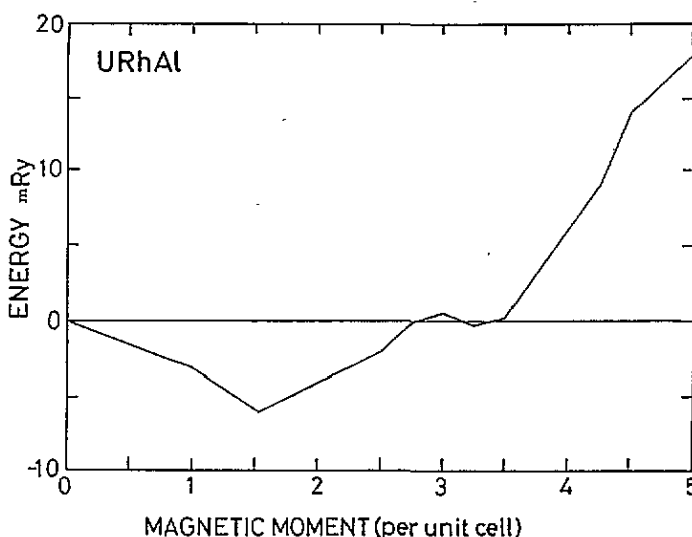


Figure 2. The total energy, E (in mRyd), as a function of unit-cell magnetization, M , for URhAl. The two stable states are seen for (spin-only) moments of 1.5 and $3.3\mu_B$.

4.4. Metamagnetism

A paramagnetic material has a minimum in its curve for energy (E) versus magnetization (M) at $M = 0$. Similarly, a ferromagnetic material has its minimum at $M = M_0$. There is a class of materials which possess at least *two* local minima in their E - M curve. The simplest case of this is *metamagnetism*, where one of the minima is at $M = 0$ but a second minimum exists for a non-zero moment. An example of this is UCoAl: the low-energy state is at $M = 0$ but in an external field of 0.8 T an induced moment is found to be stable [5]. The calculations of Eriksson *et al* [20] reproduced metamagnetism in UCoAl. A second case is fcc Fe, which according to band-structure calculations has two minima in its E - M curve: a high-moment state and a low-moment state. If we follow the reasoning of section 3 we would expect the density of states for URhAl to be similar to that of UCoAl and therefore that URhAl could also have two minima in its E - M curve. A search has therefore been carried out in the E - M phase space for the spin-polarized solution, and a high-moment state has been found to be stable as shown in figure 2. The calculations presented in section 4.3 correspond to the lower stable state, with a magnetic (spin-only) moment of $1.5\mu_B$ per unit cell. We have performed further calculations for URhAl in its higher-moment state (that with a spin-only moment of $3.3\mu_B$). The moments were then calculated for this state with the inclusion of spin-orbit and then orbital polarization into the Hamiltonian. Comparison of the two states including orbital polarization shows that the high-moment state has an energy 3 mRyd per unit cell higher than the low magnetic state. This means that, theoretically, the low-moment state is found to be the ground state. It is possible that calculations can find the *wrong* magnetic ground state—the most well known example is probably Fe which is found to be stable in a paramagnetic fcc state instead of its magnetic bcc state. We therefore consider this high-moment state to be a candidate for being the true ground state. The final results for this high-moment state are: uranium spin and orbital moments of 1.01, $-1.61\mu_B$; Rh spin and orbital moments of -0.13 , $-0.01\mu_B$; and a total moment of $-0.73\mu_B$ /formula unit. The two Rh sites have very similar moments. The experimental values from neutron scattering are [21]: 1.16, $-2.1\mu_B$ for the uranium

f moment; $-0.28\mu_B$ for the moment on Rh site 1; and $-0.03\mu_B$ for the moment on Rh site 2. Although the calculated moments are found to be too small when compared to experiment [21], the size has increased to within the same magnitude as the experimental moments. However, the inequality in the moments of the two Rh sites is not reproduced. This is unusual; even for very complicated systems like $\text{Nd}_2\text{Fe}_{14}\text{B}$ the *ratio* of moments on different sites tends to be well reproduced.

To summarize: for URhAl we find a second magnetic state with a higher total magnetic moment. Although our calculated moments are of the same order as the experimental values, we continue to find two shortcomings. The first is that we underestimate the uranium spin and orbital moments; the second is that we do not reproduce the inequality of the two Rh-site moments. This failure of the calculation could depend upon the fact that hybridization is strongly anisotropic in this compound and that the orbital moments are (experimentally) found to be large. Both of these points could cause a problem when using the atomic-sphere approximation as the charge density is averaged within the sphere. This could also explain why the calculated moments are smaller than the experimental values—in all other uranium intermetallic calculations the moment is overestimated.

5. Conclusions

We have reported calculations for the system U(T)Al where T is Fe, Co, Ni, Ru, Rh, Ir or Pt. By first considering the crystal structure and applying simple arguments we explain the transition from non-magnetic to magnetic behaviour as the number of transition metal d electrons increases. By performing fully self-consistent (spin-only) band-structure calculations we confirm this model for the onset of magnetism in these compounds, in agreement with experiment. Furthermore, we predict that the compounds URhAl and UIrAl, on the one hand, and UPtAl and (hypothetically ferromagnetic) UNiAl, on the other, should have similar moments.

After the inclusion of spin-orbit coupling and orbital polarization, the calculated moments are found to be in poor agreement with experiment. For UNiAl this can be explained by the antiferromagnetic ground state of the sample; for UIrAl and UPtAl the measurements are on a polycrystalline sample and the anisotropy of these materials leads to difficulties in the experiments. For the case of URhAl there are two measurements which yield a moment of magnitude $1\mu_B$ /formula unit and the calculated moment is in poor agreement with this. We have found a second, high-moment, magnetic state for URhAl but the calculated total moments (including spin-orbit coupling and orbital polarization) are too small when compared with measurements. We also do not reproduce the large difference in the moments on the two Rh sites. This may be due to a failure of the atomic-sphere approximation due to the simultaneous occurrence of both anisotropic hybridization and large orbital moments. This point requires further investigation, possibly with one of the full potential techniques that are now available.

Acknowledgments

B Johansson is grateful to the Swedish Natural Science Research Council for financial support. Support given to T Gasche in the framework of the CEC-funded training programme 'Human Capital and Mobility' is acknowledged.

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