LETTER TO THE EDITOR

Meta-magnetism in UCoAl

Olle Eriksson†, Börje Johansson† and M S S Brooks†‡

† Department of Physics, University of Uppsala, Box 530, S-751 21 Uppsala, Sweden
‡ European Institute for Transuranium Elements, Postfach 2340, D-7500 Karlsruhe, Federal Republic of Germany

Abstract. We have undertaken a detailed theoretical investigation of the meta-magnetic transition in UCoAl. Using the fixed spin moment method in our calculations we can account for the observed meta-magnetic transition and we find that the magnetic properties of UCoAl are dominated by a moment located on the uranium atom. This uranium moment is found to consist of an orbital moment that is larger and anti-parallel to the spin moment. The spin and orbital moments were calculated using the local spin-density approximation and the recently reported formalism for orbital polarisation together with the spin–orbit interaction.

The magnetic properties of UCoAl, which is a member of the series of UTX system (T $\equiv$ Fe, Co, Ni, Ru, Rh, Ir and Pt; X $\equiv$ Al, Ga and Sn), are difficult to understand [1]. The compound forms in the hexagonal ZrNiAl structure (figure 1) (a modified version of the Fe_2P structure) and the interatomic spacing between the uranium atoms is 3.49 Å [1], slightly lower than the Hill limit [2]. The ground state of UCoAl has been shown to be non-magnetic. This was concluded from the measured temperature dependence of the susceptibility and the specific heat [1]. However, in the presence of a small magnetic field ($B < 0.8$ T), a maximum in the magnetisation develops at a temperature of about 17 K [1]. Further increase of the applied magnetic field drives UCoAl into a meta-magnetic state (at $B \simeq 0.8$ T) with a total moment of about $0.34 \mu_B$ (FU)$^{-1}$ [1]. The applied field is directed along the easy axis, i.e. the c axis. The critical temperature for the meta-magnetic state was also determined, and it was found to be 17 K [1]. When the applied field is increased further the magnetic moment also increases but no saturation is shown even for very high fields. At the highest applied field (35 T) the total moment is measured to be about $0.6 \mu_B$(FU)$^{-1}$ [1]. From a modified Curie–Weiss law, with the applied field larger than 0.8 T and directed along the c axis, it was concluded that the effective moment is $1.6 \mu_B$(FU)$^{-1}$.

Hence it seems that the magnetic properties of UCoAl are quite complex and it is of considerable interest to examine the nature of the meta-magnetic transition. Especially intriguing is the role of the 5f electrons, namely whether they are delocalised or not. In connection with this it is also important to investigate the influence of orbital magnetism, since it has recently been realised that delocalised band states may sometimes carry an appreciable orbital moment [3]. The distribution of the magnetic moment between the different types of atoms is also of interest, since one might suspect that both the U and Co atoms carry a magnetic moment.
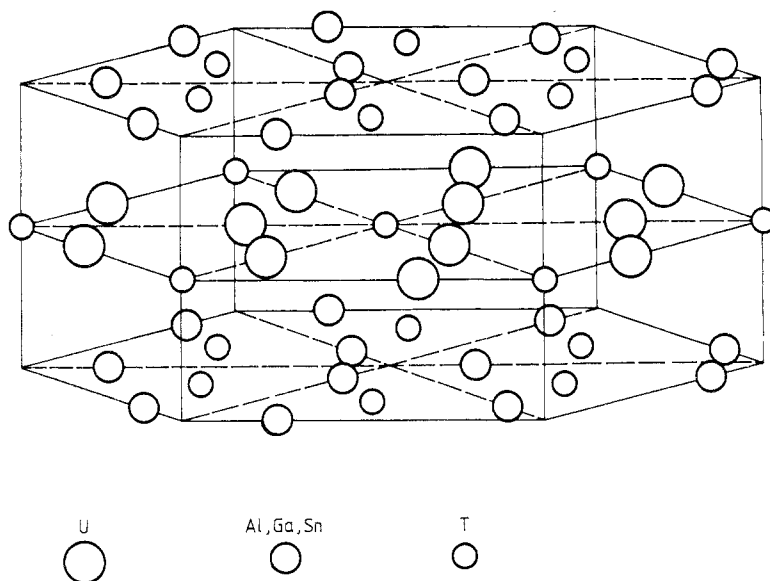
Figure 1. Crystal structure of UCoAl (ZrNiAl-type structure).

In order to investigate the magnetic properties of UCoAl we first performed a conventional scalar relativistic band calculation for the paramagnetic state, using the LMTO-method with the combined correction terms [4] and we calculated the density of states (DOS) using the analytical tetrahedron method [5]. In the calculation of a self-consistent potential we used the frozen-core approximation together with the von Barth–Hedin parametrisation of the exchange and correlation potential [6], in the local spin-density approximation. Furthermore, in the calculations, the ratios between the atomic sphere radii, $S_U:S_{Co}:S_{Al}$, were chosen to be $1.07:0.9:1.0$.

We also performed calculations using the so-called fixed spin method (FSM) [7]. In this method one uses the magnetic moment (M) as an external parameter and the total energy is calculated as a function of M. The number of valence electrons Z_{val} and M are calculated from

$$Z_{val} = N^\uparrow + N^\downarrow = \int_{-\infty}^{E_F^\uparrow} D^\uparrow(E)\,dE + \int_{-\infty}^{E_F^\downarrow} D^\downarrow(E)\,dE \tag{1}$$

and

$$M = N^\uparrow - N^\downarrow \tag{2}$$

where $D^\uparrow(E)$ and $D^\downarrow(E)$ are the spin-up and spin-down DOS, respectively. These two equations determine the values for $E_F^\uparrow$ and $E_F^\downarrow$, and for a general value of M we have $E_F^\uparrow \neq E_F^\downarrow$. Only when a maximum or a minimum in the total energy is found, are the two Fermi levels equal, i.e. $E_F^\uparrow = E_F^\downarrow$.

The DOS from the paramagnetic calculation is shown in figure 2. Here we notice that the 3 eV broad Co 3d band is nearly filled and has its major weight at 1.5 eV below E_F, whereas the 5f band is pinned at the Fermi level with a band width of about 3 eV. The hybridisation between these two bands is seen to be quite strong. It has been shown that the hybridisation between actinide 5f electrons and ligand orbitals is often vital for the
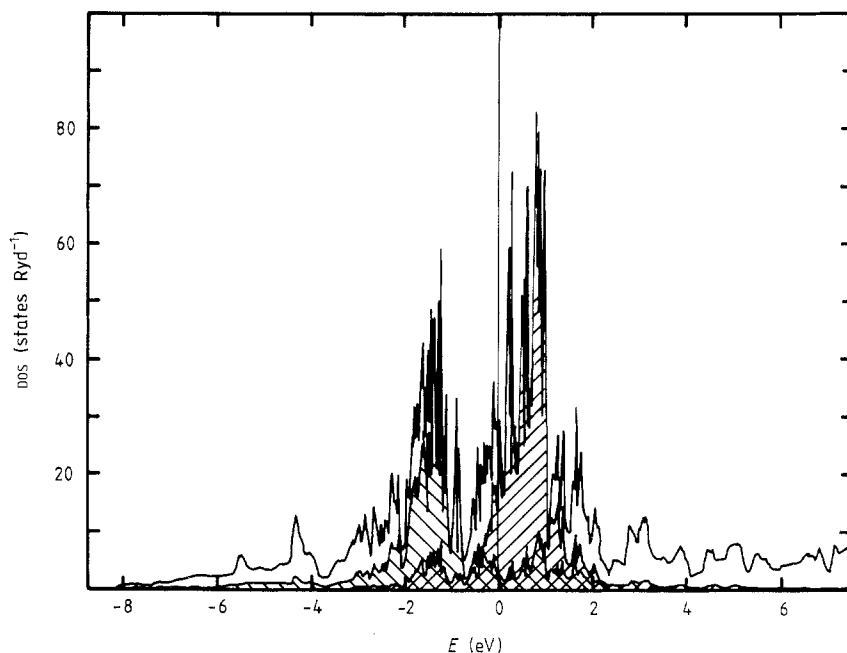
Figure 2. Self-consistently calculated scalar relativistic density of states (DOS) for paramagnetic UCoAl. The Fermi level is at zero and energies are in eV.

5f band formation and band width in compounds [8]. This is also the case for UCoAl since an estimate of the 5f band width with no hybridisation can be written [4, 9].

$$W_{5f} = [(12/N_{5f})\,|S^{5f}_{5f}|^2]^{1/2}\,\Delta_{5f}. \tag{3}$$

Here $|S^{5f}_{5f}|^2$ is the second moment of the 5f block in the structure constants. N_{5f} is $(2l + 1)n_u$, where $l = 3$ and n_u is the number of uranium atoms in the unit cell. Furthermore Δ_{5f} can be written [4, 9]

$$\Delta_{5f} = 1/[\mu_{5f}S_u^2(S/S_u)^7]. \tag{4}$$

In (4), S is a characteristic radius of the lattice, S_u is the radius of the uranium atomic sphere and μ_{5f} is the band mass for the 5f states. Using (3), with a calculated $\Delta_{5f} =$ 8.9 mRyd and $|S^{5f}_{5f}|^2 = 57$, we estimate the unhybridised band width to be 0.7 eV. This is considerably smaller than the band width of about 3 eV obtained from the fully hybridised calculation (figure 2).

The Stoner product [10], i.e. the criterion for the onset of ferromagnetism, was calculated to be 0.61, which clearly suggests that UCoAl is paramagnetic. In figure 3 we show the results for the energy versus spin magnetisation from our FSM calculation, and here we notice that the $M = 0$ state indeed is the stable one. However, most interestingly, there exists a metastable state for a finite magnetic moment at $M = 2.15\ \mu_B$ (unit cell)$^{-1}$. This state lies 0.7 mRyd (FU)$^{-1}$ higher in energy than the paramagnetic state and can thus only be reached when a sufficiently strong external field is applied. Hence it seems that our delocalised picture of the 5f electrons can explain this complicated aspect of the magnetic properties UCoAl. The meta-magnetic transition from a paramagnetic to a ferromagnetic state can be understood as follows. The applied external field shifts the
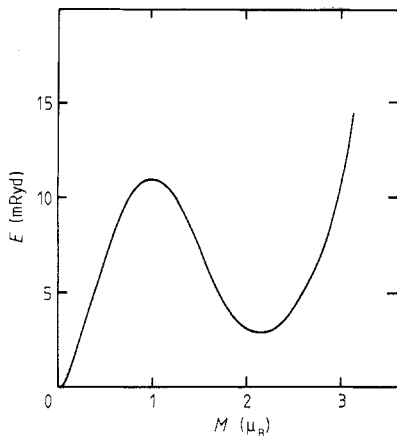
Figure 3. Calculated total energy per unit cell as a function of magnetic moment (unit cell)$^{-1}$. Energies are in mRyd and the magnetic moment is given in units of Bohr magnetons (μ_B).

up and down spin bands by a small amount. By doing this the system gains potential energy due to a reduced Coulomb interaction, but at the same time loses energy due to an increase of the kinetic contribution. The final induced magnetic moment will be determined from a balance between these two terms. However, in some systems there will be, for a certain critical value of the applied field, a sudden gain in potential energy that is not sufficiently counterbalanced by the kinetic term, and a meta-magnetic spin state develops. More quantitatively, the criterion for the onset of metamagnetism may be written [11]

$$I(1/2D_\uparrow(E_F) + 1/2D_\downarrow(E_F))^{-1} = 1. \tag{5}$$

Here I is the multi-band Stoner parameter, and $D_\uparrow(E_F)$ and $D_\downarrow(E_F)$ are the DOS at the Fermi energy for the spin-up and down bands respectively. From (5) it can be seen that if the two state densities simultaneously attain sufficiently large values for a given applied field a meta-magnetic transition will take place. A glance at figure 2 shows that a small splitting of the spin bands will indeed give large values of both $D_\uparrow(E_F)$ and $D_\downarrow(E_F)$. This explains the occurrence of the magnetic transition. From (5) we also observe that the normal Stoner criterion for ferromagnetism is obtained when the applied field is zero, i.e. when the two state densities are equal.

In the high-spin state, the calculated total moment for UCoAl ($0.72\ \mu_B(FU)^{-1}$) can be decomposed into the different atomic sites and we find that the uranium atom carries a magnetic moment of $0.85\ \mu_B$. This uranium moment can be further decomposed into its partial wave contributions and is dominated by a 5f moment of $0.77\ \mu_B$ parallel with a smaller 6d moment of $0.07\ \mu_B$. Similarly we find a total moment at the Co site of $-0.18\ \mu_B$, which is dominated by a 3d moment of $-0.22\ \mu_B$. The magnetic moment at the Al site is very small, only $0.05\ \mu_B$. The sum of these moments does not compare very well with the experimentally determined total moment [1] of $\mu_{tot} = 0.34\ \mu_B\ (FU)^{-1}$; or with the site-projected moments deduced from neutron experiments [12] ($\mu_U = 0.3\ \mu_B$ and $\mu_{Co} = 0.07\ \mu_B$). We believe this discrepancy originates from the large influence of relativistic effects on the magnetism in uranium compounds, i.e. large orbital moments [3].

In order to calculate the orbital contribution to the magnetic moment we first included the spin–orbit coupling to the band Hamiltonian and iterated to self-consistency. Then the total spin moment was dramatically reduced to a value of $0.29\ \mu_B\ (FU)^{-1}$, due to the

spin–orbit-induced mixing of the spin states. The moment decomposition gave a uranium 5f spin moment of $0.37\,\mu_B$, a uranium 6d spin moment of $0.04\,\mu_B$ and a Co 3d spin moment of $-0.16\,\mu_B$. The calculated orbital moment was found to be $-0.35\,\mu_B$ for the uranium atom and $-0.06\,\mu_B$ for the Co atom. The total uranium and cobalt moments are thus $0.02\,\mu_B$ (FU)$^{-1}$ and $-0.22\,\mu_B$ (FU)$^{-1}$ respectively. Hence, although the agreement with experiment for the total moment is now quite good, the site decomposition of the moment is still far from the experimental observations. Also, our finding of a ferrimagnetic alignment between the uranium and cobalt moments is in disagreement with the measured ferromagnetic coupling.

Recently we have shown that a $(-\frac{1}{2})E^3L^2$ term added to the total energy of a system accounts for Hund's second rule [13]. This term reproduces quite well the energies derived by Nugent [14] in his description of the tetrad effect in the liquid–liquid extraction data for the partition of the lanthanides and actinides between various solvents. Here E^3 is the Racah parameter [15] and L is the 5f orbital moment of the electrons of a given spin on a uranium site. Introducing this term into the previous spin-polarised band calculations, with a self-consistently calculated E^3-value of 3.4 mRyd, thus corresponds to taking into account Hund's first (exchange), second (orbital polarisation) and third (spin–orbit interaction) rules. The self-consistently calculated values for the site-decomposed and total magnetic moments are now in acceptable agreement with experiment. The magnitude of the calculated total moment is $-0.60\,\mu_B$ (FU)$^{-1}$. The uranium atom carries a 5f spin moment of $0.66\,\mu_B$ and an orbital moment of $-1.22\,\mu_B$ and thus the total 5f moment is $-0.56\,\mu_B$. The Co atom has a spin moment of $-0.14\,\mu_B$ and an orbital moment of $-0.06\,\mu_B$, whereas the aluminium atom carries essentially no magnetic moment. Hence the agreement between theory and experiment has improved considerably as compared to the calculations without the orbital polarisation. In particular we obtain a parallel moment for uranium and cobalt. To investigate the influence of the magnitude of E^3 on the above results, we also performed a calculation with E^3 equal to 2.6 mRyd. This value of E^3 reproduces, according to Nugent [14], the atomic 5f data. In contrast to findings in earlier investigations of orbital magnetism in actinide systems, we find that the results of the magnetic properties in UCoAl depend quite strongly on the value of E^3. Hence this value for E^3 gives a total moment of $-0.53\,\mu_B$ (FU)$^{-1}$. The cobalt spin moment is $-0.15\,\mu_B$, whereas the orbital moment is $-0.06\,\mu_B$. For the uranium atom the spin moment now becomes $0.59\,\mu_B$ and the orbital moment $-1.02\,\mu_B$, and its total moment is therefore $-0.43\,\mu_B$. This compares rather well with the experimental values deduced from neutron experiments.

An important probe for magnetic moments in solid systems is neutron scattering. Very recently a thorough investigation of the magnetic properties of UCoAl was performed, using this method [13]. In order to make a theoretical comparison with the data we have calculated the form factor from our self-consistent results. The calculation of the magnetic form factor was performed within the dipole approximation [16].

$$f(Q) = \langle J_0 \rangle + C_2 \langle J_2 \rangle. \tag{6}$$

Here $\langle J_n \rangle$ is the average of the spherical Bessel function J_n. Furthermore, $Q = 4\pi \sin\theta / \lambda$ is the momentum transfer and C_2 is the ratio between the orbital moment and the total moment, μ_{orb}/μ. Since the neutron scattering experiments measure the 5f contribution to the uranium moment, we have used the 5f partial moments for the calculation of C_2 in (6). From our calculations we get a C_2-value of 2.2, to be compared to an experimentally determined value of 2.5. The calculated uranium form factor (6) is shown in figure 4. Unfortunately we cannot at present compare this form factor with the experimental one.
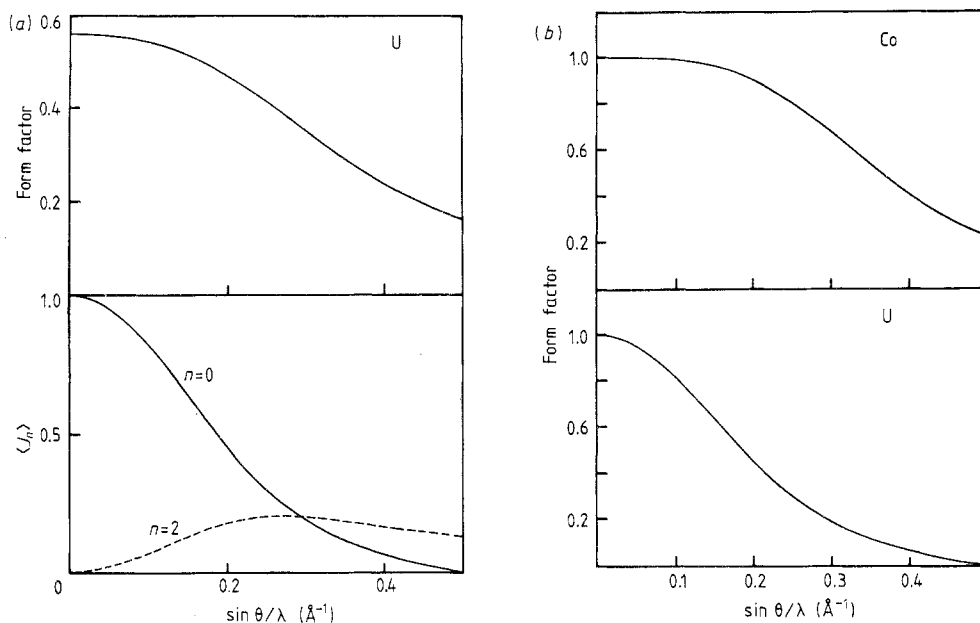
Figure 4. (*a*) Calculated magnetic form factor times the magnetic moment for the uranium atom in UCoAl (upper panel) and calculated spin density averages over spherical Bessel functions (lower panel). (*b*) Calculated magnetic form factor for the uranium and cobalt atoms in UCoAl. The spin density was obtained here from the scalar relativistic calculation without the spin–orbit interaction.

The large influence of the $\langle J_2 \rangle$ term is obvious, as can be seen from the lower part of figure 4(*a*). To illustrate the influence of the orbital contribution further we show in figure 4(*b*) the rather different shape of the form factor obtained from the scalar relativistic calculations without the spin–orbit interaction. This difference has become an almost classical characteristic of the magnetic form factors in uranium systems.

In conclusion, we have shown that the complex magnetic behaviour of the hexagonal UCoAl compound can be described as a delocalised 5f electron system with a para-magnetic ground state and a meta-magnetic state at higher energies. The meta-magnetic state was found to have a magnetic moment that compares rather well with magnetisation and neutron scattering experiments. We find from our calculations that the magnetism is dominated by a large orbital part, which is larger in magnitude and anti-parallel to the spin moment on the uranium atom. A complete theoretical account of this could, however, only be achieved by the inclusion of all three of Hund's rules (exchange splitting, orbital splitting and spin–orbit interaction). We also obtain the result that the magnetic form factor of the uranium atom is characterised by a large influence from the orbital magnetic moment. This can, for example, be seen from the relatively high value of the parameter C_2, which we calculate to be 2.2. In agreement with experiment, we calculate that the uranium and cobalt moments are parallel and conclude that the cobalt moment is very small in this system, much smaller than one normally finds in magnetic Co compounds. The reason for this is that the Co 3d band is almost filled in UCoAl, which only allows a small moment. This high filling of the 3d band is due to the strong hybridisation with the uranium 5f states. The size of the calculated Co moment is also in agreement with experiment, as is our finding of a negligible moment on the Al site.

References

[1] Sechovský V, Havela L, de Boer F R, Franse J J M, Veenhuizen P A, Sebet J, Stehno J and Andreev A V 1986 *Physica* B **142** 283

Sechovský V, Havela L, Pillmayr N, Hilscher G and Andreev A V 1984 *J. Magn. Magn. Mater.* **63 + 64** 99

Havela L, Sechovský V, de Boer F R, Brück E, Veenhuizen P A, Bouwer J B and Bushow K H J 1988 *J. Magn. Magn. Mater.* **76 + 77** 89

[2] Hill H H 1970 *Plutonium 1970 and Other Actinides* ed. W N Miner (New York: The Metallurgical Society of the AIME) p 2

[3] Brooks M S S and Kelly P J 1983 *Phys. Rev. Lett.* **51** 1708

[4] Andersen O K 1975 *Phys. Rev.* B **12** 3060

Skriver H L 1984 *The LMTO Method* (Berlin: Springer)

[5] Jepsen O and Andersen O K 1971 *Solid State Commun,* **1** 1763

[6] von Barth U and Hedin L. 1972 *J. Phys. C: Solid State Phys.* **5** 1629

[7] Williams A R, Moruzzi V L, Kübler J and Schwarz K 1984 *Bull. Am. Phys. Soc.* **29** 278

Schwarz K and Mohn P 1984 *J. Phys. F: Met. Phys.* **14** L129

[8] Brooks M S S and Glötzel D 1980 *Physica* B **102** 51; 1980 *J. Magn. Magn. Mater.* **15–18** 873

Koelling D D, Dunlap B D and Crabtree G W 1984 *Phys. Rev.* B **31** 4966

Albers R C 1985 *Phys. Rev.* B **32** 7646

[9] Andersen O K, Skriver H L, Nohl H and Johansson B 1979 *Pure Appl. Chem.* **52** 93

[10] Vosko S H and Perdew J P 1975 *Can. J. Phys.* **53** 1385

Janak J F 1977 *Phys. Rev.* B **16** 255

Brooks M S S, Eriksson O and Johansson B 1987 *Phys. Scr.* **35** 52

[11] Cyrot M, Gignoux D, Givord F and Lavagna M 1979 *J. Physique Coll.* **40** C5 171

[12] Wulff M and Delapalme A 1989 private communication

[13] Eriksson O, Johansson B and Brooks M S S 1989 unpublished

[14] Nugent L J 1970 *J. Inorg. Nucl. Chem.* **32** 3485

[15] Racah G 1942 *Phys. Rev.* **62** 438; 1943 **63** 367

[16] Marshall W and Lovesey S W 1971 *Theory of Thermal Neutron Scattering* (Oxford: OUP)