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## Theory of orbital splittings applied to $\text{NpAl}_2$

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**Abstract.** We report on spin polarised energy band calculations for the cubic Laves phase compound  $\text{NpAl}_2$ . The calculations were performed within the local spin density formalism, with a correction that takes into account the different intra-atomic Coulomb interactions for states with different azimuthal quantum numbers. The spin–orbit interaction was included in the band Hamiltonian and thus the parameter-free calculations took into account Hund’s first, second and third rules. A description of the formalism is presented and it is found that only when treating all of Hund’s rules simultaneously do we obtain good agreement between the theoretical and experimental magnetic moments. A prediction of the magnetic form factor is also presented. It is found that the cohesive properties are strongly affected when introducing the orbital polarisation, and only when doing this do the theoretical and experimental volumes compare well.

### 1. Introduction

The local spin density (LSD) approximation has proven to be very accurate in determining magnetic structures and magnetic moments for a vast range of materials [1]. However, for heavy elements (i.e. actinides) normal spin polarised band calculations often do not give the correct magnetic moments, although they usually yield the nature of the ground state (para- or ferromagnetic) in agreement with experimental data. The main reason for this disagreement between theory and experiment lies in the orbital contribution to the magnetism. It has been shown that for uranium compounds the orbital moment accompanying the spin moment can be computed by including the spin–orbit interaction in the band Hamiltonian [2]. In most of the uranium systems studied to date it seems that with the inclusion of spin–orbit interaction in the calculations, a large part of the orbital moment can be accounted for [3, 4], but it has become clear to us that this approach sometimes underestimates the magnitude of the orbital contribution to the magnetic moment [5]. This deficiency becomes even more pronounced for the neptunium and plutonium systems [6].

We have recently suggested [7] that, particularly in narrow band materials with large spin–orbit coupling, the normal local spin density approximation is inadequate, since it leaves out those parts of the electron–electron interaction that lead to Hund’s second

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rule—namely, a coupling between the orbital moments. Furthermore we have suggested how the residual interactions may be approximately included in an extended Stoner-like theory, by splitting the eigenvalues corresponding to orbital quantum number. Such corrections have been shown to enhance the orbital moment [5–7].

In order to investigate the proposed corrections further we have performed calculations allowing for this 5f orbital polarisation for the cubic Laves phase compound  $\text{NpAl}_2$ . The reason we have chosen this system is that the magnetism of this compound has been thoroughly investigated experimentally and is anomalous.

It is found experimentally that the cubic Laves phase compound  $\text{NpAl}_2$  (lattice constant = 7.764 Å, which is larger than the Hill limit [8]) orders ferromagnetically below 56 K [9]. From magnetisation measurements it has been found that the total moment per Np atom is  $1.2 \mu_B$  [9]. Neutron diffraction and Mössbauer measurements gave, on the other hand, a moment at the Np site of  $1.5 \mu_B$  and from this it was suggested that the conduction electron polarisation was  $0.3 \mu_B$  per Np atom coupled anti-parallel to the Np 5f moment [9]. The Curie temperature and the hyperfine field were measured as a function of pressure up to 40 kbar [10]. Since the hyperfine field showed a quite strong change with pressure it was argued that the 5f electrons on the Np atom are only partially localised.

A detailed investigation of the electronic structure of  $\text{NpAl}_2$  in the paramagnetic phase has been reported earlier in connection with a general description of the  $\text{AnAl}_2$  Laves phase systems. (An = U, Np and Pu) [11]. Here it was noted that the electronic structure of all these systems is dominated by a narrow 5f band pinned at the Fermi level ( $E_F$ ). It was also stressed that the trend in the behaviour of the magnetic properties is anomalous since  $\text{UAl}_2$  is a spin-fluctuating material and  $\text{NpAl}_2$  orders ferromagnetically, whereas  $\text{PuAl}_2$ , contrary to intuitive ideas about magnetism throughout the actinide series, does not order magnetically.

## 2. The orbital splitting

We have shown earlier [7] that adding a term  $-E^3 L^2/2$  to the total energy of the spin polarised atom corresponds to a mean field correction of the intra-atomic Coulomb interaction. Here  $L$  is the total orbital moment of the 5f electrons of a given spin, and  $E^3$  is the  $E$  Racah parameter [12]. This energy term takes into account the different Coulomb repulsions between 5f electrons with different azimuthal quantum numbers  $m_1$ , and is hence an implementation of Hund's second rule in a band calculation. This gives rise to an extra contribution to the single-electron eigenvalue for a 5f electron in the  $m_1$  state of form  $-E^3 L m_1$ .

We have performed calculations with this correction together with the LSD approximation to the spin potential [13]. The spin-orbit interaction was also included in the band Hamiltonian [2] and thus the parameter-free calculation includes Hund's first, second and third rules.

The energy bands were calculated using the linear muffin tin orbital (LMTO) technique with the combined correction terms [14]. The density of states (DOS) was then calculated from these energy bands by using the analytical tetrahedron method [15]. We used the frozen core approximation and the valence charge density was converged to one part in 1000.

### 3. Results

We first made a normal scalar relativistic band calculation and from this we calculated the Stoner product [16] to be 2.7. Since this is larger than one, we predict  $\text{NpAl}_2$  to have a ferromagnetic state with lower energy than the paramagnetic one, and when in our treatment we allow for different potentials for the different spin directions a finite moment develops. The magnitude of the total self-consistent spin moments is  $3.94 \mu_{\text{B}}/\text{FU}$  (FU  $\equiv$  formula unit) and is essentially composed of an Np f moment ( $3.56 \mu_{\text{B}}$ ) and an Np d moment ( $0.25 \mu_{\text{B}}$ ). We then included the spin-orbit splitting in the band Hamiltonian [2], and the total spin moment from this calculation is  $3.60 \mu_{\text{B}}/\text{FU}$ . Here the spin moment is composed of an Np f moment of magnitude  $3.28 \mu_{\text{B}}$  and an Np d moment of magnitude  $0.21 \mu_{\text{B}}$ . The calculated orbital moment of the Np atom is  $-3.00 \mu_{\text{B}}$ , and the total Np 5f moment is thus  $0.28 \mu_{\text{B}}$ . The results from both these calculations compare very badly with the reported experimental values.

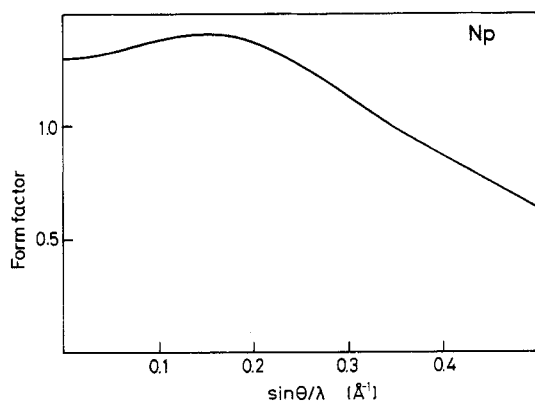
When we include Hund's second rule, as described in § 2, the orbital 5f moment increases in magnitude to a value of  $-4.5 \mu_{\text{B}}$ . The spin moment changes only marginally and we calculate it to be  $3.5 \mu_{\text{B}}/\text{FU}$ . Thus we calculate the total moment to be  $-1.0 \mu_{\text{B}}/\text{FU}$  in fair agreement with the experimental data. The Np f spin moment is  $3.2 \mu_{\text{B}}$  and the total 5f moment is thus  $-1.3 \mu_{\text{B}}$ ; this also compares quite well with the experiments. We find that the conduction electron polarisation reduces the total moment by about  $0.3 \mu_{\text{B}}/\text{FU}$ , which agrees with the difference between the moment derived from the neutron experiment and the moment from magnetisation measurements. We also find that this negative conduction electron spin splitting is mainly of 6d character. The reason for the anti-parallel coupling of the conduction electron polarisation to the total moment can be understood as follows. The 5f-6d exchange interaction produces parallel 5f and 6d spin moments. However, since we are dealing with a less than half-filled shell, the 5f spin and orbital moments are anti-parallel and since the orbital moment is larger in magnitude than the spin moment, the anti-parallel 6d spin polarisation follows.

Neutron scattering experiments are often used to monitor the f partial moments and we have computed the form factor from our self-consistent results using the dipole approximation [17]

$$f(Q) = \langle j_0 \rangle + C_2 \langle j_2 \rangle. \quad (1)$$

Here  $Q = 4\pi \sin \theta/\lambda$  is the momentum transfer and  $\langle j_n \rangle$  are averages of spherical Bessel functions of the spin density.  $C_2$  is calculated from the ratio of the orbital and total moment, i.e.  $C_2 = \mu^{\text{orbital}}/\mu$ . Since the neutron experiments are expected to resolve only the 5f contribution to the magnetic moment, we calculated the value of  $C_2$  from the Np 5f partial moments. The form factor (figure 1) is characterised by a maximum at  $\sin \theta/\lambda$  equal to  $0.18 \text{ \AA}^{-1}$ , with the calculated  $C_2$ -value of 3.5. In a recent series of experiments on the cubic Laves phase compounds  $\text{UFe}_2$  [18] and  $\text{PuFe}_2$  [19], a maximum in the form factor at finite values of the scattering vector  $Q$  has been found. This characteristic maximum arises because the orbital contribution to the moment is larger than, and opposite to, the spin moment. Hence a detailed investigation of the experimental form factor of  $\text{NpAl}_2$  would be valuable in order to investigate to what extent the present formalism can account for such a sensitive probe.

The calculated occupation numbers are summarised in table 1. Here we have also given the total pressure [20] from the two calculations and we note that the effect of spin and orbital splitting reduces the total pressure by about 47 kbar. This reduction in



**Figure 1.** Calculated magnetic Np form factor multiplied by the magnetic moment for  $\text{NpAl}_2$ .

**Table 1.** Self-consistently calculated electronic pressures and occupation numbers for  $\text{NpAl}_2$ , both from the paramagnetic calculation (Para) and the calculation including Hund's rules (Full).

	Para	Full
$P$ (kbar)	-78	-31
$n_{5f}$	4.16	4.22
<b>Spin up</b>		
$n_{5f}(m_1 = -3)$		0.94
$n_{5f}(m_1 = -2)$		0.91
$n_{5f}(m_1 = -1)$		0.82
$n_{5f}(m_1 = 0)$		0.56
$n_{5f}(m_1 = 1)$		0.33
$n_{5f}(m_1 = 2)$		0.10
$n_{5f}(m_1 = 3)$		0.07
<b>Spin down</b>		
$n_{5f}(m_1 = -3)$		0.04
$n_{5f}(m_1 = -2)$		0.04
$n_{5f}(m_1 = -1)$		0.06
$n_{5f}(m_1 = 0)$		0.09
$n_{5f}(m_1 = 1)$		0.09
$n_{5f}(m_1 = 2)$		0.07
$n_{5f}(m_1 = 3)$		0.10

chemical bonding emanates from loss of the 5f partial pressure. This comes about since magnetism reduces the chemical bonding [21]. In our present calculation for  $\text{NpAl}_2$ , the loss of chemical bonding is even more pronounced since the spin polarised 5f band is also split into its different  $m_1$ -components. This can be understood using an approximate rectangular-shaped 5f DOS and then calculating the pressure from the so-called first-order pressure relation. In this expression one divides the electronic pressure into two

**Table 2.** Self-consistently calculated magnetic moments from a spin polarised (Spin only) and a spin and orbital polarised (Full) calculation, together with the experimentally determined moments (see text). The calculated  $C_2$ -ratio is also given as well as the first-order calculation of the electronic pressure ( $P^{est}$ ) from equation (3) (Spin only) and equation (5) (Full).

	Spin only	Full	Exp
$P^{est}$ (kbar)	-43	-2	0
$\mu_{5f}$ ( $\mu_B$ )	3.56	1.3	1.5
$\mu_{tot}$ ( $\mu_B$ )	3.94	1.0	1.2
$C_2$		3.5	

components, a band-centre term and a band-width term. For 5f electrons it is the band-width term that dominates, and for the paramagnetic case it can be written [22] as

$$(3PV)_W = 3.5 W n_f (n_f / 14 - 1). \quad (2)$$

Here  $W$  is the 5f band width and  $n_f$  is the occupation number for the 5f electrons. For 5f states this term is negative (bonding), except when  $n_f$  is 0 or 14 giving  $(3PV)_W = 0$ . When the 5f band is spin polarised with a moment  $m_s$  ( $m_s = n_f^\uparrow - n_f^\downarrow$ ), equation (2) becomes [22]

$$\begin{aligned} (3PV)_W^{spin} &= (3PV)_W^\uparrow + (3PV)_W^\downarrow = 3.5W [n_f^\uparrow (n_f^\uparrow / 7 - 1) + n_f^\downarrow (n_f^\downarrow / 7 - 1)] \\ &= (3PV)_W [1 - m_s^2 / n_f (14 - n_f)]. \end{aligned} \quad (3)$$

Here  $(3PV)_W^\uparrow$  ( $(3PV)_W^\downarrow$ ) is the contribution to the electronic pressure from the spin up (down) electrons. When the system has orbital polarisation as well as spin polarisation we can similarly divide the electronic pressure further:

$$\begin{aligned} (3PV)_W^{orb} &= \sum_{m=-3}^3 (3PV)_W^{\uparrow,m} + \sum_{m=-3}^3 (3PV)_W^{\downarrow,m} = 3.5W \sum_{m=-3}^3 n_m^\uparrow (n_m^\uparrow - 1) \\ &\quad + 3.5W \sum_{m=-3}^3 n_m^\downarrow (n_m^\downarrow - 1) \end{aligned} \quad (4)$$

where  $n_m^\uparrow$  ( $n_m^\downarrow$ ) is the occupation number for the spin up (down) states with orbital character  $m$ . However, since from (3)  $3.5W = (3PV)_W^\uparrow / n_f^\uparrow (n_f^\uparrow / 7 - 1)$  we can simplify (4) to

$$(3PV)_W^{orb} = \frac{(3PV)_W^\uparrow}{n_f^\uparrow (1 - n_f^\uparrow / 7)} \sum_{m=-3}^3 n_m^\uparrow (1 - n_m^\uparrow) + \frac{(3PV)_W^\downarrow}{n_f^\downarrow (1 - n_f^\downarrow / 7)} \sum_{m=-3}^3 n_m^\downarrow (1 - n_m^\downarrow). \quad (5)$$

Inserting the numbers in table 1 into equation (3) gives a reduction in 5f pressure of 36 kbar due to the spin splitting. Using equation (5) gives a further reduction of the pressure by 40 kbar due to the orbital splitting. The total pressures from equations (3) to (5) are given in table 2 (together with our calculated total moments) and are found to compare quite well with the pressure from the full pressure formula [20] (table 1).

#### 4. Conclusion

We have shown that by taking into account all three Hund's rules we can describe the magnetic moments in  $\text{NpAl}_2$  accurately. The inclusion of the orbital polarisation and the spin-orbit coupling, in addition to the spin polarisation, does indeed seem to be crucial for the understanding of ground state properties in this compound. This inclusion is for instance much more important than using the combined correction terms [14]. In fact the calculations presented here were first iterated to self-consistency without the combined correction terms, and after that were converged with them. No major changes were observed between these two calculations. When including all of Hund's rules into the description of the electronic states of  $\text{NpAl}_2$  we get a quite good agreement between experiment and theory. We also predict from this calculation that the magnetic form factor of  $\text{NpAl}_2$  is characterised by a maximum for  $\sin \theta/\lambda$  equal to  $0.18 \text{ \AA}^{-1}$ . An experimental investigation of this maximum would be an excellent test of the present theory. The calculated total electronic pressure from this calculation is negative but small ( $-31 \text{ kbar}$ ) and shows that if an equation-of-state calculation had been performed we would obtain a lattice constant in good agreement with experimental values. This was not done in the present work since it would require self-consistent band calculations at several lattice parameters which for this system would be very time consuming. The dramatic reduction, when we include the orbital splitting, of the electronic pressure is due to the fact that the filling of each of the  $m_1$  sub-bands is almost complete and thus the 5f contribution to the bonding is reduced dramatically as compared with the results of the calculations for the para- or ferromagnetic (spin only) ground states. The reduction is not complete, however, leaving a small bonding 5f pressure in the system. From the calculation of the electronic structure we note that there is a small Np 5f mixing of the states at the Fermi level ( $E_F$ ). Hence this implies that the Np 5f electrons to a large extent have local character, but that there remains some Np 5f character of the states at  $E_F$  due to hybridisation with the conduction electrons.

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