The magnetic moment reduction of fullerene encapsulated gadolinium. A combined effect of spin-orbit interaction and anisotropic hybridisation

Gd moment reduction in fullerene

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Abstract. We propose a theoretical model to account for the recently observed magnetic moment reduction of gadolinium in fullerenes. While this reduction has been observed also for other trivalent rare-earth atoms (Dy^{3+}, Er^{3+}, Ho^{3+}) in fullerenes, and can be ascribed to crystal field effects, the explanation of this phenomena for Gd^{3+} is not straightforward due to the spherical nature of its ground state ($S = 7/2$, $L = 0$). In our model the momentum reduction is the result of a subtle interplay between hybridisation and the spin-orbit interaction.

PACS. 71.20.Tx Fullerenes and related materials; intercalation compounds – 73.22.-f Electronic structure of nanoscale materials: clusters, nanoparticles, nanotubes, and nanocrystals – 75.75.+a Magnetic properties of nanostructures

1 Introduction

Endohedral metallofullerenes $M@C_{82}$ are novel materials that have attracted a wide interest in physics, chemistry and in material or biological sciences for the large variety of promising applications of their peculiar properties [1–3]. In endohedral metallofullerenes, a positively charged core metal is off-centre in a negatively charged carbon cage, resulting in strong metal-cage interaction and intrafullerene charge transfer from the metal to the cage [1,4–6].

The magnetism of these systems is mainly due to the spin of the entrapped metals. In a series of average magnetisation measurements a paramagnetic behaviour has been observed [7–10], with negative Weiss temperatures. The negative Weiss temperature indicates the presence of a weak antiferromagnetic interaction between the cage and the metal, and between neighbouring cages. However, for heavy rare-earths (RE) endofullerenes [10], ferromagnetic coupling has been mentioned in the sub-20 K range. In the case of heavy RE, these experiments gave a smaller number of magnetons per encaged ion than for the free ion. This result has been phenomenologically ascribed to the cage crystal field interaction for high L ions and, for the $L = 0$ Gd case, to the antiferromagnetic interaction between the ion and the cage.

In a recent work [11], the local magnetic properties of heavy RE metallo centres have been characterised us-

ing X-ray magnetic circular dichroism and (XMCD) X-ray absorption spectroscopy (XAS) at the M_4 and M_5 resonances ($3d \rightarrow 4f$ transitions). The absorption spectra in this study were accurately fitted assuming trivalent ions ($4f^n$ electronic structure with $n = 7$ for Gd, $n = 9$ for Dy...) and XMCD confirmed that there is a strong reduction of the measured ion magnetisation compared to the free ion case.

For $L \neq 0$ ions the reduction was reproduced by a model Hamiltonian where a weak crystal field prevents the ion total angular moment J from aligning completely along the magnetic field. The $L = 0$ ion of trivalent gadolinium was more difficult and the hybridisation model did not give a satisfactory explanation.

In fact, although hybridisation gives antiferromagnetic coupling with the cage and accounts (in the Gd case) for a 14% reduction of the average moment (Gd plus cages), it cannot explain the reduction of the moment localised on the Gd ion (see next section).

We show in the present paper that the combined action of hybridisation and spin-orbit interaction can have a dramatic effect on the observed magnetic moment.

In our model the Gd ground state is basically $4f^7$ with a $4f^7 5d^1$ component and a smaller $4f^8$ one. The latter two components are due to electron backdonation from the cage. The cage orbitals backdonation is determined by the location of the gadolinium with respect to the cage. The encaged Gd ion at equilibrium is displaced off centre, and

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stands, inside the cage, at a position adjacent to a C=C$_\pi$ double bond [12]. The C=C$_\pi$ bond electrons are partly donated to the gadolinium 5d orbitals and, to a minor extent, to the 4f shell. Another source of backdonation comes from the electrons close to the Fermi energy that populate the C=C$_\pi^*$ antibonding orbitals. These orbitals are not empty because the cage is negatively charged.

This hybridisation of the C=C$_\pi$ bond with 5d is no doubt the main cause of the Gd-cage bond but for the study of the magnetic effects we consider both contributions, the one from C=C$_\pi$ and that from the C=C$_\pi^*$ antibonding orbital.

In Section 2 we consider the effect of spin-orbit interactions on the bond resulting from hybridisation between C=C$_\pi$, 5d and 4f orbitals (the Gd-cage bond). In Section 3 we consider the hopping of the unpaired cage electron on the Gd ion. In both Sections 2 and 3 we use an effective Hamiltonian on a model space obtained by applying partitioning techniques which are discussed in Section 2. In both cases we obtain a non-negligeable splitting of the Gd energy levels as a function of Gd magnetic moment projection along the Gd-cage bond axis. The splitting is calculated by our analytical formula in Sections 2 and 3 and its origin is discussed qualitatively in Section 4.

The effect of this splitting on the magnetic properties is calculated using a realistic set of parameters, and is compared to experiments in Section 5 where we explain the Gd moment reduction and anomalies in the low temperature magnetisation profiles [10] that had not been understood so far.

2 Hybridisation model and spin-orbit for the C=C$_\pi$ hybridised orbital

In the following discussion we denote the angular momentum quantisation axis by z and define it to be parallel to the displacement axis passing through the cage centre and the Gd position. The Hamiltonian that we use for the treatment of the C=C$_\pi$ hybridised orbital is:

$$
\begin{aligned}
H = H_{\text{Gd}} &+ t_d \sum_\sigma (d_\sigma^+ c_\sigma + c_\sigma^+ d_\sigma) \\
&+ t_f \sum_\sigma (f_\sigma^+ c_\sigma + c_\sigma^+ f_\sigma) - J_p(c_\sigma^+ u_\sigma + u_\sigma^+ c_\sigma). \quad (1)
\end{aligned}
$$

In this equation σ represents the electron spin, d is the annihilation operator for an electron in the 5d orbital with $3z^2 - r^2$ symmetry (which is the orbital with the strongest hybridisation), f annihilates the electrons in the 4f shell with $5z^3 - 3z$ symmetry, c^+ creates an electron in the C=C$_\pi$ bonding orbital and u is the operator for the unpaired electron. The hopping strengths are given by parameters t_d and t_f while J_p is the exchange between the unpaired orbital and the C=C$_\pi$ one. Finally H_{Gd} is the Hamiltonian of an isolated Gd ion.

A non-perturbative solution for our Hamiltonian can be obtained in a concise form using partitioning techniques. Good descriptions of this technique can be found

in the literature [13]. First we divide the full Hilbert space into a model space and the remaining space, then we define the effective Hamiltonian acting in the model space. Our model space is formed by all the states in which the gadolinium has a $4f^7 5d^0$ configuration, the C=C$_\pi$ bonding orbital is full, and one unpaired electron is in the u orbital. The remaining space is formed by all the states in which the gadolinium has a $4f^7 5d^1$ or $4f^8$ configuration, the C=C$_\pi$ bonding orbital has one electron, and one unpaired electron is in the u orbital. Denoting by P the projector on the model space and by Q the projector on the remaining space, the effective Hamiltonian H_{eff} is written [13]:

$$
H_{eff} = PHP + PHQ \frac{1}{E - QHQ} QHP \quad (2)
$$

where E is the eigenenergy of the eigenstate. In this formula, with our definition of the model space, the hopping terms are isolated in PHQ and QHP, while the atomic interactions H_{Gd} and the J_p exchange term are isolated in PHP and QHQ. Switching off the hopping causes the ground state of the Hamiltonian to become the ground state of PHP which is the ground state of a free Gd ion with a $4f^7$ configuration plus an unpaired electron on the cage. The ground state of the $4f^7$ configuration is characterised by a total spin $S^{f^7} = 7/2$ and an angular moment $L = 0$. Without hybridisation the ground state of the system, considering also the unpaired electron, has a degeneracy of 16. If we switch on the hopping, the QHP and PHQ terms are no longer zero and degeneracy is removed. We can neglect the H_{eff} terms connecting the ground state of $4f^7$ to other excited states of the $4f^7$ configuration because of the strong gap due to the exchange interaction between $4f$ electrons. Within this approximation our model space is simply the degenerate ground-space. Another important simplification is made by considering that equation (1) has rotational symmetry around the z axis and, thanks to angular moment conservation, we are left with a two-dimensional model space which is spanned by the two states $|S_z^{f^7}, \sigma\rangle$ and $|S_z^{f^7} + 2\sigma, -\sigma\rangle$ where S_z, in the expression $|S_z^{f^7}, \sigma\rangle$, is the $4f^7$ spin z component and σ is the spin of the unpaired electron. The matrix elements of H_{eff} between two states a and b of the model space can be calculated with a summation over the eigenstates of QHQ

$$
\langle a|H_{eff}|b\rangle = \sum_n \langle a|H|n\rangle \frac{1}{E - \langle n|H|n\rangle} \langle n|H|b\rangle \quad (3)
$$

where $|n\rangle$ are eigenstates of QHQ and belong to the remaining space. The term $\langle a|PHP|a\rangle$, being a constant, has been removed. The sum can be split in two by dividing the remaining space in two subspaces which block-diagonalise QHQ: one with the gadolinium in its $4f^7 5d^1$ configuration and another with the Gd in its $4f^8$ configuration. We write:

$$
H_{eff} = t_d^2 H_{eff}^{f^7 d^1} + G^2 t_f^2 H_{eff}^{f^8}. \quad (4)
$$

In this equation the $H_{eff}^{f^7 d^1}$ term is obtained from equation (3) restraining the sum over $|n\rangle$ to the $4f^7 5d^1$

subspace and, analogously, the $H_{eff}^{f^8}$ term is obtained by summing only over the f^8 subspace. The factor G, appearing in the the $H_{eff}^{f^8}$ term, will be discussed in detail later, but we anticipate now that its value is $\sqrt{8/7}$ and has been abstracted out to allow writing, in the rest of the paper, the same analytical formula for both $H_{eff}^{f^8}$ and $H_{eff}^{f^7d^1}$.

The complete expression for $H_{eff}^{f^7d^1}$ and $H_{eff}^{f^8}$ requires writing the complete set of eigenstates of the remaining subspaces in terms of a complete set of commuting observables (CSCO).

As the QHQ operator does not correlate cage variables with Gd ion ones, the CSCO is the union of the CSCO for an isolated ion and the CSCO for the cage.

The cage is characterised, in the remaining space (which is obtained by moving one electron from the bonding orbital to the gadolinium), by the total spin moment S^{cage} and by S_z^{cage}. These result from the coupling of the unpaired electron spin with the spin of the electron left on the C=C$_\pi$ orbital.

The ion is characterised, in SL coupling by S, L, J and J_z. For the $4f^7 5d^1$ configuration S may take the values 3 and 4, L the value 2 and J the values from $S - L$ up to $S + L$. For the $4f^8$ configuration S may take the value 3, L the value 3 and J the values from 0 up to 6. The $4f^7 d^1$ configuration is obtained adding a d electron with $m_z = 0$ ($3z^2 - r^2$ orbital) to the $4f^7$ ground state:

$$d_{0\sigma}^+ |4f^7 S^f S_z^f\rangle =$$
$$\sum_{S,L=2,J,Jz} |4f^7 5d^1 SLJJ_z\rangle C(S^f, 1/2, S_z^f, \sigma; S, S_z^f + \sigma)$$
$$C(S, L, S_z^f + \sigma, 0; J, J_z) \quad (5)$$

in this equation the symbols C are the Clebsch-Gordan coefficients. The expression for the $4f^8$ states is analogous, but the sum over S is fixed to $S = 3$, and, due to the equivalence of $4f$ electrons, a parentage coefficient appears [14–16]:

$$f_{0\sigma}^+ |4f^7 S^f S_z^f\rangle =$$
$$-\sqrt{8} \sum_{S=3,L=3,J,Jz} G_{S^f L f}^{SL} |4f^8 SLJJ_z\rangle$$
$$C(S^f, 1/2, S_z^f, \sigma; S, S_z^f + \sigma) C(S, L, S_z^f + \sigma, 0; J, J_z) \quad (6)$$

where $G_{S^f L f}^{SL} = 1/\sqrt{7}$. We have factored out $\sqrt{8/7}$ in equation (3) and we can now write the same analytical expressions H_{eff}^{conf} for $H_{eff}^{f^7d^1}$ and $H_{eff}^{f^8}$. These expressions are, for the diagonal elements:

$$H_{eff}^{conf}(S_z^f, \sigma \to S_z^f, \sigma) =$$
$$\sum_S \sum_J \frac{F1(S, J, S_z^f, \sigma)}{E - \Delta^{conf} - E^{conf}(S, J) - E_{cage}(1)}$$
$$+ \sum_S \sum_J \sum_{S^{cage}} \frac{F2(S, J, S_z^f, \sigma)}{2(E - \Delta^{conf} - E^{conf}(S, J) - E_{cage}(S^{cage}))}$$
$$(7)$$

where

$$F1(S, J, S_z^f, \sigma) = C(S^f, 1/2, S_z^f, -\sigma; S, S_z^f - \sigma)^2$$
$$\times C(S, L^{conf}, S_z^f - \sigma, 0; J, S_z^f - \sigma)^2$$
$$F2(S, J, S_z^f, \sigma) = C(S^f, 1/2, S_z^f, +\sigma; S, S_z^f + \sigma)^2$$
$$\times C(S, L^{conf}, S_z^f + \sigma, 0; J, S_z^f + \sigma)^2.$$

In equation (7) E is an eigenvalue, L^{conf} takes the value 2 for $f^7 d^1$, and value 3 for f^8. The symbol Δ^{conf} is defined as the difference between the energy of the system having Gd in a configuration $conf$ with quantum numbers S, L^{conf}, having one electron less on the cage, and the energy of the configuration f^8 in absence of hopping, spin-orbit coupling and cage electron exchange. The energy corrections for intra-atomic interactions and for cage electron exchange are represented by $E^{conf}(S, J)$ and $E_{cage}(S^{cage})$ respectively.

In a similar manner the off-diagonal interaction terms are calculated:

$$H_{eff}^{conf}(S_z^f, \sigma \to S_z^f + 2\sigma, -\sigma) = \sum_S \sum_J \sum_{S^{cage}} (-1)^{S^{cage}}$$
$$\times C(S^f, 1/2, S_z^f, \sigma; S, S_z^f + \sigma)$$
$$\times C(S^f, 1/2, S_z^f + 2\sigma, -\sigma; S, S_z^f + \sigma)$$
$$\times \frac{C(S, L^{conf}, S_z^f + \sigma, 0; J, S_z^f + \sigma)^2}{2(E - \Delta^{conf} - E^{conf}(S, J) - E_{cage}(S^{cage}))}. \quad (8)$$

The effective Hamiltonian described by equations (4, 7, 8) has the following remarkable property: in the limit of zero spin-orbit $E_{conf}(S, J)$ is independent of J and, as a consequence, the matrix describing H_{eff} in the two dimensional space spanned by the two vectors (S_z^f, σ) and $(S_z^f + 2\sigma, -\sigma)$ can be written, after some algebra, in the following form:

$$H_{eff}|_{so=0} = A + \sum_S B_S v_S \otimes v_S \quad (9)$$

where A is a constant, B_S depends on S, and v_S is the versor:

$$v_S = (C(S^f, 1/2, S_z^f, +\sigma; S, S_z^f + \sigma),$$
$$C(S^f, 1/2, S_z^f + 2\sigma, -\sigma; S, S_z^f + \sigma)). \quad (10)$$

This versor represents a state where the Gd spin is coupled with the unpaired electron spin to give a total system spin S. To derive equation (9) from equations (7, 8) we have used the identity

$$C(S^f, 1/2, S_z^f, -s_z; S, S_z^f - s_z)^2 = \frac{1/2 + S}{1/2 + S^f}$$
$$- C(S^f, 1/2, S_z^f, +s_z; S, S_z^f + s_z)^2. \quad (11)$$

In the case of zero spin-orbit coupling we have therefore a system described by the Hamiltonian (9) which has two eigenspaces corresponding to a total spin $S = 3$ (antiferromagnetic coupling with the cage) and $S = 4$ (ferromagnetic coupling with the cage). With some further algebra

Table 1. Dependence of $4f^8$ ground state energies as a function of total moment J. First order formula (first line) is compared to numerical results (second line) obtained using parameters from reference [18]. Units are eV.

	$J = 6$	$J = 5$	...	..	..	..	$J = 0$
Equation (15)	-0.295	-0.098	0.065	0.197	0.295	0.361	0.394
$E_{4f^8}(3, J) - E_{4f^7}$	-0.302	-0.066	0.076	0.189	0.268	0.321	0.346

one can show that for positive J_p (cage electron exchange in Eq. (1)), and considering $t_d \gg t_f$, one has $B_3 < B_4$. The ground state is therefore given by antiferromagnetic coupling with the cage and, for zero spin-orbit coupling, is represented by the versor v_S that can be written explicitly:

$$v = ((7/2 + S_z)^{1/2}, -(7/2 - S_z + 1)^{1/2}) \frac{1}{\sqrt{8}}. \quad (12)$$

The local moment of Gd, in the antiferromagnetic ground state, can be almost fully aligned along the magnetic field. In fact, on the basis of equation (12) one should observe, at saturation

$$\langle S_z^f \rangle = (7/2 \times 7 + 5/2)/8 = 3.375 \quad (13)$$

corresponding to a 3.6% reduction which is very much less than the 20% reduction of the local magnetic moment observed with XMCD at the M_4 and M_5 resonances [11]. We deduce that the observed X-ray spectra [11] are a signature of a non-negligible spin-orbit effect. To check the effect of spin-orbit coupling, all we have to do is to switch on the $E^{conf}(S, J)$ term in equations (4),(7) and (8), using a realistic set of parameters for $\Delta^{f^7 d^1}$, Δ^{f^8}, t_d, t_f, J_p and the spin-orbit interactions ζ_{5d} and ζ_{4f}.

2.1 Choice of parameters

The atomic energies $E^{conf}(S, J)$ can be calculated using standard methods [17]. For $4f^7 d^1$ configuration, in LS coupling, they are:

$$E_{4f^7 d^1}(4, J) = -J_{ex} + \zeta_{5d}(J^2 + J - 26)/16 \quad (14)$$
$$E_{4f^7 d^1}(3, J) = J_{ex}/7 + \zeta_{5d}(18 - J^2 - J)/16.$$

We take $\zeta_{5d} = 0.1 eV$, while J_{ex}, which modulates the $4f5d$ interaction given by $-J_{ex}(1 + 4(S_f.S_d)/7)/2$, is $J_{ex} = 0.7$ eV. These coefficients have been calculated using the Cowan's code [18].

The $4f^8$ energies, in LS coupling, are:

$$E^{4f^8}(3, J) = \zeta_{4f} \frac{24 - J(J + 1)}{12} \quad (15)$$

and we take $\zeta_{4f} = 0.1975$ eV [18]. The exact values of $E^{conf}(S, J)$ are very important because the J dependency represents the action of the spin-orbit interaction and breaks the degeneracy in the J_z variable. We have checked numerically , with an atomic multiplet code [18], the validity of expressions (14) and (15). We get a very good agreement for the $4f^7 d^1$ configuration but we found small differences between the formula (15) in LS coupling

and the exact numerical values for a $4f^8$ configuration. We show in Table 1 the comparison between the two sets of energies, one obtained numerically and the other from equation (15). In the following section the numerical set of energies will be used for the $4f^8$ configuration.

The cage energy is expressed as a function of the intra-cage exchange J_p, which enters the following expression for the cage energy:

$$E_{cage}(1) = -J_p \quad (16)$$
$$E_{cage}(0) = J_p. \quad (17)$$

The intra-cage exchange J_p depends on the wavefunction of the unpaired cage electron, which is not known, and we consider values between zero and a maximum given by the atomic value of a $2p_x 2p_y$ exchange that is about 0.8 eV. We show in the next section that the exact value of J_p has only a small influence on the magnetic results

The parameters governing the hopping to the $5d$ orbital are chosen to be $t_d = 2$ eV and $\Delta^{f^7 d^1} = 1$ eV. For the hopping to the $4f$ shell we chose $t_f = 0.4$ eV and $\Delta^{f^8} = 2$ eV. On the basis of these parameters we can already estimate the average number of electrons back-donated to the gadolinium and compare it with ab-initio calculations [12]. To calculate the $5d$ and $4f$ occupancies we can neglect spin-orbit coupling and exchange which influence mainly the magnetic properties. These properties will be studied later. We now write the effective Hamiltonian which accounts for hopping and zero spin-orbit coupling. It is given by equation (9) setting $B = 0$ and retaining only the diagonal A term. More precisely we have:

$$H_{eff}|_{so=0,J_p=0} = t_d^2 \left(\frac{9/8}{E - \Delta^{f^7 d^1} + J_{ex}} \right.$$
$$\left. + \frac{7/8}{E - \Delta^{f^7 d^1} - J_{ex}/7} \right) + t_f^2 \frac{1}{E - \Delta^{f^8}}. \quad (18)$$

To get the fractional back-donated charge, so, we solve the equation $E = H_{eff}|_{so=0,J_p=0}$ and then calculate the derivatives of E as a function of $\Delta^{f^7 d^1}$ and Δ^{f^8} to get the fractions on $5d$ and on $4f$.

Our parameter choice gives 0.44 electrons on $5d$ and a very small amount of 0.005 electrons back-donated to the $4f$ shell. These fractions have to be compared with ab-initio calculations [12] which give 0.48 electrons on $5d$ and 0.02 electrons back-donated to $4f$. We are in good agreement concerning $5d$ electrons but the fraction for $4f$ is four times smaller. In the framework of our model we could not do any better for $4f$ without some unphysical assumptions like $\Delta^{f^7 d^1} > \Delta^{f^8}$ or $t_f \simeq t_d$.
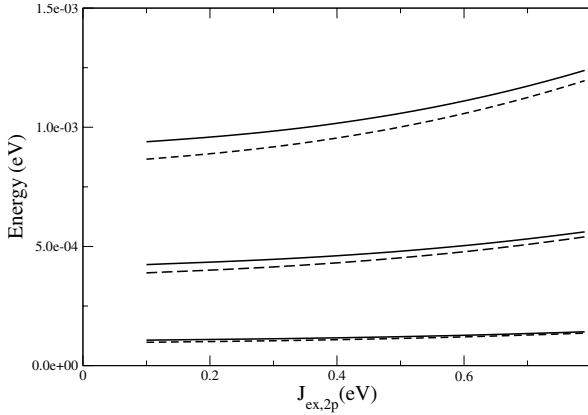
Fig. 1. Energies as a function of intra-cage exchange for S_z between 1 (smallest energy) and 3 (highest energy). The ground state for $S_z = 0$ is taken as the origin of the energy scale. The dashed lines are calculated without any $4f^8$ contribution.

2.2 Numerical results

We diagonalise the effective Hamiltonian (Eq. (4)) in the model space. As explained above H_{eff} can be block-diagonalised on the two-dimensional subspaces spanned by the couples of vectors $(|S_z^{f^7}, \sigma\rangle,\ |S_z^{f^7} + 2\sigma, -\sigma\rangle)$. Each two-dimensional subspace has a definite total spin J_z.

The lowest eigenvalue of each subspace corresponds to antiferromagnetic coupling between the Gd and the cage. Using the set of parameters discussed in the previous section we calculate the antiferromagnetic eigenstates for $J_z = 0$ up to $J_z = 3$ (as a consequence of time reversal the J_z space is degenerate with $-J_z$).

Without spin-orbit coupling all these four eigenstates would be degenerate, but this is not the case with our set of parameters discussed above where the spin-orbit coupling is correctly accounted for. For the magnetic properties of our system, the important quantities are the energy differences between eigenstates $E(S_z)$. We plot in Figure 1 the energy differences $E(S_z) - E(0)$ for $S_z = 1$ up to $S_z = 3$ versus the unknown parameter J_p.

In this figure we show, with solid lines, the energies obtained from the diagonalisation of the equation (4) Hamiltonian using the full set of parameters discussed in the previous section. To check the effect of the $4f^8$ component, we show with dashed lines the energies calculated by setting $t_{4f} = 0$. The lowest lines correspond to $J_z = 1$ and the highest to $J_z = 3$, while the ground state always corresponds to $J_z = 0$. We can see that our model is tolerant with respect to the choice of J_p.

3 Hybridisation model and spin-orbit correction for the unpaired cage electron

We have seen in the previous section that the spin-orbit interaction induces a J_z dependency in the ground state energy. The effect of this J_z dependency on magnetisation

profiles is calculated in the following section and compared with experiment. We have already found, however, a discrepancy between the $4f$ occupancies predicted by equation (18) and those predicted by ab-initio calculations [12]. This discrepancy is an evidence that hopping from orbitals different from the C=C$_\pi$ one need to be taken into account. In this section we consider hopping of the unpaired cage electron onto the $4f$ orbital. The hopping onto the $5d$ orbital could, at first sight, be considered more important. However this is not the case because the $5d$ orbital is already hybridised with C=C$_\pi$ and this raises the energy of the antibonding hybridised $5d$ orbital. The following Hamiltonian matrix, for one hybridised electron, provides numerical insight into this phenomenon. We consider:

$$\begin{bmatrix} E_p & t_{pd} & 0 & 0 \\ t_{pd} & E_d & t_{ud} & 0 \\ 0 & t_{ud} & E_u & 0 \\ 0 & 0 & 0 & E_f \end{bmatrix} \qquad (19)$$

where $E_p < E_d < E_u < E_f$ represent the bare energies of an electron on the C=C$_\pi$ orbital, the $5d$ energy, the bare energy of the unpaired electron orbital and that of the $4f$. As an example we consider $E_p = 0$, $E_d = 1$, $E_u = 1.5$ and $E_f = 2.0$. The hopping between p and d is taken as in the previous section $t_{pd} = 2$ while $t_{ud} = t_{pd}/4$. With this choice of parameters we find that the lowest energy eigen-orbital is the hybridised $5d$-C=C$_\pi$ with $E = -1.6$, but the second lowest has $E = 1.4$ and has a surprisingly strong u character, despite of the high energy of the unpaired electron orbital. At energy $E = 2$, slightly greater than the u orbital, we have the $4f$ orbital, and finally it is at the highest energy $E = 2.7$ that we find the hybridised antibonding $5d$-C=C$_\pi$ orbital. By the way we note that, in such a simple model, the $5d$ spectral weight of the hybridised $5d$ orbital is split into two main components: a bigger one at the upper end of the spectra, corresponding to an empty $5d$ orbital, and a smaller one, which has a predominant C=C character, corresponding to a filled orbital. This explains why resonant photoemission spectroscopy [19] cannot provide spectral evidence of the non-negligeable Gd^{2+} component. Within this simple picture the u orbital maintains its character. If we introduce an hypothetical uf hybridisation term we could effectively couple u to the f orbitals because of the small energy difference. The real system is of course much more complicated than our one particle picture, with complex electron-electron correlations and screenings but we set a limit in order to address the problem with a phenomenological model. We consider the hopping of the unpaired electron to $4f$ orbital by the following Hamiltonian:

$$H = H_{\mathrm{Gd}} + t_{fu} \sum_\sigma (f_\sigma^+ u_\sigma + u_\sigma^+ f_\sigma). \qquad (20)$$

The model is solved with the same partitioning technique that we used in the previous section. After some algebra we get the effective Hamiltonian matrix in the two dimensional subspace

$$H_{eff} = F(S_z) v_{S_z} \otimes v_{S_z} \qquad (21)$$

where

$$F(S_z) = t_{uf}^2 \frac{8}{7} \sum_J \frac{C(3,3,S_z,0;J,S_z)^2}{E - \Delta - E_J^{4f^8}}. \qquad (22)$$

The energy $E_J^{4f^8}$ is the spin-orbit energy of the state $S = 3$, $L = 3$ as a function of J and has been given in the previous section. Our choice of parameters is $\Delta = 0.7$ eV and $t_{uf} = 0.1$ eV. With this choice the energy differences $E(S_z) - E(0)$ for $S_z = 1$ up to $S_z = 3$ are 0.4, 1.5 and 2.8 meV.

4 Qualitative comments on the origin of the splitting

Without hybridisation the ground state of our system is formed by a trivalent Gd^{3+} ion and a negative cage. The ion-cage bond forms because cage electrons, in particular those on the $C=C_\pi$ bond, lower their kinetic energy by delocalising themselves on the Gd ion. The magnitude of this decrease in energy is governed by two factors: the *overlap* between the cage and ion orbitals, and the denominator appearing in equations (7, 8) and (22). Such a denominator is negative because the empty orbitals on the Gd ion are at higher energies than the cage ones. The main contribution in the sums appearing in such equations will be due to the Gd^{2+} ion eigenstates having lower energy. According to whether the cage electron hops to a more than half-filled or less than half-filled Gd shell, the Gd^{2+} lowest state has S parallel or anti-parallel to L. As the hopping brings an electron onto a $m_z = 0$ orbital, the orbital angular moment Gd^{2+} has a zero component along z axis. The lowest energy state spin S, being parallel or antiparallel, will also have a zero z component. This is visible, for example, in the Clebsch-Gordan coefficient $C(3,3,S_z,0;J,S_z)$ of equation (22) which, for $J = 6$ (S parallel to L), takes its largest value for $S_z = 0$.

5 Comparison with experiments

The energy splitting has to be compared with the magnetic field strength. Considering a typical XAS-XMCD experimental case [11] with a 7 Tesla field, the energy gain, obtained by aligning 7 Bohr magnetons from a perpendicular to a parallel direction with the field, is 0.4 meV. This energy is of the same order of magnitude of, or lower, than the splitting caused by hybridisation plus spin-orbit coupling.

This effect can therefore, depending on t and Δ, prevail over the magnetic polarising field and suppress partially, or completely, the magnetisation.

At zero temperature, the magnetisation parallel to the Gd-cage bond, would be a discontinuous function of the magnetising field. For a perpendicular polarising field the magnetisation curve would be instead continuous.

In a real system one should take into account temperature and disorder. Temperature effects would tend to
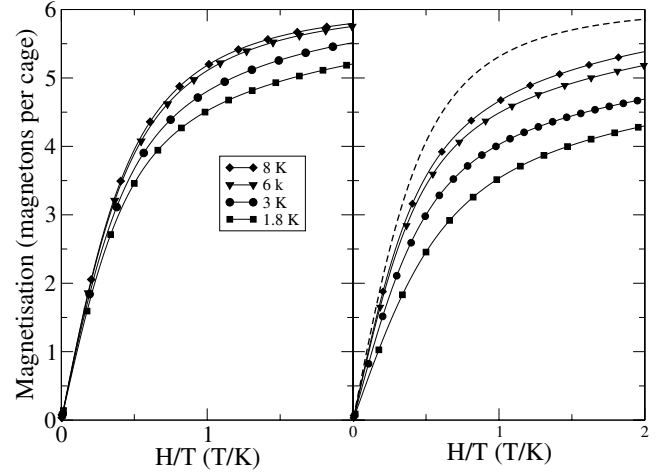
Fig. 2. Magnetisation for temperatures of 1.8, 3, 6 and 8 K. Left side: hybridised $C=C_\pi$ model. Right side: hybridised unpaired electron model. Dashed line: magnetisation curve without spin-orbit coupling.

smear out discontinuities. Any disorder of the gadolinium displacement axis direction in the sample would have a similar effect.

To compare with experiment we have calculated magnetisation curves at different temperatures in the case of a random orientation of the displacement axis. We consider the parameters discussed in the previous section and our analytical formulas. The magnetisation is calculated, for a given orientation of the displacement axis, by writing the Hamiltonian matrix M in the antiferromagnetic subspace of the model space. In the case of a magnetic field parallel to the displacement axis, J_z is still a good quantum number and the energies are $E(J_z) - BJ_z$. In the general case, the interaction with the magnetic field needs to be similarly transformed by rotation matrices:

$$M_{ij} = E(i)\delta(i,j) - B\sum_k R_{ik}^{-1} k R_{kj} \qquad (23)$$

where the indexes i, j, k may take the values from –3 up to 3, representing the possible values of J_z, and R is the representation of rotation in the $J = 3$ space. To calculate the average magnetisation at finite temperature we do a Boltzmann average over the eigenvectors of M, and another average over an uniform distribution of the displacement axis orientation.

The magnetisation is shown in Figure 2 for temperatures of 1.8, 3, 6 and 8 K. The calculations on the left side have been done for the hybridised $C=C_\pi$ model, using the energies $E(S_z)$ calculated using formula (4) and the atomic value of J_p. The calculations on the right side have been done by adding to the energies $E(S_z)$ the energy corrections calculated in the previous section for the hybridised unpaired electron model. We plot also, with a dashed line, the calculated magnetisation for zero spin-orbit coupling. The XMCD experiment [11] corresponds to $H/T = 1$ and a temperature of 7 K. We see in Figure 2 that a strong reduction of the magnetisation compared
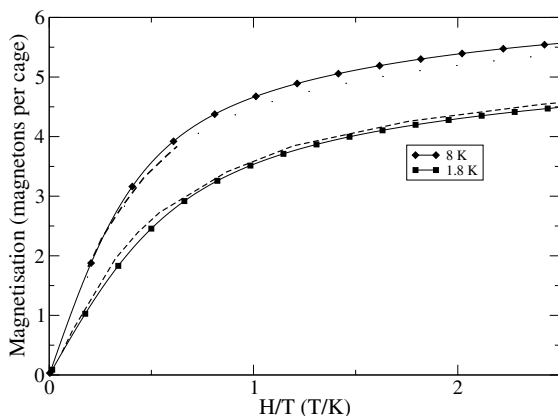
Fig. 3. Comparison with the experiment (dashed line, Ref. [10]) for temperatures of 1.8 and 8 K.

to the dashed line (ideal value), is observed and that it is not far from the 20% one observed with XMCD. The hybridised $C=C_\pi$ model (left graph) under-estimates this reduction. The magnetisation profile of Figure 2 can be compared with Figure 8 of reference [10]. The experimental behaviour is reproduced qualitatively and, quantitatively. Figure 3 shows a comparison of our hybridised unpaired electron model (solid lines) with the experimental magnetic profiles taken by reference [10] (dashed lines). The derivative of $E(S_z)$ with respect to Δ gives the occupancy of the $4f$ orbital due to the hybridised unpaired electron and we get a value of 0.039. Considering that we have also 0.005 electrons due to the hybridised $C=C_\pi$ bond, the predicted $4f$ occupancy is therefore a factor 2 bigger than the one predicted by ab-initio calculations.

6 Conclusions

The highlighted effect can be resumed in the following way: the combined effect of a non-isotropic hybridisation and spin-orbit interaction induces systematically a S_z dependence of the ground state energies of encaged ions. The spin-orbit interaction tends to align S in a parallel or antiparallel direction with respect to L. In our case the gadolinium angular moment component M_z is zero both for the $4f^7$ component and for the Gd^{2+} component due to hopping and, for this reason, the lowest energy has a spin moment $S_z = 0$ which is perpendicular to the hybridisation axis. We have studied, within a model Hamiltonian, this effect using the partitioning technique of the Hilbert space [13] which allows a concise treatment of the problem. We have compared our model to experiments using a realistic set of parameters. These parameters have been determined with an atomic code [18], except for the hybridisation parameters for which a guess has been made trying to respect as much as possible the $5d$ and $4f$ occupancies predicted by ab-initio calculations. We have discovered unexpectedly that, concerning the magnetic properties, it is the weak $4f^8$ component which plays the major role, rather than the stronger $4f^75d^1$ one. Our analytical formulas explain the local moment reduction observed

with XMCD, and the anomalous magnetisation profiles of encaged gadolinium observed at low temperatures. Both these effects had not been fully understood so far.

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