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Structural and Energetic Aspects of Spin Pairing in Lanthanides

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Abstract

Numerical Hartree–Fock calculations on the lanthanide ions confirm the earlier results of Marcantonatos and coworkers, by showing that the excitation from the ground state of a given f^n-configuration to a state with lower spin multiplicity is accompanied by a change in size and shape of the orbitals. This orbital change is also shown to be at the basis of a new interpretation of the spin pairing phenomenon in lanthanides. This interpretation is significantly different from the picture offered by conventional multiplet theory; indeed, the spin pairing energy, calculated on the basis of Hartree–Fock theory is accompanied by a decrease in interelectronic repulsion.

Although the relevant energetic (repulsion) effects are obviously quite large, the underlying size effects are very much smaller. Therefore, it seems highly unlikely that they are responsible for the change in coordination number of $Gd(H_2O)_8{}^{3+}$ upon excitation, as suggested by Marcantonatos.

Introduction

In a series of recent papers [1–3], Marcantonatos and coworkers have argued that ligand field excitation of $Gd(H_2O)_8{}^{3+}$ from its $^8S_0$ ground state to the lowest lying sextet terms, gives rise to the expulsion of two water molecules from the first coordination sphere, thereby producing the hexacoordinated $^*Gd(H_2O)_6^{3+}$ in the excited state.

The authors [2, 3] propose a rationalization of their observations, based on the size difference between the orbitals in the ground state and in the excited state. A number of Xα-calculations are presented in support of this hypothesis.

It is the purpose of the present note: (i) to investigate the relevant orbital sizes at the Hartree–Fock level of approximation; (ii) to extend the calculation to the complete range of the lanthanide series; (iii) to discuss certain energetic and conceptual aspects related to the changes in orbital size; (iv) to discuss the available evidence in favour of a six-coordinated species in the excited state of the Gd^{3+}-aquo-ion.

Conventional Multiplet Theory

The f^n-energy levels of free lanthanide ions are determined by both interelectronic repulsion and spin–orbit coupling interactions [4]. In the present analysis, we will focus our attention exclusively on the interelectronic repulsion effects, and more specifically on the general features of the excitation process from the ground state – always characterized by maximal multiplicity S – to one of the excited states, characterized by multiplicity $S-1$, $S-2$, ... If the quantity $E(S)$ denotes the average energy of all f^n-states with multiplicity S,

$$E(S) = \frac{\sum_L (2L+1)E(L,S)}{\sum_L (2L+1)} \tag{1}$$

then $E(S-1) - E(S)$ measures the average energy required to flip the spin of one electron.

In conventional multiplet theory [5], all levels corresponding to a given f^n-configuration are described by the same set of frozen orbitals, and the energy gap $\Delta E = E(S-1) - E(S)$ is expressed in terms of electron repulsion parameters. We adopt the following notation:

$$E = T + V = T + L + C = H + C$$

where T and V are the kinetic and potential energy components, L the electron–nuclear attraction, C the interelectronic repulsion and H the total one-electron energy. Obviously, in the conventional picture

$$\begin{aligned} \Delta E &= E(S-1) - E(S) = \Delta C = \Delta C_{ff} \\ \Delta L &= \Delta T = \Delta H = \Delta C_c = \Delta C_{cf} = 0 \end{aligned} \tag{2}$$

where C_{ff} is the valence repulsion, within the open f-shell; C_c is the repulsion of the core, and C_{cf} is the core-valence repulsion.

On the basis of first-order perturbation theory, Jϕrgensen [6] and Slater [7] have shown that it is possible to introduce a spin pairing parameter D, so that

$$\Delta E = E(S-1) - E(S) = 2SD \tag{3}$$

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TABLE I. Hartree–Fock Spin Pairing Parameter $D' = \Delta E'/2S$ and its Components for the Tripositive Lanthanide Ions Pr^{3+} to Tm^{3+} (all Energies in cm^{-1}). For Comparison, the Last Column Gives the Values of the Open-shell Repulsion Calculated on the Basis of Conventional Multiplet Theory [8] (Frozen Orbital Set for all Multiplicities): $D = \Delta C_{ff}/2S = \Delta E/2S$

	$S \rightarrow S-1$	$\Delta E'/2S$	$\Delta T'/2S$	$\Delta L'/2S$	$\Delta C'/2S$	$\Delta C'_{ff}/2S$	$\Delta E/2S$
$f^2(Pr^{3+})$	$1 \rightarrow 0$	7367	−7365	55320	−40587	6259	7389
$f^3(Nd^{3+})$	$3/2 \rightarrow 1/2$	7680	−7678	53357	−37999	5645	7668
$f^4(Pm^{3+})$	$2 \rightarrow 1$	7979	−7980	51931	−35972	5100	7936
	$1 \rightarrow 0$	7903	−7907	52634	−36824	4911	7936
$f^5(Sm^{3+})$	$5/2 \rightarrow 3/2$	8265	−8268	50875	−34342	4609	8194
	$3/2 \rightarrow 1/2$	8188	−8184	51527	−35155	4405	8194
$f^6(Eu^{3+})$	$3 \rightarrow 2$	8542	−8541	50088	−33005	4155	8445
	$2 \rightarrow 1$	8464	−8465	50704	−33775	3943	8445
	$1 \rightarrow 0$	8417	−8422	51088	−34249	3814	8445
$f^7(Gd^{3+})$	$7/2 \rightarrow 5/2$	8811	−8812	49515	−31892	3732	8688
	$5/2 \rightarrow 3/2$	8733	−8734	50086	−32619	3515	8688
	$3/2 \rightarrow 1/2$	8681	−8680	50478	−33117	3367	8688
$f^8(Tb^{3+})$	$3 \rightarrow 2$	8996	−8997	49635	−31642	3111	8927
	$2 \rightarrow 1$	8940	−8939	50027	−32148	2951	8927
	$1 \rightarrow 0$	8907	−8905	50267	−32455	2854	8927
$f^9(Dy^{3+})$	$5/2 \rightarrow 3/2$	9195	−9195	49699	−31313	2559	9160
	$3/2 \rightarrow 1/2$	9156	−9158	49968	−31654	2445	9160
$f^{10}(Ho^{3+})$	$2 \rightarrow 1$	9403	−9403	49759	−30953	2058	9389
	$1 \rightarrow 0$	9378	−9374	49925	−31173	1980	9389
$f^{11}(Er^{3+})$	$3/2 \rightarrow 1/2$	9617	−9618	49826	30591	1596	9615
$f^{12}(Tm^{3+})$	$1 \rightarrow 0$	9834	−9849	49925	−30242	1165	9837

Thus for one given f^n-system, it requires $S/(S-1)$ times more energy to induce the transition $S \rightarrow S-1$ than to induce the transition $S-1 \rightarrow S-2$. The spin-pairing parameter D is ion-specific and can in general be expressed as a function of the Slater–Condon F_k (4f; 4f)-parameters [5]:

$$D = \frac{1}{8}(70F_2 + 231F_4 + 2002F_6) \tag{4}$$

The F_k-parameters are positive quantities, and in the framework of conventional multiplet theory, spin pairing is an energy-requiring process because it corresponds to an increase of the valence shell repulsion.

The last column of Table I contains the conventional spin-pairing parameter $D = \Delta E/2S$ for all f^n-systems, as calculated on the basis of a frozen orbital set, and by using a method described elsewhere [8].

Hartree–Fock Calculations

Equation (2) cannot possibly be strictly valid, because they violate the virial theorem, requiring that $\Delta E + \Delta T$ be zero. The latter condition can only be satisfied by abandoning the frozen orbital approximation, and by allowing the orbitals to change their shape from one state to another state. This change of shape (or 'relaxation') of the orbitals obviously induces a difference between the L and T values of two different states.

The best possible orbitals corresponding to any specific situation are obtained from numerical given f^n-configuration are obtained from numerical Hartree–Fock (NHF)-calculations. From previous Hartree–Fock studies on transition metal ions [8] (later confirmed by more exacting calculations [9]), the ΔL and ΔT values can turn out to be quite important, indicating that the shape and size of the orbitals depend to a significant extent on the state under consideration.

The Hartree–Fock equations can be solved for the different spin averages of any given f^n-configuration, thereby corresponding to the energy expression of eqn. (1). We will introduce a prime in order to distinguish the Hartree–Fock results from the conventional results of eqs. (1)–(4).

$$\begin{aligned} E'(S) &= T'(S) + L'(S) + C'(S) \\ \Delta E' &= E'(S-1) - E'(S) = \Delta T' + \Delta L' + \Delta C' \end{aligned} \tag{5}$$

Table I and Fig. 1 show the Hartree–Fock values of $\Delta E'/2S$ and some of its components for the tripositive lanthanide ions. For the different transitions within one single configuration ($S \rightarrow S-1$; $S-1 \rightarrow S-2$; $S-2 \rightarrow S-3$), the values of Table I are quite close to each other; in Fig. 1, they are practically superimposed, and indistinguishable at the scale of

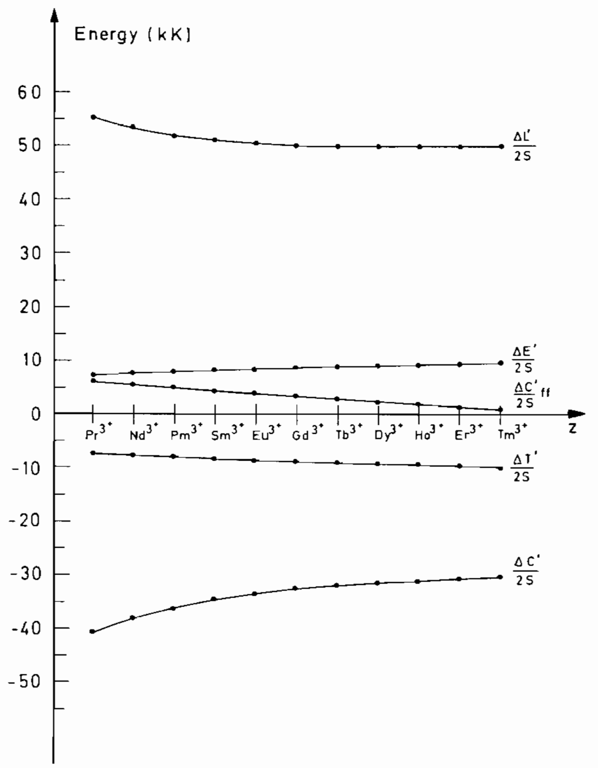

Fig. 1. Spin pairing energy $D' = \Delta E'/2S$ and its components as a function of Z. The definition of the symbols is given in eqns. (2), (5) and (6).

the Figure. Therefore, also at the Hartree–Fock level of approximation, it is possible to define a spin pairing parameter $D' = \Delta E'/2S$: to a very good approximation, the equivalent of eqn. (3) holds, and moreover, $D' \approx D$. This means that the total relaxation energy $\Delta E' - \Delta E$ is negligibly small: the change from the single frozen orbital set to the optimal set for the S-multiplets leaves the total energy virtually unaffected, but it does change the energy components to a very significant extent.

The most striking difference between Fig. 1 and the conventional picture of eqns. (2) is that $\Delta C'$ is now negative. Therefore spin pairing actually decreases the interelectronic repulsion. Since $\Delta T' = -\Delta E'$ is necessarily negative, the only positive component in $\Delta E'$ is the electron-nuclear attraction term. Therefore, at the Hartree–Fock level – quite similarly to what had been found for p^n and d^n systems [8–10] – the meaning of the spin pairing phenomenon becomes definitely more subtle than in conventional multiplet theory.

It is very unlikely that the above conclusions would be altered significantly in going from the Hartree–Fock results to the exact solutions of the Schrödinger equation. Indeed, both for p^n and d^n systems, Hartree–Fock and (nearly) exact treatments give rise to very similar conclusions [8–10]. Moreover, Pyper and Grant have shown that also the incorporation of relativistic effects does not affect the main conclusions to a significant effect [11].

The origin of the negative values of ΔC is not a decrease of the open-shell repulsion however. As a matter of fact, $\Delta C_{ff}'$ remains positive, although its values are lower than the conventional ΔC_{ff}-values for all Z (see Table I). Furthermore, whereas ΔC_{ff} increases with Z, $\Delta C_{ff}'$ exhibits the opposite behavior (Fig. 1 and Table I).

Table II shows a further breakdown of the $\Delta E'$-components for the Gd^{3+}-ion:

$$\Delta E' = \Delta T_c' + \Delta T_f' + \Delta L_c' + \Delta L_f' + \Delta C_c' + \Delta C_{cf}' + \Delta C_{ff}' \quad (6)$$

where c in each case refers to the core and f to the valence orbitals. It is well to stress that, of the seven components of $\Delta E'$, $\Delta C_{ff}'$ is now the smallest. Especially noteworthy is the strong reduction of the core-valence repulsion C_{cf}' upon excitation. In fact, $\Delta C_{cf}'$ is the leading term of $\Delta C'$, determining the sign of the total repulsion energy difference.

A deeper understanding of the sign and magnitude of the different energy terms in Table II can be obtained from a consideration of the orbital size in the different spin states. Table III gives a list of the expectation values r_i for the ψ_i-orbitals of Gd^{3+}, where

$$r_i = \langle \psi_i | r | \psi_i \rangle \quad (7)$$

is a measure of the size of the orbital. Obviously, the 4f-orbitals are more sensitive to multiplicity changes than any of the other orbitals: if the multiplicity decreases, the resulting increase in C_{ff} induces an expansion of the 4f-orbitals, thereby partly offsetting the original repulsion increase. The 4f-expansion allows the other (closed-shell) orbitals to come closer to the nucleus; the resulting contraction is most pronounced in the outer orbitals and gradually vanishes towards the inner core of the ion.

TABLE II. Breakdown of the L', C' and T' Energy Components into Core and Valence Contributions for the Gd^{3+} Ions

$S \rightarrow S-1$	$\Delta L'/S$	$\Delta L_c'/2S$	$\Delta L_f'/2S$	$\Delta T'/2S$	$\Delta T_c'/2S$	$\Delta T_f'/2S$	$\Delta C'/2S$	$\Delta C_c'/2S$	$\Delta C_{ff}'/2S$	$\Delta C_{cf}'/2S$
$7/2 \rightarrow 5/2$	49515	−58782	108297	−8812	28051	−36863	−31892	28415	3732	−64039
$5/2 \rightarrow 3/2$	50086	−59375	109462	−8734	28271	−37005	−32619	28754	3515	−64888
$3/2 \rightarrow 1/2$	50478	−59777	110255	−8680	28422	−37102	−33117	29016	3367	−65500

TABLE III. Orbital Radii r_i (Å) for the Gd^{3+} Ion ($4f^7$)

	$S = 7/2$	$S = 5/2$	$S = 3/2$	$S = 1/2$
1s	0.012542	0.012542	0.012542	0.012542
2s	0.053352	0.053352	0.053352	0.053352
2p	0.045317	0.045317	0.045317	0.045317
3s	0.137335	0.137334	0.137333	0.137332
3p	0.132109	0.132107	0.132106	0.132106
3d	0.117397	0.117395	0.117394	0.117393
4s	0.310213	0.310119	0.310053	0.310013
4p	0.317985	0.317867	0.317782	0.317732
4d	0.337810	0.337561	0.337465	0.337378
5s	0.756887	0.756051	0.755440	0.755068
5p	0.837622	0.836535	0.835739	0.835235
4f	0.414118	0.417432	0.419869	0.421361

The orbital relaxations, following frozen orbital excitation, are reflected in the energy terms of Table II. The contraction of the closed shells gives rise to $\Delta C_c' > 0$, $\Delta L_c' < 0$ and $\Delta T_c' > 0$, whereas the f-shell expansion results in $\Delta T_f' < 0$, $\Delta L_f' > 0$ and $\Delta C_{ff}' < \Delta C_{ff}$. The combination of core contraction and f-expansion is also at the basis of the negative $\Delta C_{cf}'$-values. Table IV shows the variation of $r(5p)$ and $r(4f)$ throughout the lanthanide series as a function of Z.

Orbital Radius and Coordination Number

Tables III and IV are more complete than the work of Marcantonatos *et al.* [3], but as far as a comparison can be made (Eu^{3+}, Gd^{3+}, Tb^{3+}), the results are qualitatively similar. The actual numbers are obviously different, because our Tables are based on Hartree–Fock calculations, whereas Marcantonatos [3] used the Xα-method. Moreover, Tables III and IV show the expectation values $\langle r \rangle$ (eqn. (7)), whereas ref. 3 gives the radius of maximal density. Still, both methods show that an excitation from the groundstate to a state with lower multiplicity is accompanied by an increase of the 4f-size and a decrease of the 5p-size. The global size of the ion as such is essentially determined by the dimensions of the 5p-orbitals. Marcantonatos [3] suggests that the decrease of the 5p-radius of ≈0.15% be responsible for the change of coordination number from 8 to 6.

Although this possibility may perhaps not be ruled out completely, it appears rather improbable if compared with the role of the ionic or orbital radii in the coordination chemistry of the lanthanides as a whole. Table IV shows that, in agreement with experimental data, the lanthanide contraction from Pr^{3+} to Tm^{3+} amounts to ≈15%, or two orders of magnitude more than the contraction of $S \to S - 1$. Even the contraction from one lanthanide ion to its nearest neighbor ($Z \to Z + 1$) amounts to ≈1.5%, still one order of magnitude more than the 0.15% involved in the spin change. Yet, it is generally accepted that the coordination number in solution varies from 9 or 8 in the lighter lanthanides to 8 or 7 for the heavier lanthanides with Gd^{3+} at the breakpoint position. Therefore, on general grounds, we would expect the size effects of spin pairing to be much too small to be responsible for a change in coordination number.

More specific structural factors will probably not affect the above conclusions. For instance the square antiprismatic conformation, supposedly characterizing $Gd(H_2O)_8{}^{3+}$ cannot be expected to exhibit significantly more steric constraints in the excited state than in the groundstate. Moreover, the 'hexacoordinated' structures proposed in reference 3 could more properly be described as seven- or eight-coordinated if the detailed crystallographic structure is taken into consideration (see Fig. 2). In solution, the 'vacant' sites of the cube in Fig. 2C and 2D will quite likely be occupied by water ligands.

Xα-calculations on the square antiprismatic $Gd(H_2O)_8{}^{3+}$ and on the octahedral $Gd(H_2O)_6{}^{3+}$ may

TABLE IV. Orbital Radii of the 4f- and 5p-Orbitals for the Weighted Average of the States with S_{max} and $S_{max} - 1$

Ion	S_{max}	$r(5p; S_{max})$	$r(5p; S_{max} - 1)$	$r(4f; S_{max})$	$r(4f; S_{max} - 1)$
Pr^{3+}	1	0.909066	0.908538	0.491439	0.497190
Nd^{3+}	3/2	0.892860	0.892164	0.472513	0.477537
Pm^{3+}	2	0.877762	0.876935	0.455684	0.460141
Sm^{3+}	5/2	0.863604	0.862672	0.440530	0.444533
Eu^{3+}	3	0.850282	0.849240	0.426660	0.430378
Gd^{3+}	7/2	0.837622	0.836535	0.414118	0.417432
Tb^{3+}	3	0.824495	0.823593	0.405451	0.407860
Dy^{3+}	5/2	0.812036	0.811345	0.396717	0.398359
Ho^{3+}	2	0.800238	0.799717	0.487981	0.389095
Er^{3+}	3/2	0.789015	0.788646	0.379433	0.380150
Tm^{3+}	1	0.778312	0.778080	0.371143	0.371556

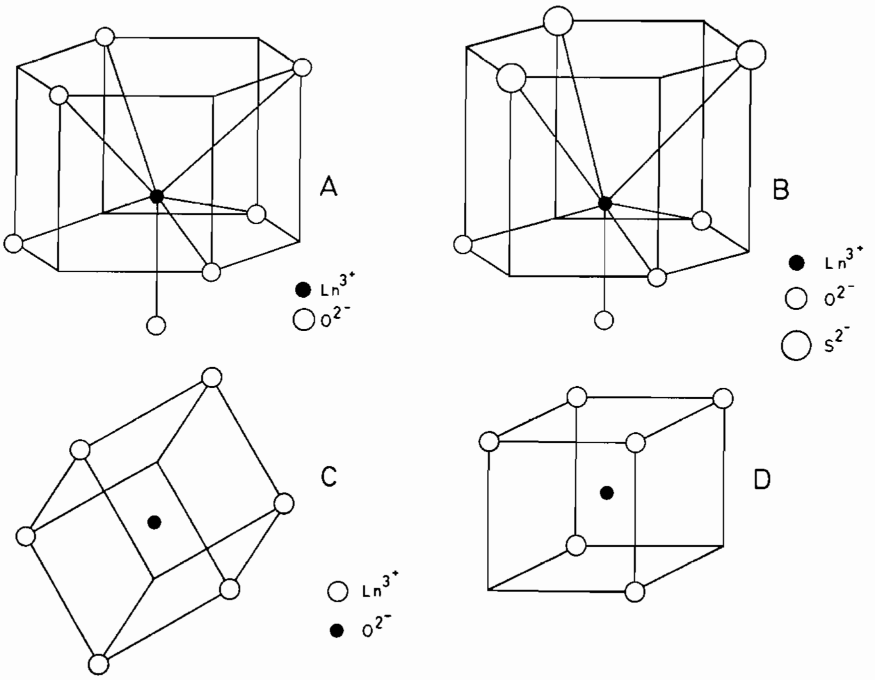

Fig. 2. Different site symmetries for lanthanide ions in Ln_2O_3 and Ln_2O_2S (see also ref. 3) surrounded by oxygen and/or sulphur ligands. The coordination number is often larger than 6, as evident in A or B (where a seventh very close-lying ligand is shown), or in C and D, where neighboring fragments of the unit cell have ligands very close to the 'vacant' sites of the cube.

not provide us with a completely realistic picture [12] of the bonding phenomenon in solution. Differential covalency or different strength of certain specific bonds within the square antiprismatic structure might be more relevant for the study of ligand substitution processes [13, 14] than for the prediction of coordination numbers.

Conclusions

(1) Hartree–Fock studies confirm the work of Marcantonatos [2, 3] by indicating that the size of lanthanide ions slightly decreases upon excitation from the ground state to excited states with lower multiplicity. In the present paper, this contraction and the corresponding 4f-expansion, are shown to be at the basis of the remarkable (non-classical) prediction that the total interelectronic repulsion energy decreases upon excitation.

(2) The relevance of the present considerations obviously depends on the validity of the multiplicity concept. Whereas the ground and first excited states of the central lanthanides (Gd^{3+} and its nearest neighbors) can be expected to be sufficiently pure spin states [4], the first and the last members of the lanthanide series exhibit heavily mixed spin character, and the size effects can be expected to be correspondingly smaller.

(3) In all cases, the lanthanide contraction upon excitation is quantitatively so small, that it is unlikely to be the cause of a possible change in coordination number, either in $Gd(H_2O)_8{}^{3+}$, or in any lanthanide complex.

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