Comparison between magnetic-hyperfine-structure parameters in Sci and TII

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COMPARISON BETWEEN MAGNETIC-HYPERFINE-STRUCTURE PARAMETERS IN ScI AND TiI

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Résumé. — Les effets de second ordre dus à l'interaction de configuration sur les paramètres concernant les parties de structure hyperfine magnétique dépendant de l'orbite ont été évalués *a priori* dans les termes fondamentaux du Scandium et du Titane. Les importances relatives des différentes excitations sont discutées. Les valeurs du rapport $\alpha = a_l/a_{sC}$ obtenues dans Sc et Ti sont respectivement 1,07 et 1,05.

Abstract. — *Ab initio* calculations of the second-order effects of the configuration interaction on the orbit-dependent magnetic-hyperfine-structure parameters in the $3d^N\,4s^2$ configuration have been performed. The importance of the contributions of the different excitations is discussed and a comparison is made between Sc and Ti. The ratio $\alpha = a_l/a_{sC}$ is found to be 1.07 and 1.05 in Sc and Ti respectively.

To take into account the effects of the configuration interaction on the hyperfine structure, three radial parameters are needed, for a given pure Russell-Saunders term. They correspond to the three parts of the magnetic effective hamiltonian : the orbital part, the spin dipole part and the core polarization part. This means that the $\langle r^{-3} \rangle$ quantities are different for the orbital part and for the spin dipole part. It is convenient, in the case of a pure Russell-Saunders term αSL of an l^N configuration, to define correction factors Δ_x such as

$$\langle r_x^{-3} \rangle = (1 + \Delta_x) \langle r^{-3} \rangle \quad (x \equiv l \quad \text{or} \quad sC)$$

where Δ_x depends on αSL.

Using the second order perturbation theory, the Δ factors can be written as linear combinations of radial integrals arising from the different excitations which occur. Bauche-Arnoult [1] gives the formal expression of the Δ factors for the Hund terms of d^N and f^N configurations. These expressions exhibit some striking features : the formal expression of $\Delta_l - \Delta_{sC}$ is the same for d and d^2, d^3 and d^4, d^6 and d^7, d^8 and d^9, except for the part arising from the excitation d → g. The ratio of hfs parameters

$$\alpha = \frac{a_l}{a_{sC}} = \frac{1 + \Delta_l}{1 + \Delta_{sC}},$$

which can be written $1 + (\Delta_l - \Delta_{sC})$ since the Δ correction factors are small compared to unity, should therefore have the same value for the Hund terms of two neighbouring elements (if we assume that the similar radial integrals change very little from one element to the next one in the series and if we neglect the contribution of the d → g excitation).

In the $3d^N\,4s^2$ series, the pairs are (Sc, Ti), (V, Cr), (Fe, Co) and (Ni, Cu). Childs and Greenebaum [2] have gathered the experimental data avialable in this series. For Fe and Co the data agree well with the prediction since $\alpha_{Fe} = 0.94 \pm 0.03$ and $\alpha_{Co} = 0.924$. Unfortunately the ground configurations of Cr and Cu are not of the $3d^N\,4s^2$ type and therefore these hyperfine structures have not been measured by atomic beam resonance. Furthermore, in Cu, the distance between $^2D_{3/2}$ and $^2D_{5/2}$ is 2 042 cm^{-1}. This would not allow the off-diagonal hyperfine-structure studies which are necessary if we consider the three independent parts of the hamiltonian.

For these reasons our attention has been drawn to the pair (Sc, Ti). Several experiments have been performed. Fricke *et al.* [3] have measured the hfs of the ^2D levels of Sc. Childs [4] has been able to determine the off-diagonal hyperfine-structure, because the distance between $^2D_{3/2}$ and $^2D_{5/2}$, here, is only 168 cm^{-1}. The values of the three magnetic hfs parameters lead to the ratio $\alpha = 1.13^{+0.27}_{-0.10}$. As concerns Ti, Childs [2] has deduced, from the experimental result on the three levels ^3P of Channappa and Pendlebury [5], $\alpha = 1.03$. We concluded, at that time, that the prediction was valid. However, more recently, Gebauer *et al.* [6] have obtained in Sc a value of α with a much better accuracy : $\alpha = 1.123 \pm 0.010$.

TABLE I

	Contribution	Analytical Sc	Analytical Ti	MCHF Sc	MCHF Ti
1s, 2s, 3s, 4s → d′	$-\Delta_{sC^2}$	− 0.000 687	− 0.000 712		
	$-\Delta_{sC^2}$	− 0.010 284	− 0.010 925	− 0.010 550	− 0.009 765
	$-\Delta_{sC^2}$	− 0.004 625	− 0.002 862		
	$-\Delta_{sC^2}$	− 0.000 705	− 0.000 427		
2p → p′	$\Delta_1 - \Delta_{sC^2}$	+ 0.085 089	+ 0.079 477	+ 0.084 273	+ 0.079 383
3p → p′	$\Delta_1 - \Delta_{sC^2}$	+ 0.052 878	+ 0.018 662	+ 0.053 309	+ 0.017 725
2p → f′	$-\Delta_{sC^2}$	− 0.016 008	− 0.015 251	− 0.016 014	− 0.015 509
3p → f′	$-\Delta_{sC^2}$	− 0.020 286	− 0.017 684	− 0.020 610	− 0.017 557
1s → 3d	$-\Delta_{sC^2}$	− 0.000 020	− 0.000 024		
2s → 3d	$-\Delta_{sC^2}$	− 0.003 364	− 0.003 632		
3s → 3d	$-\Delta_{sC^2}$	− 0.009 363	− 0.007 931		
4s → 3d	$-\Delta_{sC^2}$	+ 0.000 316	+ 0.000 122		
3d → s′	$-\Delta_{sC^2}$	0	0		
3d → d′	$\Delta_1 - \Delta_{sC^2}$	0	0		
3d → g′	$-\Delta_{sC^2}$	0	+ 0.008 635		
	Total	+ 0.072 941	+ 0.047 448		

Therefore, in order to understand the discrepancy between α_{Ti} and α_{Sc}, we performed *ab initio* evaluations of the α quantities.

For each configuration of the type : $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^N\ 4s^2$, seven kinds of excitations can occur :

i) excitations from a closed shell to an empty shell :

$$1s, 2s, 3s, 4s \rightarrow d'$$
$$2p, 3p \rightarrow p'$$
$$2p, 3p \rightarrow f'$$

ii) excitations from a closed shell to the open shell :

$$1s, 2s, 3s, 4s \rightarrow 3d$$

iii) excitations from the open shell to an empty shell:

$$3d \rightarrow s', d', g'$$

(we note that the excitations of a closed shell 1s, 2s, 3s, 4s to an empty shell s′ give a contribution only to the Fermi contact term, that we do not consider here).

From Bauche-Arnoult [1] the formal expression of $\Delta_1 - \Delta_{sC}$ is the same for Sc and Ti for the excitations i) and ii). In the third case, $\Delta_1 - \Delta_{sC}$ is zero for $3d \rightarrow s'$ and d′ for both elements. $3d \rightarrow g'$ gives 0 for Sc and a non zero value for $3d^2\ 4s^2\ {}^3F$ of Ti.

The separate effects of each excitation can be described in terms of one virtual orbital since the excitations involve only one electron. Each virtual orbital was determined as an analytical function by optimization [7]. For each of the largest contributions to Δ_1 and Δ_{sC} (> 0.01), it appeared feasible to check our result by making another calculation, using a Multiconfigurational Hartree-Fock program (MCHF) [8]. The MCHF procedure has been used here for obtaining the virtual orbital relevant to the true second order effect, that is, with vanishing weights for all excited configurations. In the five cases that we considered, the results obtained by the two methods are very close (Table I).

If we examine each excitation separately, we see that 2p, 3p → p′ give contributions much larger than the other ones, due to the large spatial overlapping of the radial functions. The following ones in order of importance are 2p, 3p → f′, the excitations of the *n*s closed shells being ten times weaker.

Comparing Sc and Ti we see that, except for 3p → p′, the large contributions do not differ by more than 20 %. For the inner shells 1s, 2s and 2p, the differences are very small : less than 10 %. For 3s and 4s they are somewhat larger.

The sum of the contributions of the different excitations to $\Delta_1 - \Delta_{sC}$ is given at the bottom of the table. Omitting the last figures, we have summarized the results in table II. The effects of relativity are expected to be about 1 % for both Sc and Ti, reducing the calculated value of α [9].

In conclusion, as it was expected [1], when we consider the second order effects, the *ab initio* evaluations of α for Sc and Ti lead to values which are close (in spite of the excitation d → g in Ti, which turns

TABLE II

	Sc	Ti
$\alpha_{\text{calculated}}$	1.07	1.05
$\alpha_{\text{calc. with relativity}}$	1.06	1.04
$\alpha_{\text{experimental}}$	1.12 ± 0.01	1.03

out to be 1 % of the α_{Ti} value). The problem of the bad agreement with the experimental α_{Sc} value remains. However : on the one hand, the configuration-mixing wave functions are not yet known for the even low levels of ScI ; on the other hand, calculations including higher-order effects, in particular near-degeneracy effects, would be of great interest. In order to check the agreement with other experimental results, similar second-order calculations for the other elements of the series would be instructive.

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