Pseudo-Zeeman factors for transition ions in silicon

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ABSTRACT

Frequently the analysis of a magnetic resonance experiment is carried out describing the ground state in which the resonance is observed by a spin-Hamiltonian expression introducing an effective spin in accordance with the number of observed transitions. However, if a low-lying excited state coupling to the ground state is present the parameters as determined will deviate from their true physical value. The general theory for interactions mediated by orbital momentum and by electron or nuclear spin is outlined. A specific examination is presented for transition ions of the iron group and of some of their complexes in silicon in a spin quartet state. The examples include the interstitial titanium ion of cubic symmetry, and several iron-acceptor complexes in either trigonal or orthorhombic symmetry. The analysis accounts in a satisfactory manner for the large deviations of the g tensor components from their free-electron value $g = 2.0023$. Also the tensor for the nuclear Zeeman effect can deviate substantially from the scalar value for the free nucleus and it appears to be possible to account for apparent strongly anisotropic coupling tensors. Both the presence of low-lying excited states and the Zeeman tensors applicable to them are predictable from the analysis.

1. INTRODUCTION

Electron paramagnetic resonance (EPR) is a powerful technique for the identification and characterization of centers in solids. For silicon about three hundred centers have been observed by their EPR spectra and their spectroscopic parameters have been determined. These spectroscopic parameters, such as Zeeman splitting factors and hyperfine components and the symmetry of these tensors, serve as a unique fingerprint of the centers, with few exceptions only. The parameters are obtained by analysis with an appropriate spin-Hamiltonian expression taking into account the electronic and nuclear spins present and their mutual interactions and those with the host crystal. The interpretation of the parameters in terms of physical properties of the centers usually is less straightforward. Deviation of the electronic g values from the free-electron value $g = 2.0023$ indicates presence of (non-quenched) orbital momentum or values of electron spin higher than $S = 1/2$. This is extremely valuable as without these deviations all centers would have equal electronic g values, $g \approx 2$, rendering the g values useless for identification. To large extent this situation applies to and forms a handicap for the study of centers in diamond. In general the nuclear Zeeman splitting factor is equal to that of the free nucleus. This, again, is a very positive feature as it allows the identification of the nucleus. However, as discussed in the present paper, situations may arise where also the nuclear g factor deviates from its textbook value due to indirect interactions which also have the form $\mathbf{B} \cdot \mathbf{I}$. Hyperfine constants provide valuable information on the spatial extension of unpaired spin density and are often more easily interpretable using a linear combination of atomic orbitals (LCAO) description.

In this paper a discussion is given of indirect interactions of the form $\mathbf{B} \cdot \mathbf{S}$ or $\mathbf{B} \cdot \mathbf{I}$ which add to the regular Zeeman energies of electrons and nuclei, respectively, creating pseudo-Zeeman factors. In the next section of the paper the general theoretical framework to assess these indirect contributions is outlined. The effects will be large if low-lying excited states exist, too high in energy to be within reach of the exciting microwave quantum and

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not thermally populated, but close enough to have appreciable mixing to the ground state functions. Effects on the electronic g tensor can be huge and their existence is well confirmed by analysis of experimental data. For nuclei a much less prominent effect in an EPR experiment is expected. First of all, transitions with change of nuclear quantum number will be present only if due to complexity of the spin system these so-called forbidden transitions become allowed, but then, most probably, still with low intensity. Even when present, due to the small nuclear energies the shifts in EPR line positions will be hardly noticeable. The purely nuclear energy terms, such as Zeeman splitting and quadrupole interactions, will appear in the EPR spectrum as small second-order effects. Their unambiguous identification requires careful analysis of data. As a consequence the appearance of nuclear pseudo-Zeeman factors has been reported only occasionally and their positive implementation for structure analysis has hardly been used.

2. THEORETICAL ANALYSIS

2.1. Introduction

The regular direct Zeeman effect of an electron with spin **S** in a magnetic field **B** involves the energy $g\mu_B \mathbf{B}\cdot\mathbf{S}$, with $g = 2$ and μ_B the Bohr magneton. The equivalent energy for a nucleus is $-\gamma\mu_N \mathbf{B}\cdot\mathbf{I}$, where for practically all free nuclei the value of γ is known accurately.[1] However, also indirect ways are effective in which the magnetic field makes itself perceptible to the spins. The best known of these is via orbital momentum. In this mechanism the magnetic field induces a change of the orbital momentum expectation values which is felt by the spins through spin-orbit interaction.[2] The theoretical treatment of this mechanism is outlined in section 2.2. In a second mechanism the interaction between field **B** and electron spin **S** is mediated by a nuclear spin **I**. A similar mechanism couples **B** and **I** with **S** as the intermediate quantity,[3,4] as detailed in section 2.3. These two mechanisms exhaust the (two step) possibilities existing within a set of interactions consisting of the electron spin-orbit coupling $\lambda\mathbf{L}\cdot\mathbf{S}$, nuclear spin-orbit coupling $P\mathbf{L}\cdot\mathbf{I}$, hyperfine interaction $A\mathbf{S}\cdot\mathbf{I}$, and the interactions due to magnetic field including the electron Zeeman energy $g\mu_B\mathbf{B}\cdot\mathbf{S}$, nuclear Zeeman energy $-\gamma\mu_N\mathbf{B}\cdot\mathbf{I}$ and electron orbital energy $\mu_B\mathbf{B}\cdot\mathbf{L}$. Interactions of the mentioned set will change the energy in a paramagnetic ground state (gs), as well as in excited states (es). Of particular importance in the present context is that also non-zero matrix elements may exist between ground and excited states. Using second-order perturbation theory expressions the energy in the ground state will be changed by an amount of order $\langle \mathrm{gs}|\mathcal{H}|\mathrm{es}\rangle^2/(E_{\mathrm{es}} - E_{\mathrm{gs}})$. Cross terms in the numerator produce pseudo effects. If excited states low in energy are existent these may appreciably affect the regular values.

2.2. Mediation via orbital momentum

A pseudo electronic Zeeman interaction of the form $\mathbf{B}\cdot\mathbf{S}$ is produced by the combined action of orbital energy in magnetic field $\mu_B\mathbf{B}\cdot\mathbf{L}$ and the spin-orbit interaction $\lambda\mathbf{L}\cdot\mathbf{S}$. The perturbation of the ground state energy is of order $\Delta E = (\mu_B B + \lambda)^2/(E_{\mathrm{es}} - E_{\mathrm{gs}})$ and corresponds to a change of g factor equal to $\Delta g = \Delta E/\mu_B B$:

$$\Delta g = 2\lambda/(E_{\mathrm{es}} - E_{\mathrm{gs}}). \tag{1}$$

A relative change of electronic g value is thus

$$\Delta g/g = 2\lambda/g(E_{\mathrm{es}} - E_{\mathrm{gs}}). \tag{2}$$

An equivalent treatment of the effect on the nucleus, using the interactions $\mu_B\mathbf{B}\cdot\mathbf{L}$ and $P\mathbf{L}\cdot\mathbf{I}$, results in $\Delta E = (\mu_B B + P)^2/(E_{\mathrm{es}} - E_{\mathrm{gs}})$. The change in nuclear Zeeman factor γ is

$$\delta\gamma = 2\mu_B P/\mu_N(E_{\mathrm{es}} - E_{\mathrm{gs}}), \tag{3}$$

with the relative effect

$$\Delta\gamma/\gamma = 2\mu_B P/\gamma\mu_N(E_{\mathrm{es}} - E_{\mathrm{gs}}). \tag{4}$$

The effects on electron and nucleus are compared by

$$\Delta g/g = (\gamma\mu_N\lambda/g\mu_B P)\,\Delta\gamma/\gamma. \tag{5}$$

Inserting known or typical numbers, it may be concluded that effects tend to be small, with those on the nuclear parameter even smaller than that on the electron.

2.3. Mediation via spin

In an entirely similar manner an electronic pseudo-Zeeman factor is created via the nuclear spin **I**. The interactions $\gamma\mu_N\mathbf{B}\cdot\mathbf{I}$ and $A\mathbf{S}\cdot\mathbf{I}$ together provide an indirect way of coupling the electron spin to the magnetic field. The energy by which the ground state is perturbed $(\gamma\mu_N B + A)^2/(E_{es} - E_{gs})$ leads to change of g factor by

$$\Delta g = 2\gamma\mu_N A/\mu_B(E_{es} - E_{gs}), \tag{6}$$

or on a relative scale by

$$\Delta g/g = 2\gamma\mu_N A/g\mu_B(E_{es} - E_{gs}). \tag{7}$$

For the nucleus the required interactions to produce the pseudo-Zeeman effect are $g\mu_B\mathbf{B}\cdot\mathbf{S}$ and $A\mathbf{S}\cdot\mathbf{I}$. These will give the change of ground state energy by $\Delta E = (g\mu_B B + A)^2/(E_{es} - E_{gs})$, with the effect on the Zeeman factor given by

$$\Delta\gamma = 2g\mu_B A/\mu_N(E_{es} - E_{gs}), \tag{8}$$

and

$$\Delta\gamma/\gamma = 2g\mu_B A/\gamma\mu_N(E_{es} - E_{gs}). \tag{9}$$

The electronic and nuclear shifts are related by

$$\Delta g/g = (\gamma\mu_N/g\mu_B)^2\,\Delta\gamma/\gamma. \tag{10}$$

A summary of results is given in table 1. With $\gamma < 1$, as for many nuclei, and $g \approx 2$, an estimate on the basis of equation (10) becomes $\Delta g/g \approx 10^{-8}\Delta\gamma/\gamma$. Contrary to the result as expressed by equation (5) the **S**, **I**-mediated process can induce a sizeable effect on the nucleus, accompanied by an entirely negligible effect on the electronic factor. As mentioned before, the change of the nuclear parameter will be difficult to observe in an EPR experiment where it constitutes only second-order contributions. The appropriate way to measure possibly spectacular changes of γ is through nuclear magnetic resonance (NMR) or electron-nuclear double resonance (ENDOR).

2.4. Excited states

As indicated by the results of the previous sections, appreciable pseudo contributions to the Zeeman factors can be expected when low-lying excited states exist, provided these have non-zero matrixelements coupling them to the ground state. Several cases where this situation is practically realized can be mentioned.

	Electron		Nucleus
L mediated	$\Delta g/g = 2\lambda/g(E_{es} - E_{gs})$	$>$	$\Delta\gamma/\gamma = 2\mu_B P/\gamma\mu_N(E_{es} - E_{gs})$
S, **I** mediated	$\Delta g/g = 2\gamma\mu_N A/g\mu_B(E_{es} - E_{gs})$	$\ll$	$\Delta\gamma/\gamma = 2g\mu_B A/\gamma\mu_N(E_{es} - E_{gs})$

Table 1: Summary of the pseudo-Zeeman effects on electrons and nuclei created by mediation of orbital momentum **L** or by electron spin **S** and nuclear spin **I**.

In a first example the orbital momentum **L** and spin **S** of a many-electron system couple to a total momentum **J** by spin-orbit interaction $\lambda\mathbf{L}\cdot\mathbf{S}$, with $|L-S| \leq J \leq |L+S|$. Such situations where orbital and spin momenta of several electrons couple to form the maximum value of **L** and **S** do exist for transition metals. The excitation energies are given by

$$E_{\text{es}} - E_{\text{gs}} = (1/2)\lambda[J(J+1) - L(L+1) - S(S+1)]. \tag{11}$$

The lower values of excitation energy will be found for the lighter nuclei, in this case represented by $3d$ transition metals. Even here, though, the spin-orbit coupling constant λ for the free ion will be quite large, of order 10^6 MHz (100 cm^{-1}). Embedded in a solid the effective values of λ were found to be much reduced. Mechanisms causing the reduction are reported to be dynamical Jahn-Teller effect and covalent electron delocalisation. A convincing experimental confirmation of substantial reductions in the effective spin-orbit interaction is given by the observation of spin resonance at low temperatures in the excited states of Mn^0, Mn^+ and Cr^0 in silicon.[5]

The several states in a high-spin multiplet can also be split by a crystal field, for instance a cubic crystal field represented by an operator $a(S_x^4 + S_y^4 + S_z^4)$. In general these splittings tend to be large, but again situations are not uncommon where the effective crystal field strength operating on the paramagnetic electrons is strongly reduced. The characteristic examples here are rare-earth ions, in which the internal 4f electrons are shielded from the crystal field by outer electrons in $5s$ and $5p$ shells. Low-lying excited states have been reported to give spectacular nuclear pseudo-Zeeman contributions for holmium in calciumfluoride[6] or for neodymium in LaCl_3 (Ref. 7). Zero-field splittings are also produced by spin-orbit interaction as a small second-order effect. In the spin Hamiltonian these interactions between spins are accounted for by terms like $\mathbf{S}\cdot\mathbf{D}\cdot\mathbf{S}$, required for centers of lower than cubic symmetry and electron spin $S \geq 1$. Well-known examples illustrating this case are trigonal or orthorhombic iron-acceptor complexes; values of D in the range of 10^5 MHz are often found.

3. SPIN-QUARTET STATES

3.1. Cubic symmetry

An illustrative example of well-established pseudo-Zeeman factors is provided by titanium as an impurity in silicon.[8] This impurity from the $3d$ series of transition elements occupies an interstitial site with $T_d(\bar{4}3m)$ symmetry. In the observed positive charge state the electronic configuration is $[\text{Ar}]3d^3$. Obeying the Ludwig-Woodbury model all outer electrons are in $3d$ orbitals. In its ground state all spins are parallel, following Hund's rule, resulting in an electron spin $S = 3/2$ and orbital momentum $L = 0$, i.e., an orbital singlet $^4A_2$ ground state. Figure 1 illustrates the splitting of the atomic ^4F state, also giving excited states of $^4T_2$ and $^4T_1$ character.

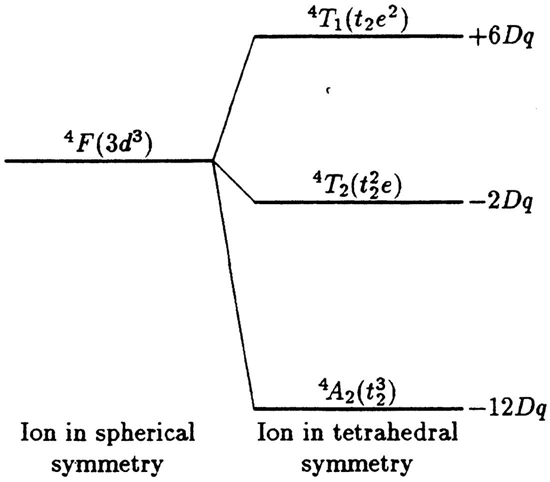


Figure 1: Energy level scheme for positive interstitial titanium in silicon, configuration $3d^3$ in tetrahedral symmetry.

For self-ENDOR experiments both titanium isotopes with nuclear moment, ^{47}Ti with $I = 5/2$ and ^{49}Ti with $I = 7/2$, were applied.[9] Some of the spin-Hamiltonian constants obtained by analysis of the ENDOR data are given in table 2. The deviation of the electron g factor from its free-electron value $g = 2.00232$ amounts to $\Delta g = -0.00426$. The values of the nuclear factors, taken from Ref. 1, are $\gamma = -0.31488$ for ^{47}Ti and $\gamma = -0.31496$ for ^{49}Ti. These are the values as measured by NMR for nuclei with diamagnetic screening by the $1s$, $2s$ and $3s$ electrons. Since such screening will also be present for the impurity in silicon, these uncorrected values will be used for comparison with the Si:Ti data as given in table 2. The shifts $\Delta\gamma$ are then found to be $\Delta\gamma = -0.00026$ for both nuclei. It is concluded from the experiment that the electronic shift is larger than the nuclear one: $\Delta g \approx 16\Delta\gamma$. This is as expected for the **L**-mediated process. On a more quantitative basis equation (5) can be applied. Constant P is given by $P = (\mu_0/4\pi)g\gamma\mu_B\mu_N\left\langle r^{-3}\right\rangle_{3d}$

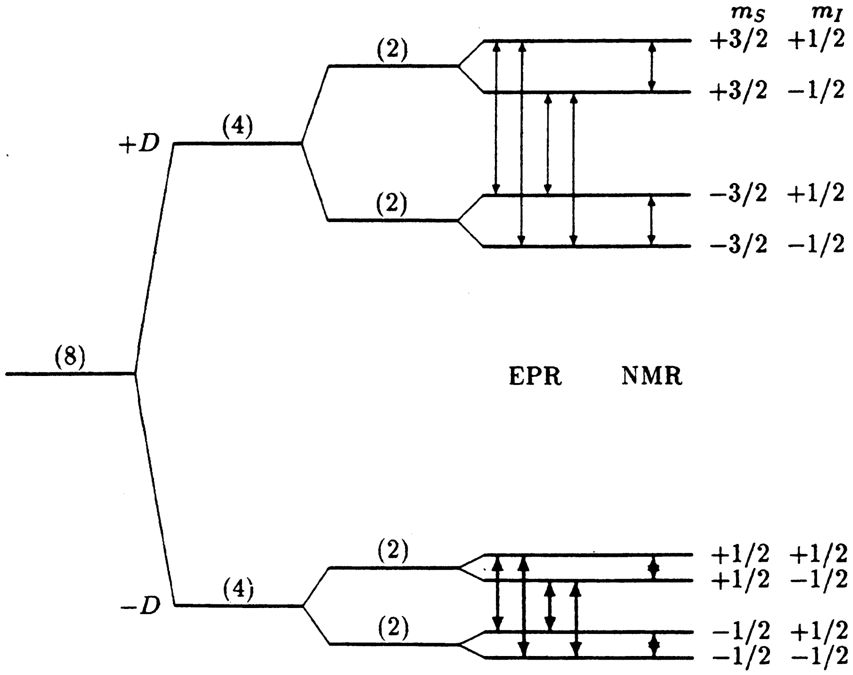
	^{47}Ti^{+}	^{49}Ti^{+}
Electron Zeeman factor	1.99806 ± 0.00004	1.99806 ± 0.00004
Nuclear Zeeman factor	-0.31514 ± 0.00001	-0.31522 ± 0.00001

Table 2: Some spin-Hamiltonian parameters for interstitial ^{47}Ti^{+} and ^{49}Ti^{+} in silicon.[9,10]

and, using $\langle r^{-3} \rangle_{3d} = 1.651 \times 10^{31}$ m^{-3} from Ref. 11, is calculated to be $P = -0.00245$ cm^{-1}. The spin-orbit coupling parameter $\lambda = 30$ cm^{-1} is taken from Ref. 12. The theoretical estimate then is $\Delta g \approx 7\Delta\gamma$. Reversing the argument, the excitation energy $E_{es} - E_{gs}$ can be calculated from the shifts of the Zeeman factors. From equation (1), $E_{es} - E_{gs} = 2\lambda/\Delta g$, the excitation energy is determined as $E_{es} - E_{gs} \approx 1.8$ eV. This value is larger than $10Dq \approx 5500$ cm^{-1} as used in earlier analysis.[9] The crystal field model gives agreement in the sign of the shifts and can provide a reasonable estimate for the magnitudes, but its limitations in providing an accurate quantitative description are apparent.

3.2. Trigonal symmetry

In a lower-symmetry environment the degeneracy of the levels of the electron spin quartet will be partially lifted. An illustrative energy level diagram for a spin system with electron spin $S = 3/2$ and nuclear spin $I = 1/2$ is given in figure 2. The crystal field, in this case considered to be trigonal, splits the electron quartet into two



$$\mathcal{H} = \mathbf{S} \cdot \mathbf{D} \cdot \mathbf{S} + g\mu_B \mathbf{B} \cdot \mathbf{S} - \gamma\mu_N \mathbf{B} \cdot \mathbf{I}$$
$$D \gg g\mu_B B$$

Figure 2: Energy level diagram for a spin system with electron spin S=3/2 and nuclear spin I=1/2 in axial crystal field. Energy splittings due to hyperfine interaction are omitted for simplicity. EPR and NMR transitions between levels are indicated by arrows. Total degeneracy of levels, electronic plus twofold nuclear, is indicated by numbers in parentheses.

Kramers doublets, at the energies $+D$ and $-D$, respectively. Zeeman interactions on both the electrons and the nucleus further remove all degeneracy. The total degeneracies of the levels, electronic plus nuclear, are given by the numbers in parentheses near the levels. EPR and NMR (ENDOR) transitions are indicated by the arrows connecting levels. Since considerable mixing between states takes place, the quantum numbers to the right are for labeling purposes only. The quantitative description and analysis of the spectroscopic features uses the spin Hamiltonian, for the present case given by

$$\mathcal{H} = +\mathbf{S}\cdot\mathbf{D}\cdot\mathbf{S} + \mu_B\mathbf{B}\cdot\mathbf{g}\cdot\mathbf{S} - \gamma\mu_N\mathbf{B}\cdot\mathbf{I} + \mathbf{S}\cdot\mathbf{A}\cdot\mathbf{I}, \qquad (12)$$

with all tensors, zero-field splitting tensor $\mathbf{D}$, electron Zeeman energy $\mathbf{g}$ and hyperfine interaction $\mathbf{A}$, having axial symmetry. It is assumed for the present application that $D \gg g_{\text{eff}}\mu_B B$. Therefore, the splitting between the upper set of four levels and the lower set is too large to be connected in the EPR experiment. Also, at the low temperatures of the experiment there is negligible thermal population of the upper states. The system is therefore only monitored by the transitions in the lower set of levels. This resonance will be described by an effective spin $S = 1/2$ and correspondingly adjusted parameters. Straightforward analysis relates the pseudo parameters in the $S = 1/2$ formalism to the real ones in equation (12) with $S = 3/2$ as indicated in table 3. The large modifications of the effective g value for electrons is not a result of the mixing as outlined in section 2 of this paper. It is another manifestation of the disturbance of the spin alignment of the three electrons by an axial field. On the other hand, the changes of the nuclear Zeeman factor are the result of the $\mathbf{S}$, $\mathbf{I}$-mediated indirect coupling as described in section 2.3 and have the form as derived there. It is seen that the scalar coupling constant γ of the nuclear Zeeman effect is to be replaced by a tensor quantity. Its parallel value $\gamma_\parallel$ is still equal to the regular value for the nucleus, allowing identification of the nucleus by inspection of nuclear tables. The perpendicular value $\gamma_\perp$ is, however, modified carrying information on the ground to excited state splitting. For small zero-field splittings the pseudo contributions may dominate over the real nuclear Zeeman factor. The trigonal FeB complex may serve as an illustrative example.[5,13] With $g_\perp = 2.0452$, $A_\perp = (\pm)21.3$ MHz and $D = 81$ GHz the correction to the nuclear Zeeman factor will be $(\pm)0.74$. It will change the regular value $\gamma = 0.18$ to $\gamma'_\perp = +0.92$ and -0.56 for the doublets. With $\gamma_\parallel$ remaining equal to 0.18, the pseudo tensor for the nucleus has become strongly anisotropic.

	Doublet $+D$	Doublet $-D$
Electron Zeeman factor	$g'_\parallel = 3g_\parallel$	$g'_\parallel = g_\parallel$
	$g'_\perp = 0$	$g'_\perp = 2g_\perp$
Nuclear Zeeman factor	$\gamma'_\parallel = \gamma$	$\gamma'_\parallel = \gamma$
	$\gamma'_\perp = \gamma - 3\mu_B g_\perp A_\perp / 4\mu_N D$	$\gamma'_\perp = \gamma + 3\mu_B g_\perp A_\perp / 4\mu_N D$
Hyperfine constant	$A'_\parallel = 3A_\parallel$	$A'_\parallel = A_\parallel$
	$A'_\perp = 0$	$A'_\perp = 2A_\perp$

Table 3: Pseudo-constants for an effective electron spin $S = 1/2$ Hamiltonian for the two (electron spin) doublets of a true $S = 3/2$ spin system in a trigonal crystal field.

Center	Principal g values			Scale	Scaled principal g values			Dou-	E/D	Refe-
	g_x	g_y	g_z	factor	g_x	g_y	g_z	blet		rence
FeB	4.0904	4.0904	2.0676	1.0239	3.9951	3.9951	2.0194	$-W$	0.00	13
trigonal	(0.00)	(0.00)	(6.14)		(0.000)	(0.000)	(6.000)	$+W$		
FeAl	1.138	1.138	6.389	1.0981	1.036	1.036	5.818	$+W$	0.18	14
trigonal	(4.29)	(4.29)	(2.00)		(2.878)	(4.940)	(1.819)	$-W$		
FeAl	1.612	1.236	5.885	1.0376	1.554	1.191	5.672	$+W$	0.25	14
rhombic	2.51	5.36	1.73	1.0277	2.442	5.215	1.683	$-W$		15
FeGa	0.69	0.59	6.19	1.0427	0.662	0.566	5.936	$+W$	0.105	15
rhombic	3.37	4.65	2.02	1.0146	3.321	4.583	1.991	$-W$		15
FeIn	1.08	1.08	6.38	1.0934	0.988	0.988	5.835	$+W$	0.175	16
trigonal	(4.28)	(4.28)	(2.00)		(4.919)	(2.909)	(1.828)	$-W$		
FeIn	3.78	4.40	2.07	1.0265	3.628	4.286	2.017	$-W$	0.05	5
rhombic	(0.31)	(0.30)	(6.14)		(0.306)	(0.291)	(5.985)	$+W$		

Table 4: Measured and predicted electronic g values in the spin $S = 1/2$ formalism for the two doublets $+W$ and $-W$ of a true spin $S = 3/2$ system. Values predicted on the basis of the theory are shown in parentheses.

3.3. Orthorhombic symmetry

Magnetic resonance measurements have been carried out for iron-acceptor complexes for all acceptors: boron, aluminum, gallium and indium. In some of these complexes iron occupies the closest interstitial site to the acceptor creating a center of trigonal symmetry. For other complexes the distance is larger and the symmetry is found to be orthorhombic. In table 4 the principal g values of six such complexes are given, all of them showing large deviations from $g \approx 2$. Extending the treatment of the previous section, an orthorhombic crystal field of form $E(S_x^2 - S_y^2)$ is introduced in addition to the axial field $D(S_z^2 - 5/4)$. Again the four levels in the spin $S = 3/2$ system will be split by the crystal field into two doublets, at the energies $\pm W$ with $W = \sqrt{D^2 + 3E^2}$. The action on these states of electron and nuclear Zeeman interactions and of hyperfine interaction are treated as a perturbation. The results will be accurate as long as these latter energies are small compared to the doublet splitting. Both doublets are treated as an effective $S = 1/2$ system with their internal splittings described by pseudo-parameters. The results obtained are listed in table 5. It is concluded that all parameters are a function of E/D. Figure 3 gives the plot of pseudo g values in the range $0 \leq E/D \leq 1/3$ corresponding to a

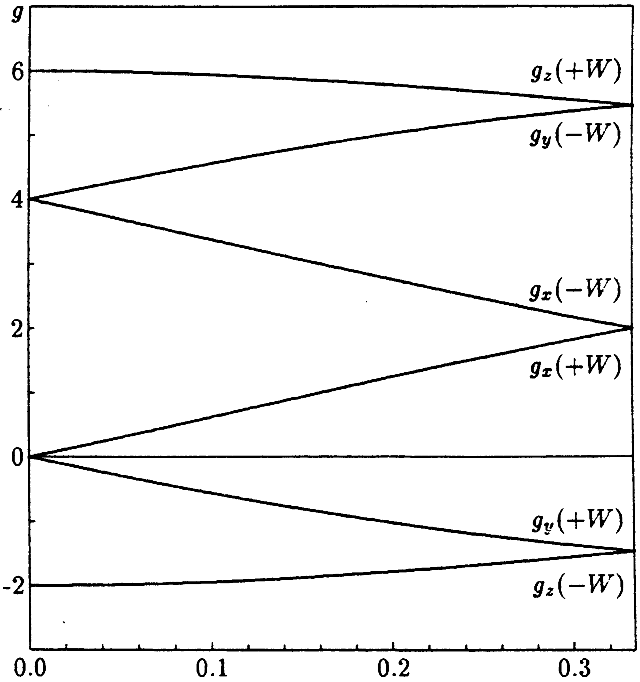


Figure 3: Theoretical principal g values g_x, g_y and g_z of the electronic pseudo-Zeeman tensor in the spin $S = 1/2$ formalism for the doublets $+W$ and $-W$ of a true spin $S = 3/2$ system. g Values are given as a function of the ratio E/D of orthorhombic to axial crystal field in the range $0 \leq E/D \leq 1/3$, correponding to a crystal field with main axial component along the z axis.

crystal field with the axial component mainly along the z axis. For other directions of the crystal field suitable transformations should be made. In drawing figure 3 it was assumed that $g_x = g_y = g_z = 2$. With this assumption of isotropic $g = 2$ the pseudo g values should obey the relation $\sqrt{g_x'^2 + g_y'^2 + g_z'^2/3} = g = 2$. The quantity of the left hand side of this equation is therefore calculated for the experimental data and the results are included in

	Doublet $+W$	Doublet $-W$
Electron Zeeman factor	$g_x' = g_x[1-(D-3E)/(D^2+3E^2)^{1/2}]$ $g_y' = g_y[1-(D+3E)/(D^2+3E^2)^{1/2}]$ $g_z' = g_z[1+2D/(D^2+3E^2)^{1/2}]$	$g_x' = g_x[1+(D-3E)/(D^2+3E^2)^{1/2}]$ $g_y' = g_y[1+(D+3E)/(D^2+3E^2)^{1/2}]$ $g_z' = g_z[1-2D/(D^2+3E^2)^{1/2}]$
Nuclear Zeeman factor	$\gamma_x' = \gamma - \frac{(D+E)^2}{D^2+3E^2}\frac{3g_x\mu_B A_x}{4\gamma\mu_N W}$ $\gamma_y' = \gamma - \frac{(D-E)^2}{D^2+3E^2}\frac{3g_y\mu_B A_y}{4\gamma\mu_N W}$ $\gamma_z' = \gamma - \frac{E^2}{D^2+3E^2}\frac{3g_z\mu_B A_z}{\gamma\mu_N W}$	$\gamma_x' = \gamma + \frac{(D+E)^2}{D^2+3E^2}\frac{3g_x\mu_B A_x}{4\gamma\mu_N W}$ $\gamma_y' = \gamma + \frac{(D-E)^2}{D^2+3E^2}\frac{3g_y\mu_B A_y}{4\gamma\mu_N W}$ $\gamma_z' = \gamma + \frac{E^2}{D^2+3E^2}\frac{3g_z\mu_B A_z}{\gamma\mu_N W}$
Hyperfine constant	$A_x' = A_x[1-(D-3E)/(D^2+3E^2)^{1/2}]$ $A_y' = A_y[1-(D+3E)/(D^2+3E^2)^{1/2}]$ $A_z' = A_z[1+2D/(D^2+3E^2)^{1/2}]$	$A_x' = A_x[1+(D-3E)/(D^2+3E^2)^{1/2}]$ $A_y' = A_y[1+(D+3E)/(D^2+3E^2)^{1/2}]$ $A_z' = A_z[1-2D/(D^2+3E^2)^{1/2}]$

Table 5: Pseudo-constants for an effective electron spin $S = 1/2$ Hamiltonian for the two (electron spin) doublets of a true $S = 3/2$ spin system in an orthorhombic crystal field.

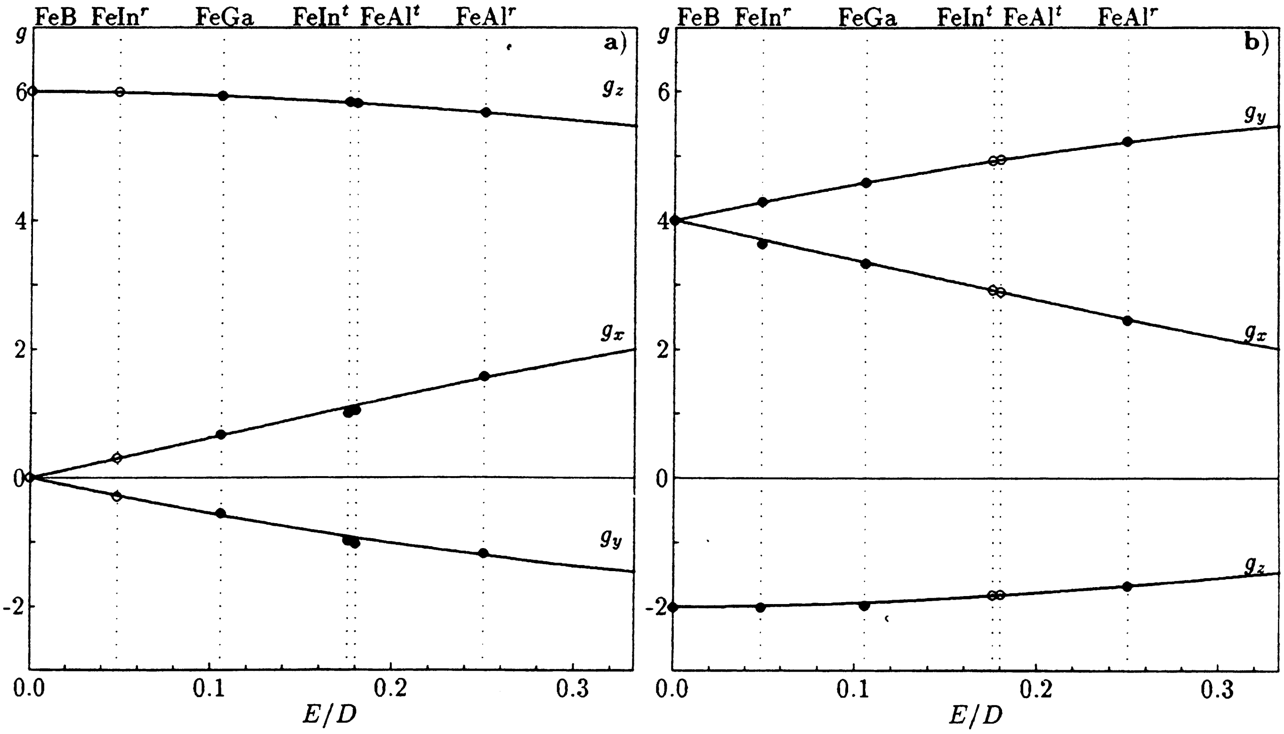


Figure 4: Principal g values g_x, g_y and g_z in the two electron spin doublets of a true spin $S = 3/2$ system. **a)** doublet at the energy $+W$, **b)** doublet at $-W$. Solid curves were calculated with expressions as given in table 5; experimentally measured data for trigonal (^{t}) and orthorhombic (^{r}) iron-acceptor complexes are represented by •, predicted values by ○.

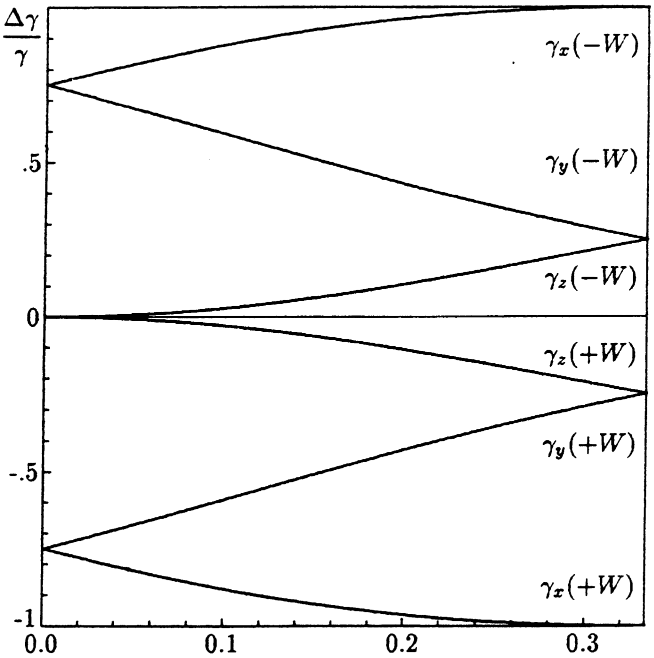


Figure 5: Relative change of the pseudo-nuclear Zeeman tensor, in units $g_i\mu_B A_i/\gamma\mu_N W$ $(i = x, y, z)$, in the spin $S = 1/2$ formalism for the doublets $+W$ and $-W$ of a true spin $S = 3/2$ system as a function of the ratio E/D of orthorhombic to axial crystal field.

table 4. A somewhat larger value $g' > 2$ is obtained. Actually the results on average are close to 2.0700, the g value of the neutral iron atom in silicon. To allow for a better comparison with calculated g values on the basis $g = 2$, the experimental data are divided by the scaling factor $g'/2$ and are as well included in table 4. The comparison between experimental values and those from analysis is illustrated by figure 4. It may be concluded that convincing agreement is obtained. The orthorhombic FeAl and FeGa pairs are observed in both doublets. For the other centers the g tensor for observation in one doublet only is thusfar available. On the basis of the presented analysis the g values valid for the other doublet can be predicted. These data are as well included in figure 4, on the basis of $g = 2$, and in table 4 both before and after rescaling. The parameter E/D for all complexes is obtained. Among the trigonal centers only FeB behaves normally with $E/D = 0$. Remarkably, the other two trigonal centers FeAl and FeIn can very well be fitted with the theory, but with non-zero values for E/D. Strong deviations of the pseudo-Zeeman factor from 2, such as $g'_\perp \approx 4$, are a clear indication of the true $S = 3/2$ character of the spin system. In this case the better analysis is obtained using this larger spin value. Advantages of the high-spin analysis are **1**) a better fit of experimental data is obtained in the analysis, as the low-spin analysis is only correct to second order, **2**) physically correct values for the spin-Hamiltonian parameters are obtained, in particular $g \approx 2$, allowing remaining small deviations to be interpreted as orbital-momentum induced, **3**) information is obtained about the crystal fields to which the center is exposed by the determination of E/D, **4**) the spin value $S = 3/2$ is confirmed to be the physically significant one, bearing evidence of a $3d^3$ or $3d^7$ electronic configuration of the center which is related to its charge state. Results as presented in the tables 3 and 5 demonstrate that the pseudo-parameters for the hyperfine interaction have the same mathematical relation to their true values as those applicable to the g tensor. When analyzed in the $S = 1/2$ formalism the hyperfine constants must be converted to their true values before any further physical analysis, such as an LCAO interpretation, is made. Pseudo contributions to the nuclear Zeeman factor are of the form as discussed in section 2.3 on the **S**, **I**-mediated interactions. They depend on the ratio of the mixture of axial and orthorhombic components in the crystal field. Results are given in graphical form in figure 5. No experimental verification of these results is available at present.

4. SUMMARY AND CONCLUSIONS

Indirect coupling of the electron spin **S** and the nuclear spin **I** to the magnetic field **B** can make significant contributions to the spectroscopic splitting factors, known as pseudo-Zeeman effect. The general equations, as shown in table 1, indicate that the **L**-mediated process is most important for electronic g tensors, whereas the **S**, **I** spin-mediated indirect interactions can effectively influence nuclear parameters with negligible effect on the electronic ones. Pseudo-Zeeman contributions lead to possibly strongly anisotropic nuclear Zeeman interaction tensors, e.g. with $\gamma'_\parallel = \gamma$, allowing chemical identification of the nucleus, and $\gamma'_\perp \neq \gamma$, revealing the existence of low-lying excited states and allowing their study.

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