

## ELECTRONIC GROUND STATE OF IRON-ACCEPTOR PAIRS IN SILICON

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## ABSTRACT

Iron-acceptor impurity pairs, consisting of a positively charged iron ion trapped on an interstitial site in the vicinity of an ionized acceptor, in silicon were observed by electron paramagnetic resonance for all common acceptor dopants (B, Al, Ga, In). The Zeeman splittings of these pairs, to which both spin and orbital momenta contribute, cover the range between 1.1 and 6.4. An interpretation of these spectroscopic splitting factors is presented, which considers the effects of the crystal field - of cubic, axial, or lower symmetry - and of spin-orbit interaction on the  $^4F$  ground state of the iron ion in a  $(3d)^7$  configuration. It is concluded that the apparent quenching of the orbital angular momentum is not due to a dynamical Jahn-Teller effect, nor due to hybridization. Rather, it is proposed that a significant reduction, by about 80%, of the orbital magnetism arises from covalency.

## INTRODUCTION

Electronic states associated with transition metal impurities in silicon are presently attracting much attention. The interest in these complexes is stimulated by the intriguing interactions between the d-electrons on the transition metal impurity and the s- and p-valence electrons of the host. Significant progress in the theoretical understanding was obtained recently by solving the wave equation using the Green's function method in self-consistent spin-unrestricted all-electron calculations [1]. As regards experimental research, the ENDOR technique, which can yield a wealth of information on impurity and ligand hyperfine interactions, made the main contribution. Extensive investigations of neutral interstitial iron, configuration  $(3d)^8$ , and positive interstitial titanium, configuration  $(3d)^3$ , were reported [2,3]. These studies have revealed interesting complexities in the charge distribution and resulting spin interactions, which are related to the many-electron character. The paramagnetic g-values of iron-acceptor pairs contain substantial contributions from the orbital angular momenta. An analysis of these spectroscopic splitting factors therefore provides information on the spatial extent of the wavefunction.

Iron-acceptor pairs in silicon consist of a positively charged iron ion, on an interstitial lattice site, in the vicinity of a negative substitutional acceptor. In the simplest model, the paramagnetism of the pair arises from the three unpaired electrons of the iron impurity, which is in a  $(3d)^7$  configuration. The spin density on the ionized acceptor is small. The iron free-ion ground state  $^4F$  is split by the cubic field of the silicon crystal leaving a  $^4T_1$  state lowest. This isolated iron ground state experiences the field of the negative acceptor, which depending on the lattice positions occupied, has trigonal or lower symmetry. With additional spin-orbit interaction the twelve-fold degenerate  $^4T_1$  level will eventually split into 6 doublets. These interactions are schematically, not to scale, depicted in figure 1. Electron paramagnetic resonance, which is performed in the lowest of these doublets, can be described with an effective spin  $J=1/2$ . The resonances are characterized by rather uncommon g-values as the result of the complicated scheme of interactions on the electrons participating. Resonances have been observed for all iron-acceptor pairs - boron [4,5], aluminum [6], gallium [4] and indium [4] - and also for two other complexes, labelled A27 [7] and A28 [7], which appear to have a similar electronic structure. g-Values are given in the tables I and

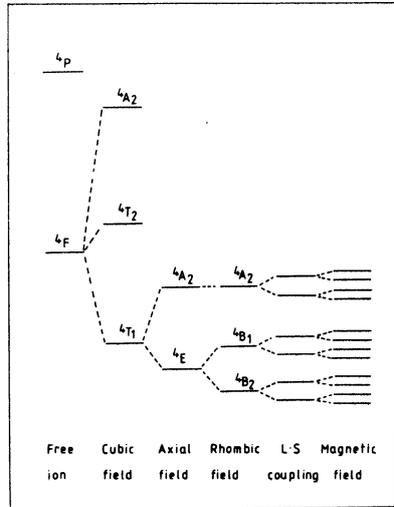


Figure 1. Energy-level diagram for the  $(3d)^7 \text{Fe}^+$ -ion.

II. It is the aim of this paper to extract from the analysis of the g-values a better understanding of the charge and spin-densities of the defect electrons.

#### AXIAL CRYSTAL FIELD

Since several of the pairs exhibit trigonal symmetry the effect of a  $\langle 111 \rangle$ -axial crystal field is considered first. Isolated interstitial iron, which occupies a cubic T-interstitial site, is automatically included as the special case with  $\Delta_{ax}=0$ . Also included in the analysis are the  $\text{FeAl}_{\text{II}}$  and  $\text{FeIn}$  pairs which, in addition to a predominant axial field, experience a smaller rhombic field component. Similarly, the centers A27 and A28, which have been observed to be monoclinic, have a marked axial character. In these latter cases an artificial perpendicular g-value  $g_{\perp}$  is derived by averaging the actual values of  $g_x$  and  $g_y$ . This mean value is shown in table I; the real values are given in table II.

Hamiltonian operators representing the actions of an axial crystal field (cf), spin-orbit coupling (so) and magnetic field (mf) are given by:

$$H_{cf} = +\Delta_{ax}(1-l_z^2) \quad (1)$$

$$H_{so} = -\alpha\lambda\vec{l}' \cdot \vec{s} \quad (2)$$

$$H_{mf} = -\alpha\mu_B\vec{B} \cdot \vec{l}' + 2\mu_B\vec{B} \cdot \vec{s} \quad (3)$$

The axial crystal field, with strength  $\Delta_{ax}$ , is taken along the z-direction; the spin-orbit coupling constant is  $\lambda$ . As indicated in figure 1 these interactions will further split the  ${}^4T_1$  ground state existing in the cubic field. Because of the three-fold orbital degeneracy an effective angular momentum  $l'=1$  is associated with the  $T_1$ -state. The Landé factor  $\alpha$ , which follows from the transformation properties of the  $T_1$  states under the angular momentum operator, is given by  $\alpha=3/2$  and determines the orbital contribution to the magnetism. The result of diagonalizing the matrix of  $H_{cf}+H_{so}$  on  ${}^4T_1$  was first reported by Abragam and Pryce [8], who also gave the g-values of the magnetic field splitting, represented by  $H_{mf}$ . Their parametric solution is

summarized by:

$$\Delta_{ax} = \alpha\lambda(x-2)(x+1)(x+6)/2x(x+2) \quad (4)$$

$$E = \alpha\lambda(x+3)/2 \quad (5)$$

$$g_{//} = +2-4(\alpha+2)(x^2-12x-12)/(x^4+4x^3+18x^2+24x+24) \quad (6)$$

$$g_{\perp} = +4\{x^4+4x^3+16x^2+24x+2\alpha x^2(x+2)\}/(x^4+4x^3+18x^2+24x+24) \quad (7)$$

For given crystal field, the parameter  $x$  is obtained by solving the cubic equation (4). Since for  $\text{Fe}^+$  the spin-orbit coupling constant  $\lambda$  is negative, the positive root of equation (4) corresponds to the lowest energy  $E$ , i.e. the ground state. The  $g$ -values are calculated in a straightforward manner from the equations (6) and (7). Elimination of  $x$  between these two equations establishes a relation between  $g_{//}$  and  $g_{\perp}$ , still as a function of  $\alpha$ . For the theoretical value  $\alpha=3/2$  this relation is shown in figure 2. Experimental data for the eight centers considered are also plotted in this figure. A comparison of the experimental  $g$ -values with the calculated ones shows quite poor agreement. However, the agreement can be made rather perfect by taking the liberty of changing the value of  $\alpha$  and adopting  $\alpha=0.3$ . The centers FeB, FeIn, A27, and A28 have  $g$ -values ( $g_{//}, g_{\perp}$ ) close to (2,4). This corresponds to the familiar case where a strong negative axial field lifts the four-fold degeneracy of an  $L=0, S=3/2$  spin-quartet and the description of the resonance in the ground state spin-doublet with an effective spin  $J=1/2$ . However, also in this case the small deviations  $\Delta g_{//}=g_{//}-2$  and  $\Delta g_{\perp}=g_{\perp}-4$  appear to be significant. In figure 3 the  $g$ -values near ( $g_{//}, g_{\perp}$ )=(2,4) calculated on the basis of the theory are shown on an expanded scale. It is clear that also the centers FeB, FeIn and A28 require  $\alpha=(0.3\pm 0.05)$  for their interpretation. Once the Landé factor is fixed on an empirical value, an optimal  $\alpha=0.3$  in the present case, an alternative plot of the results as presented in figure 4 can be made. The figure shows that the acceptors boron and indium are fitted by a positive axial field in units of negative  $\lambda$ , whereas the acceptors aluminum and gallium require an axial crystal field of the opposite sign. This meandering chemical trend is not understood. Numerical results from the analysis are included in table I; to calculate  $\Delta_{ax}$  a spin-orbit coupling constant  $\lambda=-14.3$  meV was used [9]. It may be emphasized that in the adopted way of analyzing the results, two unknown parameters  $x$  and  $\alpha$ , or alternatively  $\Delta_{ax}$  and  $\alpha$ , are derived from the two parameters  $g_{//}$  and  $g_{\perp}$  taken from the experiment. The procedure, if successful, then results in exact agreement. The theory yields a lower limit for  $g_{//}$  near 1.99, as can be seen in figure 3. Center A27, with  $g_{\perp}=1.96$ , deviates too strongly from the axial case to allow an interpretation in this approximation.

Obviously, the empirical choice of the Landé factor needs justification. In a first attempt to understand the small value of  $\alpha$ , i.e. the empirical  $\alpha=0.3$  replacing the theoretical  $\alpha=1.5$ , a quenching of the orbital magnetic moment due to the dynamic Jahn-Teller effect may be considered. For isolated interstitial iron, which has cubic symmetry,  $x=2$ , the theoretical  $g$ -value  $g=(10/3)+(2/3)\alpha$  ranges from  $g=13/3$  for  $\alpha=1.5$ , without any quenching, to  $\alpha=0$  and  $g=10/3$  for complete quenching of the orbital moment. The experimental value  $g=3.524$  then corresponds to  $\alpha=0.286$  or 81% quenching, as is easily calculated, or follows from inspection of figure 2. The reduction for  $\text{Fe}^+$  was explained by Ham in terms of the dynamic Jahn-Teller effect of the  $^4T_1$  orbital-triplet ground state [10]. Applying this concept to the pairs FeGa and FeAl<sub>I</sub> one notes that also for these centers the successful analysis requires  $\alpha=0.3$ , i.e. an equal degree of quenching. However, the ground state of these pairs is the E orbital doublet. It is remarkable that the triplet and doublet states would have an equal Ham reduction factor. Even more surprisingly, the pairs FeB, FeIn and the A28-defect have also  $\alpha=0.3$ . Since these centers have an  $A_2$  singlet ground state no Jahn-Teller instability and quenching is expected. On the basis of these results the dynamical Jahn-Teller mechanism as

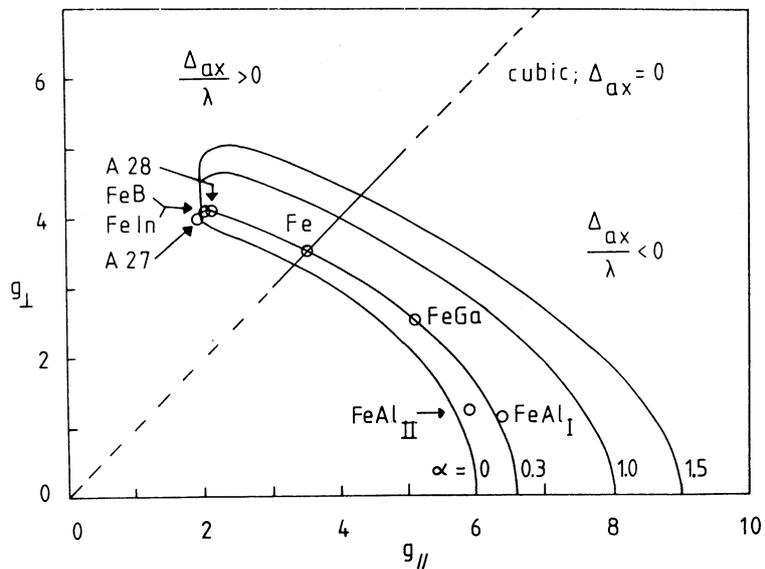


Figure 2. Experimental and theoretical Zeeman splitting factors  $g_{//}$  and  $g_{\perp}$  for a  $(3d)^7$   $Fe^+$  ion in an axial crystal field. For lower site symmetry  $g_{\perp}$  is taken as the mean of  $g_x$  and  $g_y$ .

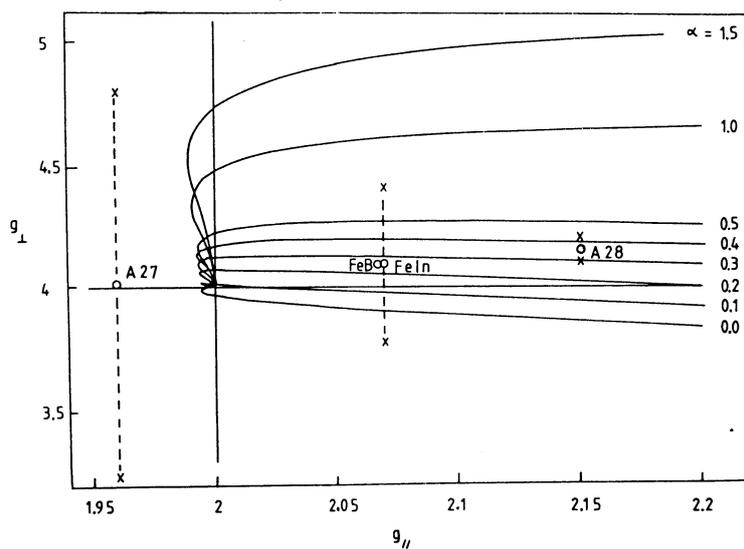


Figure 3. Experimental and theoretical Zeeman splitting factors for a large positive axial field  $\Delta_{ax}/\alpha\lambda$ .

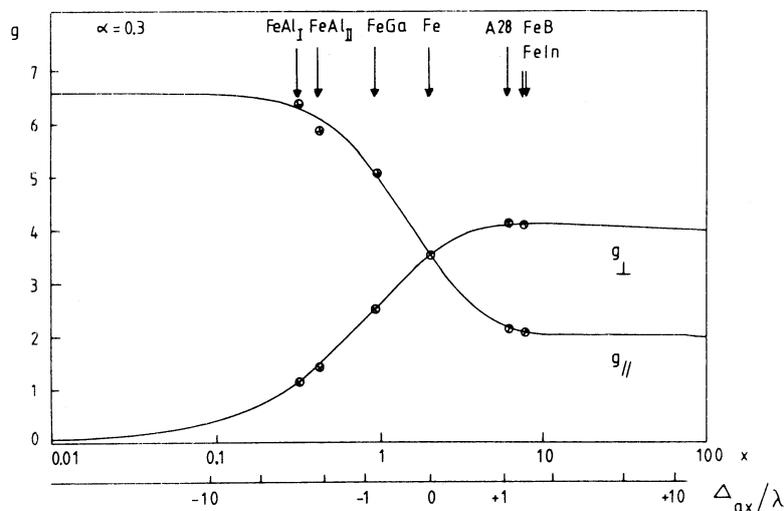


Figure 4. Experimental and theoretical Zeeman splitting factors  $g_{//}$  and  $g_{\perp}$  as a function of the axial crystal field, for an effective Landé factor  $\alpha=0.3$ .

cause of the reduction of  $\alpha$  appears unlikely.

Another way of explaining a reduction of  $\alpha$  is by hybridization. Besides lifting the degeneracy of the  $^4F$  free ion ground state, the cubic crystal field has matrixelements between the  $^4F$  and  $^4P$  excited state wavefunctions. Some P-character, derived from the  $^4P$  term, will be admixed in the  $^4T_1$  state. An improved wavefunction is thus of the form

$$\psi = \eta_F \psi_F + \eta_P \psi_P \quad (8)$$

with the normalization condition  $\eta_F^2 + \eta_P^2 = 1$ . Associated with this hybridized wavefunction the effective Landé factor is

$$\alpha = 1.5\eta_F^2 - \eta_P^2 \quad (9)$$

It can be shown that the admixture of P-functions is bound to a maximum of  $\eta_P^2 = 0.2$ . Corresponding with this maximum a lower limit of 1 is established for  $\alpha$ . Therefore, hybridization, leading to  $1 \leq \alpha \leq 3/2$ , may account for a reduction of  $\alpha$ , but its possible effect is too small to explain the required value  $\alpha = 0.3$ . The lower limit  $\alpha = 1$  corresponds to an infinite cubic field. In a more realistic estimate a maximum strength of the cubic field equal to the  $^4P$ - $^4F$  splitting,  $\approx 1.4$  eV [11], may be assumed. The lower limit for  $\alpha$  is thereby raised to  $\alpha \approx 1.4$ .

Proceeding along similar lines, the effect on the wavefunction by covalent hybridization may be examined. Though the defect electrons are certainly strongly localized on the inner 3d-shell of the transition metal impurity, some silicon ligand s- and p-orbitals will be admixed. This leads to hyperfine interactions with  $^{29}\text{Si}$  nuclei around the center, which experimentally are observable in magnetic resonance. Using electron nuclear double resonance (ENDOR) these hyperfine interactions were measured for a large number of near-neighbor atoms for  $\text{Si}:\text{Ti}^{3+}$  [3] and for  $\text{Si}:\text{Fe}^0$  [2]. In a recently introduced new way of analyzing these data, taking properly account of the many-electron aspects, an estimate for the total density in silicon neighbor orbitals of 25

Table I. Spectroscopic and crystal field data for  $\text{Fe}_i^+$ -related complexes in silicon. The g-values marked \* were obtained by averaging experimental data.

Center	Reference	Symmetry	g-Values		$\alpha$	x	$\Delta_{ax}$ (meV)
			$g_{//}$	$g_{\perp}$			
$\text{Fe}_i^+$	4	Cubic	3.524		0.286	2	0
FeB	5	Trigonal	2.0676	4.0904	0.256	7.513	-16
FeAl <sub>I</sub>	6	Trigonal	6.389	1.138	0.346	0.318	+43
FeAl <sub>II</sub>	6	Rhombic I	5.885	1.424*	0.165	0.420	+17
FeGa	4	Trigonal	5.087	2.530	0.284	0.933	+11
FeIn	4	Rhombic I	2.070	4.09*	0.256	7.444	-16
A27	7	Monoclinic I	1.96	4.01*	-	-	-
A28	7	Monoclinic I	2.15	4.15*	0.360	6.029	-18

to 40% was obtained [3]. Unfortunately, for  $\text{Si}:\text{Fe}_i^+$  the ENDOR experiment has not yet been performed. An LCAO wavefunction is represented by

$$\psi = \eta_{\text{Fe}} \psi_{\text{Fe}} + \eta_{\text{Si}} \psi_{\text{Si}} \quad (10)$$

again normalized by  $\eta_{\text{Fe}}^2 + \eta_{\text{Si}}^2 = 1$ . For the d-orbitals on the iron ion the Landé factor  $\alpha_d = 3/2$  applies and a spin-orbit coupling constant  $\lambda_{\text{Fe}} = -14.3$  meV [9]. The p-orbitals on the silicon atoms have  $\alpha_p = -1$  and for these orbitals  $\lambda_{\text{Si}} = -20$  meV was estimated [11,12]. Since  $\lambda_{\text{Si}} = \lambda_{\text{Fe}}$  an effective Landé factor for equations (2) and (3) may be approximated by

$$\alpha = (3/2)\eta_{\text{Fe}}^2 - \eta_{\text{Si}}^2 \quad (11)$$

A numerical example with  $\eta_{\text{Si}}^2 = 0.48$  results in the desired value  $\alpha = 0.30$ . Covalency can therefore account in a reasonable way for the observed reduction of orbital magnetism.

#### RHOMBIC CRYSTAL FIELD

In the preceding paragraph the rhombic centers, and also the monoclinic ones, were forced to behave as axial centers, in order to comply with the requirements of the analysis. However, the analysis can be made more general by using the appropriate crystal field potential for the lower-symmetry centers. A rhombic crystal field represented by

$$H_{\text{cf}} = \Delta_{\text{ax}}(1 - 1_z^2) + \Delta_{\text{rh}}(1_x^2 - 1_y^2) \quad (12)$$

will replace the axial crystal field of equation (1). Analytic solutions, as given in the previous paragraph, are no longer available, but numerical solutions are easily computed. The 6x6 matrix which has to be diagonalized and the formula's to calculate the g-values are given in reference [6]. Again the number of unknowns to be determined, i.e.  $\Delta_{\text{ax}}$ ,  $\Delta_{\text{rh}}$  and  $\alpha$ , equals the number of equations to be satisfied, i.e. for  $g_x$ ,  $g_y$  and  $g_z$ . As a result the unambiguous solutions as given in table II are obtained for the centers FeIn, A27 and A28. The latter center, for which it was not possible to find a solution in the axial approximation, does not present any problem using the generalized crystal field of equation (12). The analysis of these rhombic and monoclinic centers confirms the reduced value  $\alpha \approx 0.3$ . For FeAl<sub>II</sub>, which has a large positive axial field, an exact solution can not be obtained and a best fit leaves ambiguities in the crystal field parameters. The parameters as given in table II,  $\alpha = 0.3$ ,  $\Delta_{\text{ax}} = +66$  meV and  $\Delta_{\text{rh}} = 13$  meV, result in calculated  $g_x = 1.240$ ,

Table II. Spectroscopic and crystal field data for rhombic I and monoclinic I  $\text{Fe}^+$ -related complexes in silicon. The choice  $\alpha=0.3$  for  $\text{FeAl}_{\text{II}}$  is discussed in the text.

Center	Reference	Symmetry	g-Values			$\alpha$	$\Delta_{\text{ax}}$ (meV)	$\Delta_{\text{rh}}$ (meV)
			$g_x$	$g_y$	$g_z$			
$\text{FeAl}_{\text{II}}$	6	Rhombic I	1.236	1.612	5.885	0.3	+66	13
$\text{FeIn}$	4	Rhombic I	3.78	4.40	2.070	0.268	-16	1.3
A27	7	Monoclinic I	3.24	4.78	1.96	0.188	-13	2.6
A28	7	Monoclinic I	4.10	4.20	2.15	0.360	-18	0.3

$g_y=1.609$  and  $g_z=5.885$ . On the other hand, the quite different parameters as given in reference [6],  $\alpha=1.5$ ,  $\Delta_{\text{ax}}=+1.579$  eV and  $\Delta_{\text{rh}}=0.390$  eV resulting in  $g_x=1.238$ ,  $g_y=1.611$  and  $g_z=5.885$  give a fit with comparable good agreement. Reversing the argument by requiring  $\alpha=0.3$ , thus rejecting  $\alpha=1.5$ , the crystal field parameters of table II are considered preferable.

In summary, a mathematical framework, with physical background, has been presented which allows the interpretation of the electronic ground state, i.e. the Zeeman splitting factors, of the interstitial positive  $\text{Fe}_i^+$ -ion, configuration  $(3d)^7$ , in silicon, either as a cubic isolated impurity, or as part of a complex in lower symmetry. Crystal fields and spin-orbit interaction determine the ground state properties. The reduction of orbital magnetism to one fifth is not due to a dynamic Jahn-Teller effect, is possibly to a very small part caused by intra-atomic hybridization, whereas a significant reduction arises from covalency.

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