Investigation Of Selected Paramagnetic Centers In Semiconductors



Magnetic Field (mT)

Peter Stallinga

Investigation of Selected Paramagnetic Centers in Semiconductors

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Academisch Proefschrift Universiteit van Amsterdam Academic Thesis University of Amsterdam

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Abstract

The thesis describes the investigation of paramagnetic centers in silicon, GaAs, AlGaAs and SiC. Emphasis is given to hydrogen-implanted silicon, with as highlight the EPR spectrum of molecular hydrogen (Si:NL52). A possible link between this spectrum and the surface defect P_b is studied. Another defect studied is the meta-stable DX center in ternary III-V compounds. As an introduction, group theory and its application to magnetic resonance spectroscopy is presented.

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Investigation Of Selected Paramagnetic Centers In Semiconductors

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"We need more power Igor !" - Dr. Frankenstein



S.I.R.D. by the author

Aan mijn ouders Tjerk en Anna en mijn broers Eric en Thomas

Contents

1	Gro	up theory in solid state physics	1
	1.1	Introduction	1
	1.2	Definition of a group	1
	1.3	Representations	5
	1.4	Characters and character tables	6
	1.5	Reduction of representations	7
	1.6	Wave functions, energies and symmetry	10
	1.7	More than one electron \ldots \ldots \ldots \ldots \ldots \ldots	14
		1.7.1 Inequivalent electrons	14
		172 Equivalent electrons.	14
	18	Spin	15
	1.0	1.8.1 Weak crystal field	15
		1.8.2 Intermediate or strong crystal field	17
	10	Lowering symmetry	17
	1.0	Comparison with Hamiltonian method	19
	1 11	Nomenclature and magnetic resonance	20
	1.11	1.11.1 Special case: silicon-carbide	26
2	Elec	tron paramagnetic resonance of silicon carbide	29
	2.1	Introduction to EPR	29
	2.2	Introduction to SiC	29
	2.3	Experimental details	31
	2.4	Experimental results and discussion	33
3	DX	Centers in Ternary Compounds	41
-	3.1	Introduction	41
	0.2	3.1.1 Definition of DX	41
	32	Band structure and energy levels	42
	3.3	Large lattice relaxation	44
	3.4	Microscopic models	48
	0.1	3.4.1 Small lattice relaxation	51
	3.5	EPB experiments	52
	3.6	Valley-orbit splitting	55
	3.5 3.6	EPR experiments	52 55

4	Hyd	drogen in silicon	60
	4.1	Introduction	60
		4.1.1 Diffusion of hydrogen	60
		4.1.2 Lattice positions \ldots	63
		4.1.3 Hydrogen introduction into the lattice	64
	4.2	The Si-NL51 spectrum	65
		4.2.1 Experimental details	65
		4.2.2 Results	66
		4.2.3 Discussion	68
5	Ide	ntification of hydrogen molecules in silicon	72
	5.1	Introduction	72
	5.2	Results	76
	5.3	Discussion	79
6	Ар	ossible new identification of the \mathbf{P}_b defect	83
	6.1^{-1}	Introduction	83
	6.2	Comparison of the P_b and Si-NL52 spectra \ldots \ldots	84
	6.3	Intermezzo: Spectrum distortion	88
		6.3.1 Saturation of the EPR lines	88
		6.3.2 Nuclear core polarization	90
		6.3.3 Defect band formation	93
		6.3.4 Motional averaging	94
	6.4	Superhyperfine structure	95
		6.4.1 Field-scanned ENDOR	97
	6.5	Critical remarks	99
		6.5.1 Oxygen in the defect structure	99
		6.5.2 LCAO analysis	101
		6.5.3 Deuterium implantation	102
	Ар	pendix 1	.06
	A	Fundamental physical constants	106
	В	Hyperfine interactions with isotopes	107
	С	LCAO hyperfine interaction parameters for hydrogen	109
	Sun	nmary 1	11
	San	nenvatting 1	12
	Nav	voord 1	14

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Chapter 1

Group theory in solid state physics

1.1 Introduction

Group theory finds its applications in many fields, ranging from nuclear physics, where even new particles can be predicted using the techniques of this theory to more societyoriented subjects like architecture. In solid state physics, group theory can find its use where the calculations of the studied systems are too complicated or too time consuming. Other cases involve considerations of theoretical models in which the values of the parameters are not well established. In that case still a lot of information can be obtained using purely group theoretical calculations. For instance, the degeneracy of levels of electrons in a semiconductor can be calculated, even if only the symmetry of the Hamiltonian is known. To show how this is achieved, first a brief introduction into the mathematics of group theory and then its application to the field of solid state physics.

1.2 Definition of a group

A group is a set of operations that satisfy the following rules:

1. It is closed; the "product" of two elements is also a member of the group:

$$\forall A, B \in G : AB \in G. \tag{1.1}$$

NB: the product is not yet defined and can have many forms (like matrix multiplication).

2. There exists in the group a **unity** element E, such that

$$\forall A \in G : EA = AE = A. \tag{1.2}$$



Figure 1.1: An example of C_{3v} symmetry.

3. Of every element of the group there is also an inverse:

$$\forall A \in G : \exists A^{-1} \in G, AA^{-1} = E.$$

$$(1.3)$$

4. The **associative** law holds:

$$\forall A, B, C \in G : A(BC) = (AB)C. \tag{1.4}$$

As a special case, Abelian groups are those in which the elements follow the rule

$$\forall A, B \in G : AB = BA. \tag{1.5}$$

Alternatively, a group can be seen as a set of operations that leave a specific object invariant. An equilateral triangle is invariant under unity (of course), rotations of $\pm 120^{\circ}$ and $\pm 120^{\circ}$, around an axis through its centre, perpendicular to the plane of the triangle, and reflections in lines bisecting the angles of the triangle (see Figure 1.1). Thus the elements of the associated group (C_{3v}) are: $E, R_{120}, R_{-120}, m_1, m_2, m_3$. Or, in a more compact notation: $E, 2C_3, 3\sigma$. The names of the elements follow the standard Schoenflies notation, see Table 1.1. The name of the group is a direct result of the symmetry operations contained within the group, see Tables 1.2 and 1.3 and Figures 1.2a and 1.2b. In Figure 1.2a a mark is placed at a general point on a unit sphere which is then subjected to all the various symmetry operations of the group. If the point is above the projection plane the symbol \pm is used, for points below the plane a \bigcirc is used. The rotation axes are indicated by characteristic symbols. A solid circumference indicates a horizontal mirror plane, a dashed one means a vertical mirroplane, perpendicular to the plane of paper, and a solid line means a D₂ (see Table 1.2) axis.
 Table 1.1: Schoenflies notation for point group elements.

E	Identity. (Always present in the group)
C_n	Rotation over $2\pi/n$ (in crystals $n \in \{1, 2, 3, 4, 6\}$).
σ_h	Reflection in a horizontal plane with respect to principal axis.
σ_v	Reflection in a vertical plane.
σ_{d}	Reflection in a diagonal plane.
i	Coordinate inversion or parity operator $(x \rightarrow -x, y \rightarrow -y, z \rightarrow -z)$.
S_n	Improper rotation over $2\pi/n$ (a rotation C_n followed by coordinate
	inversion i). $(S_1 = i, S_2 = \sigma)$.

Table 1.2: Simple point group names.

C_n	These groups consist of E and a <i>n</i> -fold rotation C_n .
C_{nv}	In addition to the elements of C_n , C_{nv} also contains a σ_v
	reflection plane.
C_{nh}	C_n plus a σ_h reflection.
S_n	E and a n -fold improper rotation.
D_n	These groups have n twofold axes perpendicular to the principal
	C_n axis and E .
D_{nd}	Together with the element of D_n , these groups contain diagonal
	reflection planes σ_d .
D_{nh}	Identical to D_{nd} , but with <i>horizontal</i> reflection planes σ_h instead.

 Table 1.3: Point groups of higher symmetry.

T	Contains all 12 proper rotations which take a regular tetrahedron
	into itself.
T_d	The full tetrahedral group contains all operations which leave
	a regular tetrahedron invariant (24 elements). For example CH_4 or
	the silicon lattice (with respect to lattice sites).
T_h	Direct product group of T with the inversion, $T_h = T \otimes i$ (24 elements).
0	All the proper rotations which take a cube or octahedron
	into itself (24 elements).
O_h	Direct product of O and $i_{h} = O \otimes i$ (48 elements).



2-fold axis ⊥ paper 0 Mirrorplane ⊥ paper paper ≠ mirrorplane Δ 3-fold axis ⊥ paper 2-fold axis in paper ٥ Object above paper Object below paper 4-fold axis ⊥ paper paper = mirrorplane Ó ο 6-fold axis ⊥ paper proper - improper



Figure 1.2: a: (previous page) simple point groups. b: point groups of higher symmetry O and T.

A direct product group $G_{\otimes} = G_1 \otimes G_2$ is constructed by taking all combinations of the individual groups:

$$g_1 \in G_1, g_2 \in G_2 \Rightarrow g_1 g_2 \in G_{\otimes}. \tag{1.6}$$

1.3 Representations

A representation of a group is a set of mathematical entities with a function like (homomorphic) relation to the group. As an example some representations of the group C_{3v} are

• Matrix representation in 2-dimensional space:

$$E = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \quad R_{120} = \frac{1}{2} \begin{pmatrix} -1 & \sqrt{3} \\ -\sqrt{3} & -1 \end{pmatrix}, \quad R_{-120} = \frac{1}{2} \begin{pmatrix} -1 & -\sqrt{3} \\ \sqrt{3} & -1 \end{pmatrix},$$
$$m_1 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \quad m_2 = \frac{1}{2} \begin{pmatrix} -1 & \sqrt{3} \\ \sqrt{3} & 1 \end{pmatrix}, \quad m_3 = \frac{1}{2} \begin{pmatrix} -1 & -\sqrt{3} \\ -\sqrt{3} & 1 \end{pmatrix}.$$

• (Wave)functions. Any set of functions (f_g) which is invariant under coordinate transformations defined by the matrices above is a representation.

$$\forall g \in G : f_g(g^{-1}\bar{x}) = f_g(\bar{x}). \tag{1.7}$$

• Permutations. An example of a permutation representation is

$$E = (1, 2, 3) \rightarrow (1, 2, 3),$$

$$R_{120} = (1, 2, 3) \rightarrow (2, 3, 1),$$

$$R_{-120} = (1, 2, 3) \rightarrow (3, 1, 2),$$

$$m_1 = (1, 2, 3) \rightarrow (1, 3, 2),$$

$$m_2 = (1, 2, 3) \rightarrow (3, 2, 1),$$

$$m_3 = (1, 2, 3) \rightarrow (2, 1, 3).$$

This can be made clear by regarding the permutations of the corners of the triangle; for example R_{120} projects corner 1 on corner 2, corner 2 on corner 3 and corner 3 on corner 1 (see Figure 1.1). Thus $R_{120} = (1,2,3) \rightarrow (2,3,1)$.

1.4 Characters and character tables

The character χ of a group element g of a representation is defined as the trace of the accompanying matrix R_g :

$$\chi(g) = Tr R_g. \tag{1.8}$$

The set of characters of all elements belonging to the same representation (rep) is called the character vector of the rep. Some remarks on this:

- *χ*(E) = dim(R): the character of the unity element is equal to the dimension of the representation.
- χ(AB) = χ(A)χ(B): The character of the product of two reps is the product of
 the characters of the individual reps.

An example of the characters of the two- and three-dimensional matrix representations (M2 and M3) and the permutation representation (P) of the group C_{3v} are given in Table 1.4 and in short notation, using Schoenflies convention, in Table 1.5. Here the identical columns of the table are condensed in a single "class". The multiplicity of the class is indicated in the label (e.g. $3\sigma_v$). Finding the character vector for a matrix representation is straightforward, although not unique; it depends on the dimension of the matrices as can be seen directly in the character of E. The other characters also depend on the dimension of the matrices. Compare the two-dimensional (M2) with the three-dimensional matrix representation (M3) in Table 1.4. Finding the characters for other representations will prove to be more difficult. A simple method is the following:

C_{3v} .	E	R_{120}	R_{-120}	m_1	m_2	m_3
χ_{M2}	2	-2	-2	0	0	0
χ_{M3}	3	-2	-2	1	1	1
χ_P	3	0	0	1	1	1

Table 1.4: Character vectors of some representations of C_{3v} .

Table 1.5: Character vectors of reps of C_{3v} .

C_{3v}	$\mid E \mid$	$2C_3$	$3\sigma_v$
M_2	2	-2	0
M_3	3	-2	1
P	3	0	1

Expand the representation to a pseudo matrix rep. The permutation rep can for instance be written as

$$E = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \quad R_{120} = \begin{pmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix}, \quad R_{-120} = \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{pmatrix},$$
$$m_1 = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}, \quad m_2 = \begin{pmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{pmatrix}, \quad m_3 = \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}.$$

Now the trace can be taken, resulting in the character vector above. An example of matrix expansion for wave functions will be given in a next section.

1.5 Reduction of representations

Representations are often reducible which means that they can be written as a linear combination of other (non reducible) representations (reps):

$$\Gamma = \sum_{i} \alpha_{i} \Gamma_{i}.$$
(1.9)

Representations which are not reducible are said to be irreducible. In character tables the character vectors of the irreducible reps (irreps) of a group are tabulated. See for example Table 1.6 The names of the irreps indicate the dimension of these reps:

A or B for one-dimensional,

Table 1.6: Character table for C_{3v} .

C_{3v}	E	$2C_3$	$3C_2$
A_1	1	1	1
A_2	1	1	-1
E	2	-1	0

E for two-dimensional, T for three-dimensional.

Often used subscripts are g and u, which indicate an even (gerade) and an odd (ungerade) representation under inversion (if inversion is present in the group):

$$A_g, B_g: \chi(i) = 1,$$
 (1.10)

$$A_u, B_u: \chi(i) = -1. \tag{1.11}$$

To distinguish between them, different reps with the same name get an index (e.g., A_1). The character tables have some special features caused by the orthogonality theorems:

1. Columns of character tables are orthogonal:

$$\sum_{\Gamma} \chi_{\Gamma}(R_1) \chi_{\Gamma}(R_2) = \begin{cases} 0, & R_1 \neq R_2, \\ N_{group}/N_{class}, & R_1 = R_2. \end{cases}$$
(1.12)

where the sum is taken over all irreps and R_1 and R_2 are two group elements.

2. Rows of a character table are orthonormal (i.e. irreps are orthogonal):

$$\sum_{R} n(R)\chi_{\Gamma_1}(R)\chi_{\Gamma_2}(R) = \begin{cases} 0 & \Gamma_1 \neq \Gamma_2, \\ \sum_{R} n(R), & \Gamma_1 = \Gamma_2. \end{cases}$$
(1.13)

where the sum is taken over all group elements, Γ_1 and Γ_2 are two group elements and n(R) is the multiplicity factor of R (the number of times R appears in the group).

A general representation Γ does not have the orthogonality property and the orthogonality theorems provide a way to decompose it. A reducible rep can always be written as a linear combination of irreps, i.e., Γ takes the form of equation 1.9. Decomposing Γ consists of finding the coefficients α_i . According to theorem 2 and Equation 1.9 the "inproduct" of Γ with Γ_i is

$$\sum_{R} \chi_{\Gamma}(R) \chi_{\Gamma_i}(R) = \alpha_i \sum_{R} n(R) \chi_{\Gamma_i}(R) \chi_{\Gamma_i}(R), \qquad (1.14)$$

and because the sum in the right hand side of the equation can be calculated from the character table, α_i is easily found.

A different way of finding the coefficients is solving the set of equations

$$\chi_{\Gamma}(R_1) = \alpha_1 \chi_{\Gamma_1}(R_1) + \alpha_2 \chi_{\Gamma_2}(R_1) + \dots + \alpha_n \chi_{\Gamma_n}(R_1)$$

$$\vdots \qquad (1.15)$$

$$\chi_{\Gamma}(R_n) = \alpha_1 \chi_{\Gamma_1}(R_n) + \alpha_2 \chi_{\Gamma_2}(R_n) + \dots + \alpha_n \chi_{\Gamma_n}(R_n).$$

This consists of calculating the "inverse" of the character table and multiplying it by the known character vector $\chi_{\Gamma}(R_1) \cdots \chi_{\Gamma}(R_n)$, giving the coefficients $\alpha_1 \cdots \alpha_n$. The advantage of this scheme is that less information of the group needs to be known; the multiplicity factors n(R) are not necessary for the calculation and not always are they tabulated in the group tables. Moreover, because the coefficients are often simple (like zeros and ones) they are directly visible.

If one of the resulting coefficients is not a integer positive number then the representation is non-reducible, otherwise it is reducible.

Take, for example, the group C_{3v} again. Assume there is a representation with a character vector

$$\begin{array}{c|cccc} C_{3v} & E & 2C_3 & 3C_2 \\ \hline \chi_{\Gamma} & 3 & 0 & -1 \end{array}$$

Clearly Γ must be equal to $A_2 + E$. This can be proven by first calculating the inverse table which gives:

$$\frac{1}{6} \left(\begin{array}{rrr} 1 & 2 & 3 \\ 1 & 2 & -3 \\ 2 & -2 & 0 \end{array} \right).$$

Multiplying this by the character vector of Γ gives the coefficients vector α :

$$\alpha = \frac{1}{6} \begin{pmatrix} 1 & 2 & 3 \\ 1 & 2 & -3 \\ 2 & -2 & 0 \end{pmatrix} \begin{pmatrix} 3 \\ 0 \\ -1 \end{pmatrix} = \begin{pmatrix} 0 \\ 1 \\ 1 \end{pmatrix}.$$

So the starting representation is reducible because the coefficient vector consists of only positive integers. The Γ is thereby reducible to

$$\Gamma = A_2 + E. \tag{1.16}$$



Figure 1.3: Degeneracy in various symmetries.

1.6 Wave functions, energies and symmetry

These group-theoretical results can now be used in determining the degeneracy of energy levels in crystals. The principle of the calculations is that the degeneracy of the energy levels is determined by the dimensions of the representations. So if for example a representation of wave function reduces to

$$\Gamma = A_2 + E, \tag{1.17}$$

it implies that there are two energy levels: a singlet (A_2) and a doublet (E) (see Figure 1.3). Most often one is interested in the degeneracy of s,p,d ... electrons in crystals of known symmetry. The determination of the degeneracy consists of calculating the character vector and then reducing it.

Neglecting the radial dependent parts, which have no effect in this calculation, orbitals have the form of spherical harmonics:

$$Y_l^m = P_l^{|m|}(\cos\theta) \cdot e^{im\phi}, \qquad (1.18)$$

where $P_l^{|m|}$ is an associated Legendre polynomial and m has the integral values $-l, -l+1, \dots, l$. The first few spherical harmonics are:

$$s(l=0)$$
 : $Y_0^0 \propto 1$, (1.19)

$$p(l=1)$$
 : $Y_1^0 \propto z$, (1.20)

$$Y_{1}^{\pm 1} \propto x \pm iy,$$

$$d(l = 2) : Y_{2}^{0} \propto 2z^{2} - x^{2} - y^{2},$$

$$Y_{2}^{\pm 1} \propto (x \pm iy)z,$$

$$Y_{2}^{\pm 2} \propto (x \pm iy)^{2}.$$
(1.21)

These angular dependencies allow for a calculation of the character vectors of the electrons.

<u>Unity E</u>. The character is always the dimension of the representation, here the number of functions or the starting degeneracy of the energies, so

$$\chi_s(E) = 1, \ \chi_p(E) = 3, \ \chi_d(E) = 5, \ \cdots$$
 $\chi_l(E) = 2l + 1.$
(1.22)

<u>Rotations C_n </u>. The z-direction of 1.18 is not yet determined and can conveniently be choosen to lie along the rotation axis. Then

$$C_{\alpha}Y_{l}^{m}(\theta,\phi) = Y_{l}^{m}(\theta,\phi-\alpha) = e^{im\alpha} \cdot Y_{l}^{m}(\theta,\phi), \qquad (1.23)$$

or in matrix notation (basis Y_l):

$$C_{\alpha} = \begin{pmatrix} e^{-il\alpha} & 0 & \cdots & 0 \\ 0 & e^{-i(l-1)\alpha} & \cdots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \cdots & e^{il\alpha} \end{pmatrix}.$$
 (1.24)

Hence the character is

$$\chi_l(C_\alpha) = e^{-il\alpha} + \dots + e^{il\alpha}, \qquad (1.25)$$

$$\chi_l(C_n) = \frac{\sin((2l+1)\pi/n)}{\sin(\pi/n)}.$$
(1.26)

Inversion *i*. An inversion means in 1.18 substituting $\theta \to \pi - \theta$ and $\phi \to \pi + \phi$, therefore $P_l^{|m|}(\cos \theta) \to (-1)^{l+m} P_l^{|m|}(\cos \theta)$ and $e^{im\phi} \to (-1)^m e^{im\phi}$. The result is:

$$\chi_l(i) = (2l+1)(-1)^l. \tag{1.27}$$

<u>Reflections</u> σ . For the special reflections $\sigma_h(x \to x, y \to y, z \to -z)$, $\sigma_v(x \to -x, y \to y, z \to z)$ and $\sigma_d(x \to y, y \to x, z \to z)$ the characters can easily be calculated:

s-electrons. s-Electron wave functions are spherically symmetric (see Equation 1.19), so, every point group symmetry operation is a covering operation, hence $\sigma s = s$ and $\chi_s = 1$.

p-electrons. There are 3 p-electron wave functions; one in every principal cartesian direction. A horizontal reflection takes p_x and p_y wave functions into itself and p_z into its negative (see Figure 1.4).

$$\sigma_{h,p} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \Rightarrow \chi_p(\sigma_h) = 1.$$
(1.28)



Figure 1.4: p-orbitals $(p_x, p_y, and p_z respectively)$.

For a vertical reflection $\sigma_v \ (p_x \rightarrow -p_x, p_y \rightarrow p_y, p_z \rightarrow p_z)$:

$$\sigma_{v,p} = \begin{pmatrix} -1 & 0 & 0\\ 0 & 1 & 0\\ 0 & 0 & 1 \end{pmatrix} \Rightarrow \chi_p(\sigma_v) = 1.$$
(1.29)

For diagonal reflections $\sigma_d (p_x \rightarrow p_y, p_y \rightarrow p_x, p_z \rightarrow p_z)$:

$$\sigma_{d,p} = \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} \Rightarrow \chi_p(\sigma_d) = 1.$$
(1.30)

d-electrons. From Equations 1.21 can be seen:

$$\sigma_{h,d} = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{pmatrix} \Rightarrow \chi_d(\sigma_h) = 1,$$
(1.31)

$$\sigma_{v,d} = \begin{pmatrix} 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 \end{pmatrix} \Rightarrow \chi_d(\sigma_v) = 1,$$
(1.32)

$$\sigma_{d,d} = \begin{pmatrix} 0 & 0 & 0 & 0 & -1 \\ 0 & 0 & 0 & i & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 0 & i & 0 & 0 & 0 \\ -1 & 0 & 0 & 0 & 0 \end{pmatrix} \Rightarrow \chi_d(\sigma_d) = 1.$$
(1.33)

l		E	i	C_n	S_n	σ		
0	s	1	1	1	1	1		
1	p	3	-3	$Q_{3,n}$	$-Q_{3,n}$	1		
2	d	5	5	$Q_{5,n}$	$Q_{5,n}$	1		
3	f	7	-7	$Q_{7,n}$	$-Q_{7,n}$	1		
:	÷	:	:	÷		÷		
l		2l + 1	$(2l+1)(-1)^l$	$Q_{2l+1,n}$	$(-1)^{l}Q_{2l+1,n}$	1		
	$Q_{m n} = \sin(m\pi/n) / \sin(\pi/n)$							

Table 1.7:Characters for electrons.

From this the characters of reflections of all electrons can be extrapolated to be

$$\chi_i(\sigma) = 1. \tag{1.34}$$

<u>Improper rotations</u>. Because improper rotations are rotations followed by a coordinate inversion the matrices are easily found by simple multiplication of the rotation and the inversion matrices. With the knowledge that the matrix of inversion is -11, with 11 the unity matrix, this leads to the result:

$$\chi_l(S_n) = (-1)^l \chi_l(C_n).$$
(1.35)

This also proves that an improper rotation is not a reflection after a rotation, but an inversion after a rotation. Using the former definition (of Tinkham [1]), the calculation of the character gives a totally different answer. Then the representations would not have been reducible as it is now. A survey of the characters is given in Table 1.7

As an example electrons in a lattice of cubic (O) symmetry. The group table of O is given in Table 1.8. The degeneracy of levels for electrons in cubic symmetry can be calculated and is also given in Table 1.8. From these two tables it can be concluded that the f septet splits under influence of a cubic crystal field into a singlet and two triplets

$$s \rightarrow A_{1}, \qquad (1.36)$$

$$p \rightarrow T_{1}, \qquad (1.36)$$

$$d \rightarrow E + T_{2}, \qquad f \rightarrow A_{2} + T_{1} + T_{2}.$$

0	E	$8C_3$	$3C_2$	$6C_2$	$6C_4$
A_1	1	1	1	1	1
A_2	1	1	1	-1	-1
E	2	-1	2	0	0
T_1	3	0	-1	-1	1
T_2	3	0	-1	1	-1
s	1	1	1	1	1
p	3	0	-1	-1	1
d	5	-1	1	1	-1
f	7	1	-1	- 1	-1

Table 1.8: Character table for group O.

Table 1.9: Example of two inequivalent electrons.

0	E	$8C_3$	$3C_2$	$6C_2$	$6C_4$
-3d	5	-1	1	1	-1
4d	5	-1	1	1	-1
3d4d	25	1	1	1	1

1.7 More than one electron

1.7.1 Inequivalent electrons

In the case of inequivalent electrons the character of the representation is found by simply taking the product of characters of the individual reps. Take for example a 3d and a 4d electron in a cubic crystal field. The 25-fold degenerate level splits into 3 singlets, 2 doublets and 6 triplets (see also Table 1.9):

$$3d4d \to 2A_1 + A_2 + 2E + 3T_1 + 3T_2, \tag{1.37}$$

see Table 1.9

1.7.2 Equivalent electrons.

Hund's rules can be used to fill the levels: The state having lowest energy is that one having

- 1. maximum total spin (considered in the next section),
- 2. maximum total orbital momentum consistent with (1),

d	1	2	3	4	5	6	7	8	9	10	total
	x	x									
m_l	2	1	0	-1	-2	2	1	0	-1	-2	3
m_s	1/2	1/2	1/2	1/2	1/2	-1/2	-1/2	-1/2	-1/2	-1/2	1

Table 1.10: Construction of a two-electron level following Hund's rules.

3. obeyed Pauli's exclusion principle.

The spin (S) and orbital momentum (L) are then combined into a total angular momentum (J). J can have all integral or half integral (depending on S) values between L-S and L+S. The lowest state however is that one having highest J if the shell is more than half filled and lowest J otherwise. The notation for the total state is then ${}^{2S+1}X_J$, with X indicating total L (S, P, D, F, \cdots) . The orbital degeneracy can then be calculated just as before, only now with the total L. Take for instance two 3delectrons. According to Hund's rules they result in a ${}^{3}F_{2}$ -state. So the levels are just the same as with a single f-electron:

$$3d^2(=F) \to A_2 + T_1 + T_2$$
 (1.38)

1.8 Spin

To calculate the degeneracies, the spin of the electrons has been ignored, so far. The electron-spin will now be introduced in the calculations.

When there is no spin-orbit coupling, then L and S are not mixed (are still good quantum numbers) and the degeneracies can be calculated independently. When there is spin-orbit coupling, then strength of the crystal field determines the strategy for the calculations. The cases of weak and intermediate strong crystal field will be considered seperately.

1.8.1 Weak crystal field

In the case of a weak crystal field ($\approx 10^2 \text{ cm}^{-1}$), the spin-orbit coupling ($\approx 10^3 \text{ cm}^{-1}$) is of greater importance than the crystal field. The ground state is described by the total angular momentum J, as discussed in the previous section. There are two possibilities, either J is integral or J is half integral. If J is integral the characters of the wave functions can be calculated as before, only now with J instead of L. If J is half integral the characters are no longer the same. This stems from the fact that a rotation over an angle 2π no longer leaves the system invariant. This makes the character of all C_{α} 's different. The problem is solved by referring to the double groups (denoted by a prime, e.g. $C_{3\nu}$ becomes $C'_{3\nu}$). The lowest possible degeneracy is a doublet, known as a Kramers doublet, which can only be lifted by a magnetic field.

The character table of the double group can be calculated from the corresponding normal group in the following way:

- 1. Introduce a new 2π rotation R
- 2. Add to the elements of the group all combinations of R with all its C_n 's, except C_2 (if there is a C_2 axis perpendicular to the R-axis, otherwise add RC_2 anyway), because $RC_2 = C_2$.
- 3. Add as many new reps to the group table as there are introduced new classes above. The newly added character vectors should obey the orthogonality theorems (stated earlier) with all preceding vectors.
- 4. The characters of the new elements for the old reps are the same as the ones without R. So $\chi(RC_n) = \chi(C_n)$.
- 5. The characters of the new elements for the new reps have the opposite sign, so $\chi(RC_n) = \chi(C_n)$. The exception mentioned in step 2 for (R)C₂ makes the characters of these zero: $\chi(R)C_2=0$.

The character vector of the electron(s) can be calculated with the same formulae as in Table 1.7 on page 13, only now with J(j) instead of L(l). As an example, one f-electron in weak crystal field: L = 3, S = 1/2, hence J = 5/2 (the lowest state, according to Hund's rules). The character table of O' is as in Table 1.11. The lower states (J = L - S = 5/2) of an f-electron in a weak cubic crystal field are a doublet (Γ_7) and a quartet (Γ_8). The higher states (J = L + S = 7/2) are two doublets and a quartet ($\Gamma_6 + \Gamma_7 + \Gamma_8$). What can also be seen in the O' group table above is that the L=3, S=0 (J=3) state still splits into ($\Gamma_2 + \Gamma_4 + \Gamma_5$), in full compliance with the methods discussed earlier.

0'	E	R	$8C_3$	$8RC_3$	$3(R)C_2$	$6(R)C_2$	$6C_4$	$6RC_4$
Γ_1	1	1	1	1	1	1	1	1
Γ_2	1	1	1	1	1	-1	-1	-1
Γ_3	2	2	-1	-1	2	0	0	0
Γ_{4}	3	3	0	0	-1	-1	1	1
Γ_5	3	3	0	0	-1	1	-1	-1
Γ_6	2	-2	1	-1	0	0	$\sqrt{2}$	$-\sqrt{2}$
Γ_7	2	-2	1	-1	0	0	$-\sqrt{2}$	$\sqrt{2}$
Γ_8	4	-4	-1	1	0	0	0	0
J = 1/2	2	-2	1	-1	0	0	$\sqrt{2}$	$-\sqrt{2}$
J = 3/2	4	-4	-1	1	0	0	0	0
J = 5/2	6	-6	0	0	0	0	$-\sqrt{2}$	$\sqrt{2}$
J = 7/2	8	-8	1	-1	0	0	0	0
J = 3	7	7	1	1	-1	-1	-1	-1

Table 1.11: Character table of O'.

1.8.2 Intermediate or strong crystal field

When the field strength is intermediate or strong ($\approx 10^4 cm^{-1}$), then the crystal field is more important than spin-orbit (SO) coupling. The orbital momentum (L) and the spin (S) are considered separately, giving the orbital and spin representations (character vectors) as in the previous chapter. After introducing SO coupling, the representation of the state is the direct product of the orbital rep and the spin rep:

$$\Gamma_{L,S} = \Gamma_L \otimes \Gamma_S. \tag{1.39}$$

For the example of one f-electron in cubic crystal field this means

$$\Gamma_{L,S} = \Gamma_L \otimes \Gamma_S = (\Gamma_2 + \Gamma_4 + \Gamma_5) \otimes (\Gamma_6) = (\Gamma_7) + (\Gamma_6 + \Gamma_8) + (\Gamma_7 + \Gamma_8), \quad (1.40)$$

because, as stated earlier, the character vector of a direct product rep is the product of the vectors of the individual character reps. In Figure 1.5 the levels for an f-electron in a cubic crystal field are drawn.

1.9 Lowering symmetry

If the symmetry of the environment is lowered by, for example, stretching of the crystal then some of the representations are no longer irreducible. To find the coefficients for the new symmetry one proceeds as follows. Remove from the character vector of Γ



Figure 1.5: Levels of an f-electron in cubic a crystal field. a: free atom, b: strong CF (without SO coupling), c: strong CF + SO coupling, d: SO coupling + weak CF, e:SO coupling, f: free atom.

the characters of operations that are no longer present. Then decompose it as before, now with the character table of the new symmetry. If, for example, a crystal of $C_{3\nu}$ symmetry is deformed in such a way that it no longer has a 3-fold rotation symmetry axis, the previously found E is no longer irreducible with respect to the new symmetry (C_2) . The relevant character tables are:

C_{3v}	$\mid E$	$2C_3$	$3C_2$
A_1	1	1	1
A_2	1	1	-1
E	2	-1	0
C_2	E		C_2
A	1		1
B	1		-1

Thus, $A_1(C_{3v}) = A(C_2)$, $A_2(C_{3v}) = B(C_2)$ and $E(C_{3v}) = A + B(C_2)$. The earlier found Γ reduces to

$$\Gamma = A_2 + E \longrightarrow A + 2B. \tag{1.41}$$

A special case of lowering symmetry of the wave function is Jahn-Teller distortion. In this case there is no external reason for the breaking of symmetry, but the system can lose energy by going spontaneously to lower symmetry. Sometimes, as seen before, the degenerate lowest level of the system can split and since the average energy must remain unaltered, higher- and lower-energy states are produced. The system can then relax to a lower-energy configuration. Figure 1.3 shows this graphically for a system which auto-distorts from C_{3v} to C_2 .

1.10 Comparison with Hamiltonian method

A different way of calculating the degeneracies consists of explicitly calculating the Hamiltonian for the given symmetry. The energy levels and the wave functions can be found by solving the equation

$$\mathcal{H}\psi = E\psi. \tag{1.42}$$

The advantage of this method is that apart from the degeneracies also the eigenstates are calculated. Because there are often undetermined parameters in the Hamiltonian (which must be substituted by a reasonable value), the absolute positions of the levels cannot be calculated, but, because the signs of these parameters are nearly always known, the relative positions are determined by this method. This is clear advantage over the group theory method. The disadvantage lies in the fact that the calculation of the eigenvalues of the Hamiltonian is often difficult, if not a painstaking, laborious job.

As an illustration the calculation of the orbital degeneracy of f-electrons in a cubic crystal field of intermediate strength (so the spin-orbit coupling is of secondary importance). The extra term in the Hamiltonian - and the only term considered in this calculation, the others have a too large energy - is a cubic potential:

$$V_{cubic} = D \cdot (x^4 + y^4 + z^4 - \frac{3}{5} \cdot r^4).$$
 (1.43)

First this has to be translated into orbital momentum operators. Using the method of Stevens [7], it can be found that

$$\mathcal{H}_{cubic} = \lambda \{ \frac{1}{20} \left[35L_z^4 - 30L(L+1)L_z^2 + 25L_z^2 - 6L(L+1) + 3L^2(L+1)^2 \right] + (1.44) + \frac{1}{8}(L_+^4 + L_-^4) \},$$

with $\lambda = eD\beta < r^4 >$. We know

$$L^{2} |l\rangle = L(L+1) |l\rangle = l(l+1) |l\rangle, \qquad (1.45)$$

$$L_{+} |l\rangle = \sqrt{L(L+1) - l(l+1)} |l+1\rangle, \qquad (1.46)$$

$$L_{-} |l\rangle = \sqrt{L(L+1) - l(l-1)} |l-1\rangle, \qquad (1.47)$$

$$L_x = \frac{1}{2}(L_+ + L_-), \qquad (1.48)$$

$$L_y = \frac{1}{2i}(L_+ - L_-), \qquad (1.49)$$

$$L_z |l\rangle = l |l\rangle. \tag{1.50}$$

Thus, the Hamiltonian, in matrix notation, for f-electrons (L = 3) in cubic crystal fields of intermediate strength is:

	-3>	-2>	-1>	0>	1>	2>	3>
< -3	9λ	-	-	-	$3\sqrt{15}\lambda$	-	-
< -2	~	-21λ	-	-	-	15λ	-
<-1	-	-	3λ	-	-	-	$3\sqrt{15}\lambda$
< 0	-	-	-	18λ	-	-	-
<1	$3\sqrt{15}\lambda$	-	-	-	3λ	-	-
< 2	-	15λ	-	-	-	-21λ	-
< 3	-	-	$3\sqrt{15}\lambda$	-	-	-	9λ

Solving the eigen equation gives

.

$$E_1 = -36\lambda, \qquad \psi_1 \propto |-2\rangle - |2\rangle, \qquad (1.51)$$

$$E_2 = -6\lambda, \qquad \psi_2 \propto -0.775 \mid -3 > + \mid 1 >, \qquad (1.52)$$

$$E_3 = -6\lambda, \qquad \psi_3 \propto |-1\rangle - 0.775 |3\rangle, \qquad (1.53)$$

$$E_4 = -6\lambda, \qquad \psi_4 \propto |-2\rangle + |2\rangle, \qquad (1.54)$$

$$E_5 = 18\lambda, \qquad \psi_5 \propto |0\rangle, \qquad (1.55)$$

$$E_6 = 18\lambda, \qquad \psi_6 \propto |-3\rangle + 0.775 |1\rangle, \qquad (1.56)$$

$$E_7 = 18\lambda, \qquad \psi_7 \propto |-1\rangle + 0.775 |3\rangle.$$
 (1.57)

The cubic field splits the 7-fold degenerate f-electron state into two triplets and a singlet, equal to the result of the group-theoretical method.

1.11 Nomenclature and magnetic resonance

So far, only symmetry operations like rotations, reflections and inversion have been used. They have in common that they all leave at least one point unchanged, therefore they are called point group operations. However, a crystal has more than just point group symmetry, it has also translational symmetry. A crystal can be specified by a lattice, with three translation vectors, expressible in lengths (a, b, c) and angles (α, β, γ)



Figure 1.6: Labeling of translation vector parameters.



Figure 1.7: The seven crystal systems and their hierarchy.

and a basis or unit cell. Together with the translations, the point group covering operations of a crystal are called the full space group or full symmetry group of the crystal. Lattices and crystals can be labeled with their symmetry. According to what is taken into account, with or without basis and only point group operations or the full space group, the crystals can be classified in one of the following ways (see also Figure 1.8):



Figure 1.8: Relations between different classifications. PG = point group. FS = full symmetry.

- 7 Crystal systems: Only point group operations and without basis (with spherical basis).
- 14 Bravais lattices: Full space group, but without basis.
- 32 Crystallographic structures: Only point group operations together with basis (of general symmetry).
- 230 Crystals: Full space group and with basis.

In Table 1.12 the 7 crystal systems are tabulated, together with their 32 associated point groups.

In the preceding sections only the 32 crystallographic point groups of the crystal are considered. Because a magnetic resonance experiment cannot detect the translational symmetry this is by far the most important labeling scheme in these experiments.

In the magnetic resonance study as described in this thesis defects in crystals are considered. The number of possibilities for the symmetry of these defects is limited by the structure of the host lattice. Clearly some symmetries cannot occur in some crystals. A look at the silicon crystal reveals that a hexagonal defect can not exist there. The total structure of the defect plus the lattice can never have different symmetry operations than the original ones of the host. In other words the set of operations of the system must be a subgroup of that of the host crystal. The information obtained

				Sp	ectral C	lass
System	Unit cell	Pos	int groups	Si	GaAs	SiC
Cubic	a = b = c	T	23	a.	a	-
	$\alpha = \beta = \gamma = \pi/2$	T_h	$2/mar{3}$	-	-	-
		T_d	$ar{4}3m$	a	a	-
		0	432	-	-	-
		O_h	$4/mar{3}2/m$	-	-	-
Hexagonal	$a = b \neq c$	S_6	$\overline{6}$	-	-	-
	$\alpha = \beta = \pi/2,$	C_6	6	-	-	-
	$\gamma = 2\pi/3$	C_{6h}	6/m	-	-	-
		D_{3h}	$ar{6}2m$	-	-	-
		C_{6v}	6mm	-	-	-
		D_6	622	-	-	-
		D_{6h}	6/mmm	-	-	-
Trigonal	a = b = c	C_3	3	с	с	с
	$lpha=eta=\gamma$	S_3	$\bar{3}$	с	-	-
	$< 2\pi/3 \neq \pi/2$	C_{3v}	3m	с	с	с
		D_3	32	с	-	-
		D_{3d}	$\bar{3}2/m$	с	-	-
Tetragonal	$a = b \neq c$	C_4	4	-	-	-
	$\alpha = \beta = \gamma = \pi/2$	S_4	$ar{4}$	b	b	-
		C_{4h}	4/m	-	-	-
		D_{2d}	$ar{4}2m$	b	b	-
		C_{4v}	4mm	-	-	-
		D_4	422	-	-	-
		D_{4h}	4/mmm	-	-	-
Orthorhombic	$a \neq b \neq c$	C_{2v}	2mm	e	e	-
	$\alpha = \beta = \gamma = \pi/2$	D_2	222	d	d	-
		D_{2h}	2/mmm	-	-	-
Monoclinic	$a \neq b \neq c$	C_{1h}	m	g	g	g
	$\alpha = \gamma = \pi/2 \neq \beta$	C_2	2	f,g	f	-
		C_{2h}	2/m	g	-	-
Triclinic	$a \neq b \neq c$	C_1	1	h	h	h
	$ \alpha \neq \beta \neq \gamma$	$ S_1 $	1	h	-	-

Table 1.12:Crystal systems.

by magnetic resonance are the spin dependent parameters of the Hamiltonian. The symmetry of the system subjected to a study is represented by the symmetry of the Hamiltonian. This is because, if a wave function is invariant under a certain operation R

$$\mathbf{R}\boldsymbol{\psi} = \boldsymbol{\psi},\tag{1.58}$$

then, together with the fact that ψ is an eigenstate of the Hamiltonian of Equation 1.42, this can be combined into

$$\mathcal{H}\mathbf{R}\psi = \mathcal{H}\psi = E\psi, \qquad (1.59)$$

$$\mathcal{R}\mathcal{H}\psi = \mathcal{R}E\psi = E\psi. \tag{1.60}$$

Therefore the Hamiltonian commutes with the symmetry operation

$$[\mathbf{R}, \mathcal{H}] = 0, \quad \text{or} \quad \mathbf{R}\mathcal{H}\mathbf{R}^{-1} = \mathcal{H}. \tag{1.61}$$

Application of this to a term in the Hamiltonian $\mathcal{H}_{K_1,K_2} = K_1 \cdot \mathsf{M} \cdot K_2$ shows that Equation 1.61, with the condition that it should hold for all values of K_1 and K_2 , reduces to

$$\mathbf{R}\mathbf{M}\mathbf{R}^{-1} = \mathbf{M}.\tag{1.62}$$

The restrictions to a general interaction tensor

$$\mathsf{M} = \begin{pmatrix} M_{xx} & M_{xy} & M_{zx} \\ M_{xy} & M_{yy} & M_{yz} \\ M_{zx} & M_{yz} & M_{zz} \end{pmatrix},$$
(1.63)

can now be calculated. This calculation is summarized in Table 1.13 for the covering point group operations of T_d crystals. Combination of this knowledge with the earlier described crystal systems puts the 17 (11) possible symmetries of defects in unary (non unary) T_d crystals into 8 different spectral classes, see Table 1.14.

The tensor in equation 1.63 corresponds to a specific orientation of the defect and will generate a single branch in the angular dependent pattern. Application of the elements of the spacegroup of the host lattice to this tensor as in equation 1.62 generates equivalent centres. When there is no preference of one orientation over the other they will exist in equal quantity and will create branches of equal intensity. When an element of the spacegroup generates an identical tensor these orientations are degenerate and the accompanying branches will coincide, leaving a single branch with double

Oper.	Dir.	C_{i}	ryste	al *	Projection		ion	Restrictions
		1	2	3	x	у	z	
E		•	•	•	x	у	Z	
S_1 (BC)		•			-x	-y	-z	
C_2	<100>	•	•		x	-y	-Z	$M_{xy} = M_{zx} = 0$
	<010>	•	•		-x	У	-Z	$M_{xy} = M_{yz} = 0$
	<001>	٠	•		-X	-y	z	$M_{zx} = M_{yz} = 0$
C_2 (BC)	<110>	•			У	х	$-\mathbf{Z}$	$M_{xx} = M_{yy}, M_{yz} = -M_{zx}$
	<110>	٠			-у	-x	$-\mathbf{Z}$	$M_{xx} = M_{yy}, M_{yz} = M_{zx}$
	<101>	٠			z	-y	x	$M_{xx} = M_{zz}, \ M_{xy} = -M_{yz}$
	<101>	٠			-Z	-y	- X	$M_{xx} = M_{zz}, M_{xy} = M_{yz}$
	<011>	•			-x	\mathbf{Z}	У	$M_{yy} = M_{zz}, \ M_{xy} = -M_{zx}$
	<011>	•			-x	-Z	-y	$M_{yy} = M_{zz}, \ M_{xy} = M_{zx}$
σ	<110>	٠	•		-у	-X	Z	$M_{xx} = M_{yy}, M_{yz} = -M_{zx}$
	<110>	٠	•	٠	У	х	Z	$M_{xx} = M_{yy}, \ M_{yz} = M_{zx}$
	<101>	٠	٠		-Z	У	-x	$M_{xx} = M_{zz}, \ M_{xy} = -M_{yz}$
	<101>	٠	٠	٠	Z	У	х	$M_{xx} = M_{zz}, M_{xy} = M_{yz}$
	<011>	•	•		x	$-\mathbf{Z}$	-у	$M_{yy} = M_{zz}, \ M_{xy} = -M_{zx}$
	<011>	•	•	•	x	\mathbf{Z}	У	$M_{yy} = M_{zz}, \ M_{xy} = M_{zx}$
C_3	<111>	•	•	٠	Z	х	У	$M_{xx} = M_{yy} = M_{zz}, \ M_{xy} = M_{yz} = M_{zx}$
	<111>	•	٠		У	\mathbf{Z}	x	$M_{xx} = M_{yy} = M_{zz}, \ M_{xy} = M_{yz} = M_{zx}$
	<111>	•	۲		-Z	-X	У	$M_{xx} = M_{yy} = M_{zz}, \ M_{xy} = -M_{yz} = M_{zx}$
	<1111>	•	•		-y	\mathbf{Z}	-x	$M_{xx} = M_{yy} = M_{zz}, M_{xy} = -M_{yz} = M_{zx}$
	< >	•	•		Z	х	-у	$M_{xx} = M_{yy} = M_{zz}, M_{xy} = M_{yz} = -M_{zx}$
	<111>	•	•		-y	-Z	X	$M_{xx} = M_{yy} = M_{zz}, M_{xy} = M_{yz} = -M_{zx}$
	<111>	•	•		-Z	x	-y	$M_{xx} \equiv M_{yy} \equiv M_{zz}, M_{xy} \equiv -M_{yz} \equiv -M_{zx}$
\mathbf{C} (D (C))	<111>	•	•		<u>y</u>	-2 -2	-X	$\frac{M_{xx} = M_{yy} = M_{zz}}{M_{-M} - M_{-M} - M_{-M} - M_{-M}}$
$S_3(\mathbf{D}C)$	$\langle 111 \rangle$	•			-2	- X	-y	$M_{xx} = M_{yy} = M_{zz}, M_{xy} = M_{yz} = M_{zx}$
	$\langle 111 \rangle$	•			-y	-2 V	-X	$M_{xx} = M_{yy} = M_{zz}, M_{xy} = M_{yz} = M_{zx}$ M = M = M = M = M
	<111>					-7	-y v	$M_{xx} = M_{yy} = M_{zz}, M_{xy} = -M_{yz} = M_{zx}$ $M = -M = M$
					y -7	Z		$M_{xx} = M_{yy} = M_{zz}, M_{xy} = M_{yz} = M_{zx}$ $M = M = M = M = -M$
						~ <u>7</u>	у -х	$M_{xx} = M_{yy} = M_{zz}, M_{xy} = M_{yz} = M_{zx}$ $M = M = M = M = -M$
	<111>				y Z	-x	v	$M_{xx} = M_{yy} = M_{zz}, M_{xy} = M_{yz} = M_{zx}$ $M_{} = M_{} = M_{} = -M_{} = -M_{}$
	<111	•			-V	Z	x	$M_{xx} = M_{yy} = M_{xz}, M_{xy} = M_{yz} = -M_{zx}$
SA	<100>	•	•		-x	 Z	-v	$\frac{M_{uu} = M_{uu} = M_{uu} = M_{uu} = M_{uu} = M_{uu} = M_{uu} = 0}{M_{uu} = M_{uu} = M_{uu} = M_{uu} = 0}$
~4	<100>	•	•		-x	-Z	v	$M_{uu} = M_{zz}, M_{uu} = M_{uu} = M_{uu} = 0$
	<010>	•	•		-Z	-v	x	$M_{rr} = M_{zz}, M_{ru} = M_{uz} = M_{zr} = 0$
	<010>	•	•		z	-y	-x	$M_{xx} = M_{zz}, M_{xy} = M_{yz} = M_{zx} = 0$
	<001>	•	•		у	-X	-z	$M_{xx} = M_{yy}, M_{xy} = M_{yz} = M_{zx} = 0$
	<001>	•	٠		-y	x	-Z	$M_{xx} = M_{yy}, M_{xy} = M_{yz} = M_{zx} = 0$

 Table 1.13: Restrictions to a tensor as imposed by symmetry operations.

* 1: unary T_d crystals like Si, Ge, etc.

2: binary T_d crystals like GaAs, 3C-SiC, etc.

3: hexagonal SiC, ZnS, etc. with <111> being the c-axis.

Class	Spectral name	Point groups	$Distinguishable \ orientations$											
					+ (<i>extra</i>	ı for	B n a	ot in	$(0\bar{1}1)$)-pla	ne)		
a	Cubic	T, T_d	1											
b	Tetragonal	S_4, D_{2d}	1	3										
			2								*			
c	Trigonal	$C_3, S_3, C_{3v},$	1	2	4									
		D_3, D_{3d}	3											
d	Rhombic II	D_2	1	2	3									
			17	13	18									
e	Rhombic I	C_{2v}	1	2	3	4								
			5	6										
f	Monoclinic II	C_2	1	2	3	4	5	6						
			17	14	22	18	13	19						
g	Monoclinic I	C_{1h}, C_2, C_{2h}	1	2	3	4	5	6	7					
			11	g	12		8	10						
h	General	C_{1}, S_{1}	1	2	3	4	5	6	7	8	9	10	11	1
			20	15	22	18	13	19	24	17	21	14	16	2

Table 1.14:Spectral classes.

intensity. Uniaxial stress can make some orientations preferential and the intensities of the branches are then no longer necessarily equal. Another case where the orientations do not follow the regular distribution is in silicon-carbide. To explain this one has to look more closely at the SiC structure.

1.11.1 Special case: silicon-carbide

Silicon-carbide comes in many forms, called polytypes. This can be visualized by constructing the crystal in single layers. The underlying stacking order of the silicon atoms is hexagonal close packed (HCP), the carbon atoms are then above the silicon atoms. The first layer forms a triangular net as can be seen in picture 1.9. For the second layer there exist two possibilities, denoted by B and C (the first layer was of type A). The third layer can be A, B or C again. Every time there are two distinct possibilities for each layer, because consecutive layers cannot be identical. In this way there are an infinite number of different crystal structures, of which the most common ones are listed in Table 1.15. These polytypes are labeled by their shape of the unit cell (C= cubic, H= hexagonal and R = rhombohedral) and the minimum number of layers to unambigiously describe a unit cell. A special form is 3C-SiC, sometimes called β -SiC (all the other forms are called α -SiC), which is the only cubic form and has exactly



Figure 1.9: Two-dimensional triangular nets. The first layer is on position A, for the second there are then two possibilities, indicated by B and C. The solid lines are not bonds, but help to visualize the triangular arrangement.

Polytype	Stacking	No. of	inequivalent sites	Comments
		cubic	hexagonal	
2H	AB	2	0	wurtzite
$3\mathrm{C}$	ABC	3	0	GaAs, zincblende
$4\mathrm{H}$	ABCB	2	2	
$6\mathrm{H}$	ABCACB	4	2	
15R	ABCACBCABACABCB	9	6	

Table 1.15: Different polytypes for SiC.

the same structure as GaAs, or Si when the difference between the various atoms is disregarded.

Substitutional defects can replace silicon as well as carbon atoms. Apart from this distinction there still exist many possibilities, since, due to the elaborate unit cell, not all silicon atoms are equivalent. They can be classified into two groups. According to their arrangement of their first and second neighbors they are called cubic (c-sites) or hexagonal (h-sites) sites. The same applies to the branches as seen in EPR and ENDOR. In principle not all orientations are the same. For instance, the <111> direction along the (stacking) c-axis is different than the other 3 "equivalent" <111> directions, and a difference in intensity of the related branches is expected, but if the interaction with the latice does not extend beyond the first or second shell there will be no preferential <111> direction. In this case the silicon carbide acts like a normal silicon lattice, as if it contains all 24 symmetry operations of the T_d group. This can be called quasi-crystal behavior.

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Chapter 2

Electron paramagnetic resonance of silicon carbide

2.1 Introduction to EPR

Electron paramagnetic resonance (EPR) is one of the most powerful spectroscopic techniques. The discovery of the feasibility by Zavoisky in 1944 was made possible by the sudden availability of vast amounts of microwave equipment - necessary for radar detection - during the second world war. In later years the method was refined and in some cases combined with other techniques such as nuclear magnetic resonance (NMR), culminating in highly sensitive ENDOR (electron-nuclear double resonance) and state-of-the-art FSE (field-scanned ENDOR), see the chapters on hydrogen. Recent advances in the sensitivity of detection [1] enabled EPR to maintain its leading position in the world of spectroscopy, surviving waves of fancy methods.

The application of EPR to solid state physics is a logical step. Consequently, EPR is used in semiconductor research, where a detailed electronic picture can be drawn of a paramagnetic center, on the basis of the EPR data, such as line positions, angular dependencies and line intensities [2].

2.2 Introduction to SiC

The disadvantage of the classical semiconductors, like silicon and to some extent gallium arsenide, show there, where the devices are exposed to severe conditions. The exploration of new semiconductors was led by the need for devices which can operate at high temperature, high power and high frequency while they should be able to withstand high doses of radiation. Of all the wide band gap materials, silicon carbide and diamond have electronic, mechanical and chemical properties which can meet all these requirements. This is the reason for a new surge of interest, which has boosted the quality of the SiC technology. Pure SiC crystals of many polytypes are now readily available. The gap to the superior technology of silicon is diminishing rapidly.

What is more, the vast number of polytypes shows promising sides of this semiconductor for device engineering; a wide variety of bandgaps is available. The development of the blue light emitting diode (LED) seems possible in this respect, although for high-efficiency optical devices a direct band gap material would be required, something which is not available in the range of polytypes.

Now that the specifications of the devices are coming close to the theoretical limits, it is interesting to compare the capabilities of SiC-based devices to other compounds. It is difficult to express the "usefulness" of a material, since this greatly depends on the application, but two major ways of describing the overall performance of a semiconductor are often used [3, 4].

The Johnson's figure of merit considers the high-frequency and high-power capabilities. This is a function of the breakdown electric field (E_B) , i.e., the electric field needed to excite an electron across the bandgap into the conduction band, and the saturated electron velocity (V_s) :

$$FM-J = \left(\frac{E_B V_s}{2\pi}\right)^2.$$
(2.1)

The Johnson's figure of merit for some common semiconductors are compared in Table 2.1. The high breakdown fields of SiC, GaN and diamond are responsible for their high figure of merit.

material	band-gap	type	Johnson	Keyes
Si	1.12 eV^a	indirect	1	1
GaAs	1.4 eV^a	direct	6.9	0.46
InP	1.3 eV^a	direct	16	0.61
GaN	$3.45 \mathrm{eV}^b$	direct	280	1.8
3C-SiC	2.2 eV^b	indirect	700	5.1
6H-SiC	2.86 eV^b	indirect	1100	5.8
diamond	5.5 eV^{ab}	indirect	8200	32
a^{a} at 300 K, see Ref. [5].				3 K.

Table 2.1 Johnson's and Keyes' figures of merit, relative to silicon. After Ref. [4]

Keyes' figure of merit expresses the switching speed of transistors in logic devices. This is depending on the saturated electron velocity, the thermal conductivity (σ_T) and the dielectric constant ε_r :

$$FM-K = \sigma_T \sqrt{V_s/\varepsilon_r}.$$
 (2.2)

In Table 2.1 these numbers are printed. From these data, it is clear that SiC is a good alternative for diamond. Favoring the use of SiC, it does not need the extreme conditions for production, such as high pressure, as is required for diamond. Therefore, SiC is a promising novel material.

In spite of the renewed interest in this compound, the amount of EPR results is still rather small. In the early days of EPR, Woodbury and Ludwig made studies of the basic dopants, nitrogen for n-type and boron (or aluminum) for p-type SiC [6]. The nitrogen donor gives rise to two overlapping sets of three equally intense hyperfine These can be attributed to two spectra of the nitrogen triplet, one arising lines. from substitutional nitrogen on hexagonal lattice sites and one from substitutional nitrogen on cubic sites. The observed spectral intensity ratio of 2:1 agrees well to this assignment, since the number of cubic sites is twice the number of hexagonal sites in 6H-SiC, see the chapter on group theory and Ref. [7]. For the boron acceptor the spectrum is more complicated. Due to nuclear quadrupole interactions, which mix the "pure" nuclear quantum states, "forbidden transitions" ($\Delta m_I \neq 0$) become visible in EPR. Therefore the observed number of lines increases to more than the expected quadruplet for ${}^{11}B$ (I=3/2, natural abundance 81.2%) and septet for ${}^{10}B$ (I=3, 18.8%). Another group of measurements describes the EPR spectra produced by radiation damage (proton, electron and neutron). In many cases intrinsic defects are created, for instance (multi)vacancies [8]. In one case [9], a spectrum is found which is attributed to a point defect, presumably a monovacancy. The hyperfine interaction with the four nearest silicon atoms and twelve next-nearest carbon atoms of the host lattice results in a spectrum which exactly follows the intensity behavior as expected from combinatorics.

2.3 Experimental details

The first sample used in the experiment was supplied by Dr. V.S. Vaĭner. It was a SiC single crystal of a hexagonal polytype. Following crystal growth, two similar samples were cut from it. One of them received a short heat treatment at 2000 °C followed by

a rapid quench to room temperature. The other part served as reference. The sample and its position in the magnetic field are depicted in Figure 2.1.



Figure 2.1 Experimental orientation of the sample against the plane of the external field.

The second sample which was submitted to an EPR study was a green, transparent monocrystal of hexagonal (6H) polytype, supplied by V.S. Vaĭner of the Ioffe institute (St. Petersburg). The green color of the sample indicates the presence of "green" luminescence, or D band (470 nm to 600 nm), possibly related to divacancies [10]. In 6H-SiC:N the green luminescence is present without irradiation of the sample, see Figure 13 of Ref. [7].



Figure 2.2 Spectrum SiC-NL1 for $B \parallel < 100 >$ and a microwave frequency of 23.133236 GHz.

The measurements were performed with two superheterodyne spectrometers, operating at 23.1 and 9.2 GHz [1], respectively, and adjusted to detect the dispersion part of the EPR signal. The magnetic field was modulated at a low frequency of 83.4 Hz and could be rotated in a plane which contained the c-axis of the sample. The sample was placed in a TE_{011} mode, silver-coated, epibond cavity for both the X- and K-band spectrometers. This experimental set-up permitted *in situ* white light illumination to reach the sample. In the case where light was used, it was from a halogen source, guided through a quartz rod.



Figure 2.3 Angular dependence of SiC-NL1. A \Box represents an experimental point. Solid lines indicate a simulation for the Hamiltonian as in Equation 2.3 with parameters as in the text, and a microwave frequency of $\nu = 23.133$ GHz.

2.4 Experimental results and discussion

In the untreated reference sample no EPR signal has been found. The EPR spectrum (labeled SiC-NL1) for the heat-treated sample, as acquired by the K-band spectrometer, is shown in Figure 2.2. The angular dependence of this spectrum is depicted in Figure 2.3. Comparing this with the possible angular dependencies in silicon [11], the conclusion is that the symmetry of the defect must be rhombic II, i.e., the defect must contain three <100> twofold axes. As illustrated in the chapter on group theory, such a situation is not possible in silicon carbide. The symmetry has to be lower. When the three <100> axes are removed from the symmetry set, the resulting symmetry is triclinic. This lowering of symmetry is not observed in the spectrum. This means that this distortion is comparatively small, or, in other words, the spectrum is determined by the local environment and not by long-distance interactions. Locally, the structure of SiC is identical to that of GaAs. This permits the observation of spectra with seeming rhombic II angular dependence.



Figure 2.4 Detail of the SiC-NL1 spectrum at three different magnetic field angles $(54.74^{\circ} \text{ is parallel to the } c\text{-axis}).$

After having determined the symmetry of the g-tensor, it is interesting to know what the cause is for the splitting of the lines, as illustrated in Figures 2.2 and 2.3. At first the idea might appeal that this splitting is due to the Zeeman-interaction g-factor anisotropy. On the other hand, this is not able to account for the difference in intensity of the two outer lines and the central line, unless we assume that a second spectrum is superimposed in the middle [12]. A much easier explanation is possible if we assume a higher electron spin value. An electron spin value of S=3/2 would fit nicely to the observed intensities. In that case a complicated angular dependence is expected in the middle, as is indicated in Figure 2.3. Indeed, such a structure is revealed upon closer inspection. Figure 2.4 presents the details of the spectrum for the three characteristic angles 0°, approximately 54.74° and 90°. The spectrum can now be assigned to a spin Hamiltonian

$$\mathcal{H} = g\mu_{B}B \cdot S + S \cdot D \cdot S. \tag{2.3}$$

EPR of SiC



Figure 2.5 Influence of illumination on the spectrum as depicted in Fig. 2.4. The singly rising line is identified with SiC-NL2. The lines of lower intensity are SiC-NL3.

Figure 2.6 Dependence on temperature of the spectra as drawn in Fig. 2.4 (top). All lines show similar behavior.

A fit of the free parameters to the experimental data yields values of g = 2.00299, $D_1 = 403 \text{ MHz}$, $D_2 = -5 \text{ MHz}$ and $D_3 = -399 \text{ MHz}$. A simulation of the angular dependence of the resonances expected for the Hamiltonian as in Equation 2.3, with these values is drawn in Figure 2.3.



Figure 2.7 Angular dependence of SiC-NL3. The points are experimental points for $\nu = 23.133$ GHz, while the solid lines are interpolations.

To further analyze and decompose the spectrum shown in Figure 2.4, the influence of illumination with white light and temperature increment has been monitored. As can be seen in figure 2.5, most of the individual lines decrease their intensity upon illumination, while one line clearly increases. This indicates at least two different EPR components. The across-band-gap illumination, apart from changing the occupation of the impurity levels, may also increase the sample temperature. In order to eliminate this side effect, the temperature dependence of this part of the spectrum was checked. Figure 2.6 indicates that upon temperature increase, all components similarly lower their intensity, excluding the afore-mentioned effect on the line intensities. This leads to the conclusion that the single deviating line is belonging to a different spectrum, which is labeled SiC-NL2. Finally, the angular variation of the central part (816-838 mT) of the spectrum was measured; the result is depicted in Figure 2.7. It shows



Figure 2.8 A typical spectrum of the "green" sample. Indicated are the nitrogen spectrum [6] (N) and a still unknown spectrum (β).

two major features: the outer, lower-intensity resonances which exhibit pronounced anisotropy, and the inner, strong lines of SiC-NL1 whose anisotropy is contained in a narrow field range of approximately 2 mT. The lower intensity outside lines clearly have a different symmetry than the SiC-NL1 spectrum. On the basis of the different illumination dependence, any relation to the SiC-NL2 spectrum can also be excluded. Therefore, these lines must belong to a separate spectrum, SiC-NL3. The spectrum consists of two mirrored hyperfine patterns, while a third (isotropic) line in the middle cannot be excluded. This latter line is even expected, since the most likely candidates for the hyperfine interaction seem to be nitrogen (¹⁴N, I=1, 99.6% natural abundance, concentration $n_N \approx 10^{17} \text{ cm}^{-3}$), giving a triplet spectrum, silicon (²⁹Si, I=1/2, 4.7%; ²⁸Si+³⁰Si, I=0, 95.3%) and carbon (¹³C, I=1/2, 1.1%; ¹²C, I=0, 98.9%), all resulting in the superposition of singlet and doublet spectra. The spectrum can then be attributed to the spin Hamiltonian

$$\mathcal{H} = g\mu_B B \cdot S + S \cdot A \cdot I, \qquad (2.4)$$

with S=1/2 and I=1 or I=0 + I=1/2. The spectral class (symmetry) of SiC-NL3 at first seems to be very low; monoclinic I or lower. But a closer inspection of the patterns reveals that the loops have Moebius qualities: following a loop from 0° to 90° and back via the other branch does not make a closed loop. Even for the lowest symmetry (triclinic), such a behavior is not expected. Only misorientation of the sample - i.e., Table 2.2 Hamiltonians of the five spectra encountered in hexagonal SiC.

SiC-NL1	$\mathcal{H} = g\mu_{\scriptscriptstyle B}B \cdot S + S \cdot D \cdot S$				
	S=3/2				
	g: cubic, $g = 2.00299$				
	D: rhombic II, D = $\begin{pmatrix} 403 & 0 & 0 \\ 0 & -5 & 0 \\ 0 & 0 & -399 \end{pmatrix}$ MHz				
SiC-NL2	$\mathcal{H} = g\mu_B B \cdot S$				
	S=1/2				
	g: cubic, g = 2.0048				
SiC-NL3	$\mathcal{H} = g\mu_{\scriptscriptstyle B}B\cdot S + S\cdot A\cdot I$				
	S = 1/2, I=1 or I=0 + I=1/2				
	g: cubic, g= 1.9984				
	A: rhombic I, A = $\begin{pmatrix} 180 & 680 & 0 \\ 680 & 180 & 0 \\ 0 & 0 & 370 \end{pmatrix}$ MHz				
N	$\mathcal{H} = g\mu_{\scriptscriptstyle B} B \cdot S + S \cdot A \cdot I$				
	S=1/2, I=1				
	$g_{\parallel}=2.004, g_{\perp}=2.003$				
	A: cubic, A = 33 MHz				
β	$\mathcal{H} = g\mu_{B}B \cdot S + S \cdot A \cdot I$				
	S=1/2, I=?				
	g: cubic, g=2.003				
	A: cubic, $A \times I = 16$ MHz				

when the magnetic field is not exactly in the $\langle 01\bar{1} \rangle$ plane - can give the angular dependency such features. With this in mind. the spectral class can safely be determined as rhombic I. Table 2.2 summarizes the spin-Hamiltonians of the three spectra. For none of the here-presented spectra there seems to be a difference for the distinct inequivalent

For the second, green, sample, the isotropic EPR spectrum, recorded at the X-band spectrometer is shown in Figure 2.8. In this case the assignment to a single spectrum also seems dubious. A shell of 8 interacting equivalent silicon nuclei would produce the observed intensity ratio of the central line to the hyperfine lines (100:19.5). But, in that case, a second set of hyperfine lines with twice the distance to the central line and a relative intensity of 1.7% (see Appendix A) should have been observed. Apart from this, a shell of 8 equivalent atoms is inconceivable. Abandoning the trivial solutions, the impurities can be explored. Although the diffusion of nitrogen is low, the solubility is very high [7]. Therefore, the presence of nitrogen-related defects is expected. The distance of the outermost (indicated by N) hyperfine lines (2.38 mT) compares well to the spectrum observed by Woodbury and Ludwig [6]. This triplet spectrum was attributed to the nitrogen donor; in Figure 2.8 a third component is hidden by the central line. With part of the spectrum solved, the question still remains open as to the assignment of the rest. Clearly, the satellites, indicated by β , cannot belong to (all of) the central part, since they are located asymmetrically around it. The four β lines have, upon fitting to Gaussian lineshapes, equal intensities. The presence of other spectra makes it difficult to determine the multiplicity of the spectrum. A septet spectrum (I=3) fits best to the experimental data, but the lack of candidates makes such an assignment illogical. Either it is an octet (I=7/2), in which case it can be assigned to vanadium, or it is a sextet (I=5/2) which has aluminum as most likely source. The spectrum can then be attributed to a Hamiltonian with an electronic Zeeman term and a hyperfine interaction term. The low resolution and presence of other spectra did not allow for the determination of the angular dependence. Therefore the interactions are assumed to be isotropic. The spin-Hamiltonian parameters of all spectra, which are described here, are presented in Table 2.2.

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Chapter 3

DX Centers in Ternary Compounds

3.1 Introduction

DX is an omnipresent center in many ternary semiconductors (semiconductors containing three different components, e.g., $Al_xGa_{1-x}As$). The DX level was first observed by Lang in 1977 [1] by Deep Level Transient Spectroscopy (DLTS) and TSCAP (Thermally Stimulated CAPacitance). He later identified it with a complex of the donor (D) with an unknown intrinsic defect (X), presumably the anion vacancy (V_{As}). Later models prefer a simpler defect, for instance only a substitutional donor (e.g., Si_{Ga}), but the name DX was maintained. The metastable character of the DX defect, as well as its significant influence on the electronic properties of the material, together with its omnipresence in III-V semiconductors, make it an important subject and necessary studying in detail. The understanding of the exact nature of the DX defect and its formation kinetics may lead to a way to eliminate this mostly unwanted defect from the devices.

3.1.1 Definition of DX

The DX labeling covers a wide range of defects. In principle any donor in a compound semiconductor can act as a source for DX. Therefore it is difficult to describe, but some features are common:

- DX is a deep level of the donor.
- DX is present in many semiconductors with different dopants, like Al_xGa_{1-x}As, GaAs_yP_{1-y}, Cd_{1-z}Zn_zTe, GaSb and CdS.

• DX often shows metastability, which results in "photo persistencies" like PPC (persistent photo conductivity) or PPE (persistent photo EPR).



Figure 3.1 Stereographic view of the Brillouin zone of a crystal with T_d symmetry. The high-symmetry points are indicated with Γ , X and L.



Figure 3.2 Band structure of GaAs (left) and AlAs (right) [2].

3.2 Band structure and energy levels

The band structures of GaAs and AlAs are drawn in Figure 3.2. From this it is clear that in GaAs the Γ valley is the lowest point of the conduction band, whereas in AlAs the X valley is the lowest. As a function of the Al-mole concentration (x) in Al_xGa_{1-x}As the energy levels of the high-symmetry points (Γ , L and X) are drawn in Figure 3.3. The Γ "mountain" is always the highest point of the valence band. This implies that

at x=0.45 the crystal switches from direct to indirect gap, although this value is not generally accepted [3, 4].

As can be seen in Figure 3.3, the DX level apparently is coupled to the L valley with a binding energy of approximately 130 meV (GaAs) to 210 meV (AlAs). This means that from x=0.22 the DX level is lowest and will be filled under normal conditions.



Figure 3.3 Energy levels of the Γ , X, and L minima in the conduction band, DX and effective mass (EM) states in $Al_xGa_{1-x}As$ as a function of the Al-mole concentration (x).

Toyozawa [5] has shown that a deep level often is accompanied by a shallow level. The short-range electron-phonon interaction can trigger deep-shallow instability with large lattice relaxation which will be discussed later on. In $Al_xGa_{1-x}As$ these effectivemass (hydrogenic) levels are visible for the Γ and X valley (Figure 3.3). L-minimum related states were observed in the photoluminescence experiments of Henning [6]. The binding energy of these levels depends on the state [7], see Table 3.1. The most important thing to notice is that both the deep and the shallow level originate from the same defect.

Instead of varying the Al-mole concentration to change the band structure, hydrostatic pressure can be used. If we assume that the DX level is equally bound to the L valley, regardless of the pressure, then at 3 MPa the DX level is pushed out of the conduction band [8, 9]. According to the literature this point is at 2 MPa [7], so the assumption is not valid. The pressure coefficient of the DX level is not identical to that of the

Table 3.1 Position of the effective-mass levels relative to the conduction



Figure 3.4 Energy levels of Γ , X, L and DX in GaAs as a function of hydrostatic pressure.

L valley. This suggests that the DX state is not comprised only of L valley conduction band states but rather of states from the entire conduction band. Figure 3.4 shows some detail of the actual (conduction) band structure as a function of hydrostatic pressure. In this picture, for the DX level, a linear increasing binding energy is assumed.

An essential element of DX is that capture and emission of electrons can occur only via the L minimum. For GaAs, the energy separation between the L minimum and the bottom of the conduction band is comparatively large. Therefore, the capture crosssection at low temperatures is rather small. This is the source for the metastabilities of DX [10].

3.3 Large lattice relaxation

Direct indications for the occurence of large lattice relaxation (LLR) are:

- PPC (persistent photo conductivity) at low temperatures (T<120 K). A sample cooled in the dark has high resistivity. After illumination the sample is conductive and stays that way for long periods (even days). Apparently, electrons can be excited to conduction band (like) states, from where they cannot relax to nonconducting states.
- Small thermal capture and emission cross-sections. A sample cannot be thermally activated. For that purpose light has to be used, as mentioned above. At low temperatures the sample can also not be relaxed to nonconducting states with the help of phonons. There seems to be some kind of threshold for the electrons to switch between the two states.
- The optical ionization energy is much larger than the thermal ionization energy. This optical ionization energy is independent of the stoichiometry of the sample (i.e., independent of x in Al_xGa_{1-x}As, see Ref.[11]).



Figure 3.5 Configuration coordinate diagram of the DX center in GaAs at zero pressure. E_b , E_e and E_o are the thermal capture and emission energy and the optical ionization energy, respectively. The arbitrary zero level is chosen to be at the minimum of the conduction band $(E_L=0)$.

All these features point towards large lattice relaxation accompanying ionization or electron capture. This is normally explained with the help of configuration coordinate diagrams (CCDs). In 1977 Lang [1] already proposed to expand the then widely used interatomic CCDs to lattice CCDs in order to explain the features of DX. The idea behind CCDs is that the energy of a complex system can be described by a single (or a few in the case of multi-dimensional CCDs) coordinate. In Figure 3.5 such a CC diagram for DX is drawn. In this picture U_{DX} represents the energy of the total system with the electron in the DX level, NOT the energy of the electron in the DX level! The lowest value of this energy is E_{DX} . Likewise U_L represents the energy of the system with the electron in the conduction band (L valley).

If one assumes that the curvatures of the parabola are all equal, then the system can be described by three parameters:

- $\mathbf{E}_{\mathbf{b}}$ The thermal capture energy. An electron in the conduction band (U_L) always has a certain thermal energy. When this energy is larger than E_b the electron can pass the threshold and relax into the DX level. In real space the lattice relaxes to a new configuration (the atoms relocate to new positions) which is characterized by the parameter Q_T .
- $\mathbf{E}_{\mathbf{e}}$ The reverse process is also possible; an electron with sufficient thermal energy can cross the threshold and go into a conduction-band state. The threshold energy (E_e) needed for such a process is not necessarily equal to the capture energy E_b . The difference between E_e and E_b is the binding energy of the DX level:

$$E_{DX} = E_e - E_b. aga{3.1}$$

The binding energy is not necessarily positive. In GaAs the DX level is resonant with the conduction band because the lowest point of the conduction band is below the DX level, therefore $E_{DX} < 0$. Even then the DX level need not be empty at all times. At low temperatures it is possible to effectively stop thermal emission/relaxation and maintain the initial, non-equilibrium distribution.

A nice experiment which demonstrates this is the pressure experiment performed by Fujisawa [9], among others. In a GaAs:Si sample at room temperature the DX levels are mostly empty because this is not the lowest level and the thermal energy is still big enough to allow for relaxations. The lowest energy states are the effective mass states, but these are very shallow, therefore most of the electrons are in the conduction band and the sample is highly conductive (point A in Figure 3.6, where the conductivity of the sample is drawn as a function of hydrostatic pressure). When the pressure is increased the DX level becomes the lowest level at a certain pressure (20 kbar, point B). Because the temperature is still big enough for relaxation all electrons will relax from the conduction band to DX. Hence the conductivity of the sample decreases (point C). At this point the sample is cooled to freeze the electrons in the DX state. When the pressure is released the electrons stay in the DX level although this is no longer the lowest state but the low temperature prevents electrons from relaxing to the ground state. The sample keeps its high resistivity until the temperature is raised above a certain value (of about 100 K).



Figure 3.6 Conductance of a GaAs:Si sample as a function of hydrostatic pressure (After Fujisawa et al. [9]).

 $\mathbf{E}_{\mathbf{o}}$ Beside thermal excitation the electrons can also be optically transformed to conduction-band electrons provided the photon energy is big enough (larger than E_o). This is also demonstrated in the pressure experiment: When, with the sample in state C (high pressure, low temperature and the electrons in DX levels),

light is shone on the sample the electrons are converted to the conduction band (when the wavelength is not too big). From this level they cannot relax, as was demonstrated before. They are now trapped in the conduction band (point E in Figure 3.6) and the sample stays conductive until the temperature is increased to a value where thermal capture processes become significant again.

In Tables 3.2 and 3.3 E_e , E_b and E_o are displayed for several donors in Al_xGa_{1-x}As and GaAs_yP_{1-y} (copied from Ref. [10]). In this table E_{DX} is relative to the L valley.

Table 3.2 CCD parameters for DA centers in Al _x Ga _{1-x} AS [10].					
donor	E_e (eV)	E_b (eV)	$E_{DX} = E_e - E_b \ (eV)$	$E_o~({ m eV})$	
VI S	0.28	-	-	-	
Se	0.28	0.14	0.14	0.85	
Te	0.28	0.14	0.14	0.85	
IV Si	0.43	0.21	0.22	1.25, 1.45	
Ge	0.33	-	_	-	
Sn	0.19-0.21	0.02	0.17-0.19	1.11	

Table 3.2 CCD parameters for DX centers in $Al_xGa_{1-x}As$ [10].

Table 3.3 CCD parameters for DX centers in $GaAs_yP_{1-y}$ [10].

donor	E_e (eV)	E_b (eV)	$E_{DX} = E_e - E_b \ (eV)$	$E_o~({ m eV})$
S	0.35	0.15	0.2	1.53
Te	0.19	0.12	0.07	0.65

3.4 Microscopic models

The CC diagrams are very useful to explain the physical properties - especially metastability - of systems. The weak point of CCD's lies in the fact that they do not say anything about the microscopic model of the defect. That is why there is still much controversy about the actual structure responsible for the DX defect. The first model for DX was given by Lang [12]. He proposed that the defect is a complex of a substitutional donor atom and an intrinsic defect, for instance $Te_{As}V_{As}$, see Figure 3.7. The character of the defect is mainly determined by the vacancy. This explains the relative independence of the donor which merely acts as a supplier of electrons. Features which are not explained by this model are:



Figure 3.7 Stereographic view of the Lang model.

- The DX concentration is a fixed fraction (in most cases nearly 100%) of the donor concentration. This also indicates a simpler, easier to produce defect.
- The concentration of DX is independent of growth conditions. This makes the involvement of lattice self defects (like vacancies) unlikely. A simpler defect of, for instance, only the donor is much likelier.
- DX is present in many compounds with different donor impurities, both on the group III as on the group V sublattice.



Figure 3.8 Chadi-Chang model before (a) and after (b) reaction of Equation 3.2.

That is why recent models prefer simpler defects of only the donor atom. Chadi and Chang [13] conclude that DX is the result of the reaction

$$2d^0 \to d^+ + DX^-, \tag{3.2}$$

with d four-fold bound, substitutional donor atoms, not necessarily close to each other in real space. This equation implies negative U; it is energetically more favorable to lose two electrons than it is to lose one electron twice. In this model the formation of a DX center is acquired by breaking the bond with a nearest neighbor after which the donor atom relaxes (i.e., $Si_{Ga} \rightarrow Si_iV_{Ga}$, see Figure 3.8). So also in this model a vacancy is involved. The difference with the Lang model is that now the vacancies are a result of a reaction and are therefore not needed *ab initio*. In this way all donors can produce a DX center. Hence, drawbacks 1 and 2, mentioned earlier, do not apply to this model. The negative-U character can explain why the ground state does not show EPR: both in DX^+ and DX^- the electrons are paired, meaning non-paramagnetic states and DX^0 -which would be paramagnetic- is unstable. The absence of EPR is therefore an indication for negative U, although not a proof.

Table 3.4 Reaction equations concerning DX.					
	indirect gap	direct gap			
<i>U</i> -	$DX^- + DX^+ \to 2X^0_*$	$DX^- \rightarrow DX^+ + 2e^-$			
U^+	$DX^0 \to X^0_*$	$DX^0 \rightarrow DX^+ + e^-$			
X_* is the X-valley effective-mass state.					

The reaction schemes for optical processes are depending on the character of the crystal. For direct-gap (Γ is the lowest state in the conduction band) samples the effective-mass levels are too shallow to be occupied. Electrons are therefore residing in the conduction band. For indirect-gap (X is the lowest point of the conduction band) materials the hydrogenic level is deep enough to be filled. The reaction equations for direct and indirect gap, with and without negative U are then as in Table 3.4.



Figure 3.9 Oshiyama-Ohnishi model. The relaxation is indicated by arrows.

3.4.1 Small lattice relaxation

Kin Man Yu *et al.* observed in a particle-induced X-ray emission (PIXE) and an ion beam channeling experiment no off center displacement of Te and Se larger than 0.14 Å from substitutional sites [14]. Mizuta and Kitano carried out a fluorescence experiment to investigate directly the local environment of the DX center in $Al_{0.30}Ga_{0.70}As$:Se. They found that the difference in bond lengths between the two different states was less than 0.04 Å [15]. These are indications for small lattice relaxations. The stretching mode model of Oshiyama and Ohnishi (see Figure 3.9), in which nearest neighbors of the donor move toward each other, can explain the observed phenomena [16]. Hjalmarson and Drummond use a general model in which no large lattice relaxation is needed to account for the large difference in optical and thermal activation energies [17].



Figure 3.10 Persistent photo EPR (PPE) of a $GaAs_{0.55}P_{0.45}$: S sample. The thick trace shows the spectrum after cooling in the dark, while the thin trace was taken after illumination. The signal at 843 mT can be quenched by heating the sample to room temperature.



Figure 3.11 Persistent photo-enhanced EPR (PPEE) of the GaP: Te sample. The EPR signal in a) changes phase upon illumination b). After switching off the illumination, the intensity increases, while the phase is unaltered c).

3.5 EPR experiments

An electron paramagnetic resonance (EPR) study was performed, using several different samples, including

- 1. $GaAs_{0.55}P_{0.45}$:S
- 2. $GaAs_{0.60}P_{0.40}$:S
- 3. GaP:Te
- 4. Al_{0.5}Ga_{0.5}As:Te on GaAs substrate

Samples 1, 2 and 4 showed PPE (persistent photo EPR). With illumination an EPR spectrum is generated. This signal can only be quenched by heating the sample to higher temperatures. In Figure 3.10 this is demonstrated for the GaAs_{0.55}P_{0.45}:S sample. In this case an EPR line is already present after cooling in the dark, but the illumination produces a permanent line around 843 mT (g=1.9595). The same EPR is also present after cooling with light on. PPE can be explained with the LLR models as explained before. The center is excited to a metastable, paramagnetic state X_* . EPR is arising from this effective-mass state [18, 19] or DX⁰ (not possible with negative U).

GaP:Te already shows EPR after cooling in the dark. Illumination only increases the signal intensity (see Figure 3.11). Cooling in the dark produces a certain distribution over the two systems, which is disturbed by optical excitations. Since relaxations are effectively stopped at low temperatures, the original state of the sample cannot be reobtained. Another way of saying this, is that for GaP:Te the metastable state is not much shallower than the stable DX. In that case, not all electrons will freeze out in the DX level, leaving some of them in the metastable, paramagnetic state. This means bistability instead of metastability.



Figure 3.12 EPR spectrum of the $GaAs_{0.60}P_{0.40}$: S sample after cooling in the dark and after illumination. The sharp-effective mass resonance (EM) does not change intensity, while a very weak DX signal is generated.

All samples also show a (comparatively) narrow resonance. The narrowness indicates the absence of strong hyperfine interactions and therefore a shallow state. The g value (g = 2.0026) is close to the free-electron value g_e . This resonance may either arises from conduction-band electrons or from shallow (effective-mass) states. Since it does not change intensity upon illumination, we may tentatively ascribe it to secondary defects. Figure 3.12 shows such a typical resonance for the GaAs_{0.60}P_{0.40}:S sample after cooling in the dark and after illumination.

So far, all EPR signals as described were isotropic. Only in one case the EPR spectrum revealed a considerable anisotropy. Turning the $GaAs_{0.55}P_{0.45}$:S sample by 40° in the (011) plane resolved a small line at 860 mT (see Figure 3.13). The origin of this anisotropy is not clear. Bulk samples should produce isotropic EPR.



Figure 3.13 Two spectra of $GaAs_{0.55}P_{0.45}$: S for magnetic field directions 40° apart in the $(01\overline{1})$ plane.

Another spectrum which recurred in the study was a single, broad line around 800 mT (g = 2.07) with a line width varying from 20 mT in GaAs_{0.55}P_{0.45}:S (Figure 3.13) to 30 mT in GaAs_{0.60}P_{0.40}:S. Remarkably, in GaAs_{0.60}P_{0.40}:S this signal was only visible after etching the sample (10 minutes at 70°C in a solution of H₂SO₄:H₂O:H₂O₂ in a ratio 3:1:1). These lines do no show any connection to DX. There is, for instance, no

increasing or decreasing of the intensity after illumination. Apparently they are not related to DX.

3.6 Valley-orbit splitting

The DX center in bulk material has an isotropic EPR spectrum, because the only term in the spin Hamiltonian is a cubic Zeeman interaction $\mathcal{H} = g\mu_B B \cdot S$. Indeed, most of the measured bulk samples showed isotropic EPR. On the other hand, epitaxial layers, grown on a substrate exhibit a small anisotropy in the g factor caused by the strain between the AlGaAs layer and the GaAs substrate, which have different lattice parameters, ranging from 5.653 Å (GaAs) to 5.661 Å (AlAs) [2].



Figure 3.14 Constant energy surfaces of the conduction-band X-valley. The long axes are directed along <100> directions.



Figure 3.15 Position of the six X-valley effective-mass states for group-IV donors (a) and group-VI donors (b), as split by valley-orbit interactions, or chemical shift, (E_{12}) and strain (ΔE_s) .

The conduction-band X-valley constant-energy surfaces are ellipsoids with the long axes in the <001> directions. In face-centered cubic (FCC) crystals, like Si, GaAs and AlAs, the X minima are six-fold degenerate (see Fig. 3.1 and 3.14). In principle, the effective-mass (EM) states obey the same symmetry rules for calculating the energies

as the valleys to which they are connected and should show the same degeneracy behavior. But the electronic states of a defect do not have the crystal. To be more precise, the wavefunctions are derived from the band-structure Bloch functions and the hydrogenic effective-mass states (1s, 2s, 2p ...). The highest symmetry which the latter can have is cubic. And, as shown in the chapter on group theory, the highest degeneracy is then three-fold. Indeed, the valley-orbit interaction, or chemical shift, lifts the six-fold degeneracy to a triplet (T_2) , a doublet (E) and a singlet (A_1) . For group-IV donors on anion sites (e.g. Si_{Ga}), the T_2 triplet state lies lowest (see Fig. 3.15). This state, is further split into the $T_{2,z}$ and the $T_{2,x}$ and $T_{2,y}$ states by strain, assuming the growth direction is [001] [20, 21]. The magnitude of this splitting is proportional to the deformation potential Ξ [22]:

$$\Delta E_s = T_{2,z} - T_{2,x}(T_{2,y}) = \Xi(e_{\perp} - e_{\parallel}), \qquad (3.3)$$

where $e_{\perp}ande_{\parallel}$ are the perpendicular and parallel strains, respectively [22]. At low temperatures $T_{2,z}$ is not populated because ΔE_s is estimated to be 14 meV, much larger than the average thermal energy of 0.4 meV at 4.2 K. A field parallel to the [100] direction is parallel to the long axes of the x-pockets and parallel to the short axes of the y-ellipsoids. Two distinct g values are then observed. But a field in the (110) plane always makes equal angles with the x- and y-pockets [22], resulting in a single, anisotropic line. Table 3.5 gives a summary of data on silicon-doped $Al_xGa_{1-x}As$ on GaAs substrates.

	Lubic 0	•• y jue	010 0 00		$\frac{1}{2}$		10.
x	1.0	0.6	0.56	0.7	0.8	0.41	0.6
$g_{ }$	1.978	1.962	1.9653	1.9667	1.9690	1.947	1.966
g_\perp	1.945	1.943	1.9550	1.9543	1.9534	1.932	1.937
Ref.	[20]	[20]	[23]	[23]	[23]	[11]	[11]

Table 3.5 g factors of silicon in $Al_x Ga_{1-x}As:GaAs$.

For group-VI donors on the group-V sublattice (e.g., Te_{As}), A_1 is the lowest level. This results in an isotropic g value. The now very small anisotropy of the g factor is a result of the slight mixing of A_1 and E states, as caused by strain. The valley-orbit splitting can be calculated from the observed anisotropy in g [22]:



Figure 3.16 Angular dependence of the resonant field of sample consisting of a $Al_{0.5}Ga_{0.5}As$: Te layer on a GaAs substrate at 9.227028 GHz.

$$g(\theta) - g_0 = (g_{\parallel} - g_{\perp}) \left[1 - \frac{3sin^2\theta}{2} \right] \left[1 - \frac{1 + \frac{3}{2}y}{\sqrt{1 + \frac{1}{3}y + \frac{1}{4}y^2}} \right],$$
(3.4)

with g_0 the donor g value in absence of strain, g_{\parallel} and g_{\perp} the parallel and perpendicular independent-valley g factors, $(g_{\parallel} = 1.978, g_{\perp} = 1.945)$, taken from the results of a Si-doped AlAs epilayer on a GaAs substrate., see Ref. [20], and y the ratio of the strain energy (ΔE_s) to the valley-orbit splitting (E_{12}) :

$$y = \frac{\Delta E_s}{E_{12}}.\tag{3.5}$$

For ΔE_s a value of 7 meV is taken; halfway between a no-strain GaAs:GaAs sample and a 14 meV strain AlAs:GaAs sample [22] as the used sample was Al_{0.5}Ga_{0.5}As:GaAs. The observed anisotropy ($g_{[001]} = 1.9475$ and $g_{[110]} = 1.9434$, see Figure 3.16), yields a value for the valley-orbit splitting of $E_{12} = 110$ meV. Table 3.6 gives a comparison of this result with values for other donors.

donor	S	Se	Te
<i>g</i> _[001]	1.963	1.961	1.9475
$g_{[110]}$	1.954	1.953	1.9434
g_0	1.957	1.955	1.945
x	0.6	0.6	0.5
Ref.	[22]	[22]	this work
ΔE_s	8.4 meV	8.4 meV	7.0 meV
<i>E</i> ₁₂	19 meV*	20 meV^*	20 meV

Table 3.6 Valley-orbit parameters for some group-VI donors in $Al_x Ga_{1-x} As$.

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Chapter 4

Hydrogen in silicon

4.1 Introduction

With a mass-abundance of 78% to 81% hydrogen is the most common element in the universe [1]. What is more, the hydrogen atom is the most basic element possible, thus inspiring turn-of-the-century scientists to the theory of the quantization of the electronic levels and, more general, to the formulation of quantum mechanics. In solid state physics hydrogen still serves as model for the effective-mass states, i.e., a general, isoelectronic, impurity can be seen as a positively charged core and, lightly bound to this, an electron. In this theory the host lattice only affects the hydrogen-like states by changing the dielectric constant of the background, thereby increasing the radii of the states.

Recently hydrogen enjoys a growing interest among theoretical and experimental semiconductor physicists. This is motivated by the dramatic effect of hydrogen on the electronic properties of the material. Hydrogen can very easily satisfy dangling bonds or attach itself to donors or acceptors and thus terminate their electrical activity by compensating the charge carrier, i.e., capturing or supplying an electron [2]. Many technologically important shallow and deep levels - for instance DX in GaAs [3] (see Chapter 3) - can be readily passivated. Especially shallow acceptors (B, Al, Ga, In and Tl in silicon) are easily neutralized [4].

4.1.1 Diffusion of hydrogen

Another remarkable feature of hydrogen is its fast diffusion in the silicon lattice. The diffusion of an impurity can normally be expressed by Fick's second law

$$\frac{\partial C}{\partial t} = D\nabla^2 C,\tag{4.1}$$

where C(x,t) is the concentration as a function of space and time and the diffusion coefficient D is a function of the temperature

$$D(t) = D_0 e^{-E_a/kT},$$
(4.2)

with D_0 the prefactor, or infinite-temperature diffusion coefficient, E_a the activation energy, k the Boltzmann constant and T the absolute temperature. In Table 4.1 these parameters are tabulated for the fast diffusers (H, Au, Li, Cu), as well as some important dopants (P, B) and the silicon selfdiffusion. In Figure 4.1 the diffusion coefficients of these elements are plotted as a function of temperature. This shows that for temperatures higher than 530 °C hydrogen diffuses faster than any other element $(D=10^{-4} \text{cm}^2 \text{s}^{-1} \text{ at } 1000 \text{ °C}).$

 Table 4.1: Diffusion parameters for some fast diffusers in silicon and some other

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 [5, 6]

elements [5, 6].						
element	$D_0 \ ({\rm cm}^2 {\rm s}^{-1})$	$E_a (eV)$	T (°C)			
Н	$9.4 \cdot 10^{-3}$	0.48	450-1207			
$\mathrm{Cu}_{\mathbf{i}}$	$4.7\cdot 10^{-3}$	0.43	300-700			
Au	$2.4 \cdot 10^{-4}$	0.39	700-1300			
Li	$2.3\cdot10^{-3}$	0.72	0-877			
В	17.1	3.68	1120 - 1335			
Р	10.5	3.69	950 - 1235			
Si	$1.81\cdot 10^4$	4.77	900-1300			



Figure 4.1 Arrhenius plot of the diffusion coefficient of fast diffusers (H, Au, Cu and Li) in silicon in comparison to some other important elements. For temperatures higher than 530 °C until the melting point of silicon (1410 °C[7]) hydrogen is the fastest diffuser. Source:[6]). For the diffusion mechanism itself several models are proposed. Diffusion through diatomic, molecular hydrogen is not likely, since, although it is more stable than monatomic hydrogen, its activation energy (the threshold for diffusion) is too high; about 2.7 eV, as compared to the small energy barrier for atomic hydrogen. Even if we take into account the H-H dissociation energy of 1.6 eV, it is still energetically favorable to diffuse through a monatomic species [8].

The low activation energy of 0.48 eV indicates a simple (monatomic) species diffusing through interstitial lattice positions (see Figure 4.2 for the nomenclature of the various lattice positions). This can, however, not explain the low-temperature or high-concentration data. For this region Chang and Chadi calculated that a diatomic hydrogen complex accounts for the diffusion [9, 2]. In their model the hydrogen diffuses in pairs, changing from interstitial molecular hydrogen to the metastable H_2^* complex (a combination of a bond-centered and an anti-bonding hydrogen atom). The movement of the individual atoms is correlated, while different paths are possible.



Figure 4.2 High-symmetry positions in the silicon lattice.

4.1.2 Lattice positions

When the silicon crystal is at sufficiently low temperature and hence the hydrogen atom is frozen in the lattice, this atom can occupy various positions in the lattice with different symmetries, including bond-centered (BC) and anti-bonding (AB) sites. Both have trigonal symmetry, because in both cases the hydrogen atom is situated on a <111> crystal axis. Other possibilities are interstitial cubic (T_d) , orthorhombic (C = C_{2v} , on a <100> axis), monoclinic (M = C_{1h} , on a mirror plane) and hexagonal (Hex) symmetries. For negatively charged hydrogen the cubic interstitial position is predicted as the lowest energy state, H⁰ can be either on this T_d site [2] or on the BC site [10], whereas positively charged hydrogen is believed to relax to the high-electron-density BC site [2, 13]. Therefore, one expects BC hydrogen in p-type silicon and T_d hydrogen in n-type silicon.



Figure 4.3a The Si-AA9 spectrum at 77 K, B // <100> and $\nu = 37.47$ GHz [14].



Figure 4.3b Angular dependency of Si-AA9 with B in the $(0\overline{1}1)$ plane at T = 77K and $\nu = 37.412$ GHz [14].

Normal muonium (muonium on a T_d site) and anomalous muonium (muonium on a bond-centered position) have both been observed in μ SR [15]. Because muonium is chemically equivalent to hydrogen and deuterium, only differing in the mass of the nucleus, also EPR spectra of "normal" hydrogen (deuterium) and "anomalous" hydrogen (deuterium) are expected. The only EPR observation of hydrogen so far has been the Si-AA9 spectrum by Gorelkinskii and Nevinnyi [14]. This trigonal spectrum, observed in a hydrogen-implanted high-purity silicon sample, showed a small hydrogen hyperfine interaction doublet splitting, which changed into a triplet when switching to deuterium implantation, thereby giving direct proof for the presence of (a single) hydrogen in the defect. The evidence for the BC position of the hydrogen comes from the the trigonal symmetry of the spectrum and the small hydrogen hyperfine interaction, which in LCAO analysis (Linear Combination of Atomic Orbitals, see appendix C) means low charge density on the hydrogen nucleus and large ²⁹Si hyperfine interaction. This is expected for neutral hydrogen on the trigonal BC position, where the paramagnetic electron resides in the antibonding state (see Figure 4.4), since the bonding level is filled with the two silicon-silicon bond electrons. In this case there is no charge density on the hydrogen nucleus and therefore no Fermi-contact interaction, resulting in the absence of hyperfine structure.



Figure 4.4 Formation of the Si-H-Si bond. On the left the bonding (b) and antibonding (a) levels are drawn. The 1s state of the hydrogen electron (right) only couples to the bonding state, giving rise to a lower and a higher bonding state. The third, unpaired, paramagnetic electron has to reside in the antibonding state with a node in the wavefunction on the hydrogen core. This configuration will result in an absence of isotropic hyperfine interaction for BC-H⁰ [10].

4.1.3 Hydrogen introduction into the lattice

In contrast to to the high diffusion coefficient, hydrogen has low solubility in silicon. In the absence of any trapping impurities the solvability at 1 atm gas pressure follows the temperature dependence [5]

$$S = 2.4 \cdot 10^{21} e^{-1.88 \text{eV}/kT} \text{cm}^{-3}.$$
(4.3)

This implies that for moderate temperatures, exposing the sample to a hydrogen plasma will yield a very low concentration (e.g. 10^6 cm⁻³ at 350 °C). While this is a good method for passivating impurities, and has the advantage of not damaging the crystal, it evidently not suffices for generating a large amount of hydrogen defects.

Implantation of hydrogen has the advantage that the concentration and depth profile can be controlled by varying the dose and the proton kinetic energy, respectively. When this implantation takes place at low temperatures, large concentrations can be
maintained throughout the crystal. The range of protons is somewhat more than 1 μ m per 100 keV energy, while for high current density of 1 mA/cm² and long exposure times, total doses of more than 10¹⁷ can be achieved, with local densities up to 25 at%. On the other hand, by ion implantation a large number of (unwanted) radiation defects can be formed.

4.2 The Si-NL51 spectrum

Many years of research in the field of radiation effects in silicon have resulted in the discovery and identification of a variety of centers, including vacancies, self-interstitials and complexes of these primary defects. One of the most prominent and easy-to-produce radiation defects is Si-B3 [11, 12], which is well established to be originating from a self-interstitial complex oriented along a <100> crystallographic direction, resulting in an electron paramagnetic resonance (EPR) spectrum with fairly uncommon (tetragonal) magnetic field angular dependence. In the current study of defects created by hydrogen implantation of silicon we encountered a defect which seems to be related to Si-B3, in the sense that it has the same symmetry and similar, though not identical, formation kinetics.

4.2.1 Experimental details

As starting material for the experiments high-purity, high-resistivity (6k Ω cm), silicon was used. The material was submitted to proton or deuteron beam implantation with a starting energy of about 30 MeV (H) and 25 MeV (D) per nucleon. In between the cyclotron source and the target an aluminium absorber of 3.9 or 1.6 mm thickness was placed. The ion current of circa 0.5 μ A/cm² yielded a dose of circa $1 \cdot 10^{15}$ cm⁻². The implantation was repeated with different absorber thicknesses in order to produce a homogeneous distribution of hydrogen and the defects. The total dose was then estimated to be $5 \cdot 10^{15}$ cm⁻² in the 1 mm thick sample [14]. During implantation the sample was kept at a temperature of approximately 300 K.

After the implantation, the samples were given short (20 minutes) anneal stages at comparatively low temperatures (380-540 °C) in air, without any form of quenching afterwards. To remove surface defects, the samples were etched in a solution of HF and HNO₃ in a ratio of 1:3.

The measurements were performed on two superheterodyne EPR spectrometers, one with an operating frequency of 9.2 GHz (X band) [16] and one with 23.3 GHz (K

band). Both have low-frequency field modulation and were tuned for dispersion. The sample was kept at low temperatures in TE_{011} cylindrical cavities with high Q factors. To these cavities low-power microwave radiation, in the μ W range, was applied. The sample could be *in situ* illuminated with white light from a tungsten source, guided to the sample through a quartz rod. Quantitative details are given in Chapter 5.

4.2.2 Results

Following the sample preparations as described above, several EPR spectra could be detected upon illumination. In the hydrogen-implanted sample a superposition of three different spectra could be resolved and identified, as can be seen in Figure 4.5 (top trace), where these spectra are plotted for the magnetic field along a <100> crystallographic direction, as acquired at the X-band spectrometer. First, the figure reveals a slightly anisotropic spectrum (α), possibly AA1, but not further discussed in this study. Another spectrum, which could be identified by its angular dependence, is the spectrum associated with the self-interstitial, Si-B3 [12], first observed by Daly [11].



Figure 4.5 EPR spectra of the hydrogen (top trace) and deuterium (bottom trace) implanted samples, observed at X band, with the magnetic field parallel to <100>(T=4.2K). The first sample was annealed at 380 °C in air, while the latter underwent a likewise treatment at 540 °C.

Apart from these two spectra, Figure 4.5 discloses a third, previously undiscovered spectrum, which is labeled Si-NL51. Switching from protons to deuterons as an implantation species does not change the line positions or line widths of this spectrum. This is illustrated in the bottom trace of Figure 4.5, where a scan is shown for an identical sample, except for the implantation type (deuterium instead of hydrogen) and the anneal temperature (here 540 °C, instead of 380 °C for the top scan). Such a result suggests the absence of hydrogen in the defect, but in the next section we will present an alternative reason for this lack of difference. Comparison of the two scans in Figure 4.5 reveals another interesting feature, namely the absence of Si-B3 in the lower scan. This is caused by the difference in anneal temperature. The comparatively high temperature of 540 °C already anneals out Si-B3 (consistent with Figure 1 of Ref.[12]), while Si-NL51 is more persistent and subsists.



Figure 4.6 Angular dependence of Si-NL51 for X band (a) and K band (b) with the magnetic field in the $(01\overline{1})$ -plane. The experimental points of Si-NL51 (\Box) , α (+) and unidentified resonances (×) are marked. Along the solid lines, which indicate simulations with the Hamiltonian as described in the text for microwave frequencies of 9.226106 GHz (a) and 23.282640 GHz (b), the arbitrary labeled defect orientations are plotted (with 3 corresponding to [100]). The circles around the orientations indicate the electron spin state transitions (open circles: $m_S = -1$ to $m_S = 0$, solid circles: $m_S = 0$ to $m_S = 1$,). For (b) a misorientation of the sample of 4.1° was introduced into the simulation to more accurately follow the observed line positions. The Si-B3 spectrum was absent in this sample.

To further analyse the spectrum the angular dependencies were measured. The results are shown in Figures 4.6(a) and 4.6(b) for X and K band, respectively. The first task is to find the components of the spin Hamiltonian, in other words to determine the cause of the separation of the different parts of the spectrum. In view of this, it is interesting to note that a change of splitting of the lines occurs when going from the low-frequency X-band, to the higher-frequency K-band spectrometer. This eliminates the possibility of the splitting being caused by a hyperfine interaction, which is in first order magnetic-field independent. It can also be excluded that the spectrum is entirely due to an electronic Zeeman interaction, since this can never account for the intricate changes of the structure when altering the microwave frequency. First, a pure Zeeman interaction $\mathcal{H} = \mu_{\rm B} \vec{\rm B} \cdot {\rm g} \cdot \vec{\rm S}$ would produce a spectrum whose splitting would be directly proportional to the microwave frequency. Secondly, no symmetry gives rise to the observed patterns as disclosed in Figure 4.6. This leaves behind the involvement of a crystal-field term in the Hamiltonian for the explanation of the observed line positions. The lowest value of an electron spin for which crystal fields can affect the spectrum is S=1. The Si-NL51 spectrum can then be described with a spin Hamiltonian containing an (electronic) Zeeman and a crystal-field term

$$\mathcal{H} = \mu_{\rm B} \vec{\rm B} \cdot \mathbf{g} \cdot \vec{\rm S} + \vec{\rm S} \cdot \mathbf{D} \cdot \vec{\rm S}, \qquad (4.4)$$

where both \mathbf{g} and \mathbf{D} are tetragonal tensors of second rank possessing <100>-axial symmetry, and S=1, corresponding to a triplet state. The experimentally determined values of \mathbf{g} and \mathbf{D} can be found in Table 4.1, together with the spin-Hamiltonian parameters of the other spectra detected in the studied material.

Center	Symmetry	Spin	Term	//	<u>_</u>	Unit	Ref.
Si-NL51	tetragonal	S=1		<100>			$ ext{this}$
	<100>-axial		g	2.00707	2.00069		study
			D	-37.9	19.0	MHz	
Si-B3	tetragonal	S = 1/2		<100>			[12]
	<100>-axial		g	2.0166	2.0054		
Si-AA1	orthorhombic	S = 1/2		<011>			[14]
	<011>-axial		g	1.9954	2.0002		

Table 4.1. Spin-Hamiltonian parameters of the discussed spectra.

4.2.3 Discussion

Spectrum Si-NL51 exhibits tetragonal symmetry (point group S_4 or D_{2d}), indicating a symmetry axis along a <100> direction. This is quite rare in silicon, where

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only about 5% of the known centers [17] have this symmetry. All of them are radiation defects (without presence of the radiation species) [18, 19] or are <100>-uniaxial strain-induced signals [20, 21]. Since seemingly the identical spectrum is produced for hydrogen- and deuterium-implanted material it would be tempting to ascribe the center to a radiation defect, without incorporation of implantation particles.

An analysis of the D-tensor reveals further information about the defect. The magnitude of D is very small for a triplet spectrum. When we use the approximation of two interacting point-dipoles at a mutual distance r we get

$$\mathsf{D}_{\perp} = \frac{\mu_0}{4\pi} \cdot \frac{\mu^2}{r^3},\tag{4.5}$$

where $\mu = \mu_B = 9.2740154 \cdot 10^{-24}$ J/T and $\mu_0 = 4\pi \cdot 10^{-7}$ N/A². The experimental value of D_⊥ then yields an inter-dipole distance of nearly 9 Å. A careful search for ²⁹Si or other hyperfine lines within 50 mT of the Zeeman lines was made for the Si-NL51 spectrum, but none were found. It is important to note that there is also no hint of any structure in the Zeeman lines which can be associated with ¹H or ²⁹Si hyperfine interactions. It is also important to note that the EPR signal is very sensitive to the sample temperature; it vanishes for temperatures above approximately 20 K. In view of these results, the structure of the spin-triplet Si-NL51 center as arising from interacting dipoles which belong to two different cores at a distance of 9 Å with high localization is not very likely. More plausible is an extended, one-core defect, in which the value of 9 Å should be interpreted as a measure for the radius of the hydrogen-like effective-mass wavefunction. Such an extended core eliminates the possibility of observing hyperfine interactions of any nucleus, since even the strongest (closest) interactions would not be resolved in the spectrum. In this way we can still not exclude the involvement of hydrogen (deuterium) in the defect.

Because of the high electron spin (S=1) and the fact that it is seen only upon illumination Si-NL51 is most likely to arise from an excited state. On basis of the angular and frequency dependence we propose as a model for Si-NL51 an excited state of a <100>-oriented complex. It should be noted that the possibility of Si-NL51 and Si-B3 arising from the same structure cannot be excluded. The absence of Si-B3 from the higher-temperature heat-treated (540 °C) sample should then be explained by an annealing-induced shift of the Fermi level. In this case it would be logical to assign Si-NL51 to an excited, neutral charge state of the di-interstitial (SiSi)^{0*}_{Si}. Nevertheless, such a possibility seems not very likely, since Si-NL51 has not been observed in the elaborate study of Si-B3. On the other hand, if we do not assign it to the di-interstitial, the range of self-interstitials seems to be exhausted. This is in favor of a model which includes hydrogen (deuterium) in the structure. The involvement of hydrogen in the defect however cannot be positively deduced from the experimental data presented here.

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Chapter 5

Identification of hydrogen molecules in silicon

5.1 Introduction

In Chapter 4 a summary was given of the possible configurations of atomic hydrogen in silicon. However, for higher concentrations, hydrogen is expected to freeze out in diatomic complexes. There are many possibilities for these complexes, but the most likely ones are:

Molecular Hydrogen. This is a normal hydrogen pair, placed interstitially around a T_d site and without much interaction with the silicon lattice. The resulting symmetry is, in principle, trigonal (C_{3v}) .

BC². Two hydrogen atoms on BC positions, as described in Chapter 4, of near Si-Si bonds. This configuration is not very probable, since a hydrogen atom in a Si-Si bond stretches this bond by approximately 30% to 3.2 Å therefore causing strain in the vicinity of the defect, repelling other such structures. The symmetry of this configuration would be monoclinic (C_{1h}) . Of the structures mentioned here, this is the only one which is paramagnetic in the neutral charge state, since it does have two unpaired spins.

Satisfied Broken Bond. When a broken bond is satisfied with two hydrogen atoms the resulting symmetry is trigonal, but very likely to relax to lower symmetry (up to triclinic C_1) in order to release some of the huge stress.

Metastable Hydrogen, H_2^* . This is a pair which consists of a hydrogen atom on both sides of a silicon atom, one on the bond-centered position and one on the antibonding site. This is the only configuration in which the hydrogen atoms are non-equivalent. Because both atoms are on the <111> axis, the symmetry of this complex is trigonal.

This is an intermediate configuration in the hydrogen diffusion mechanism as described in Chapter 4. Experimentally, this structure was observed by Holbech *et al.* [4].



Figure 5.1 Various structures for monatomic hydrogen (as discussed in Chapter 4), diatomic hydrogen, and impurity-hydrogen complexes.

Figure 5.1 shows these possibilities for diatomic hydrogen complexes in comparison to the monatomic structures mentioned in Chapter 4.

Of the above-described complexes, the molecular hydrogen has the lowest calculated energy, even lower than two isolated hydrogen atoms of any type. Therefore, these molecules are presumed to be present in undoped material. Neither of these complexes has ever been observed in EPR. In doped silicon the hydrogen would be trapped by the donors or acceptors, forming defects of still lower energy, see Figure 5.2. In this chapter the observation of a new spectrum, labeled Si-NL52, will be reported. It will be argued that this spectrum arises from molecular hydrogen.



Figure 5.2 Energy as a function of the Fermi-level for some of the discussed complexes. In undoped material the hydrogen molecule has the lowest energy [2].

To produce the Si-NL52 spectrum as starting material undoped, high-resistivity ($6k\Omega cm$) silicon wafers of approximately 1 mm thickness was used. This material was exposed to a proton beam from a cyclotron source. The energy of the hydrogen particles, originally circa 30 MeV, was moderated and dispersed by placing an aluminum absorber in between the cyclotron source and the target. The ion current of roughly $0.05 \ \mu A cm^{-2}$ yielded a dose of circa 10^{17} protons per cm². After this hydrogen implantation the samples received short annealing stages at relatively low temperatures (typically 250 °C) in ambient air for approximately 20 minutes, without any form of quenching afterwards. To remove surface defects, the samples were etched in a solution of HF and HNO₃ in a ratio of 1:3. The samples were then placed in our superheterodyne K-band and X-band spectrometers operating at 23.3 GHz and 9.2 GHz, respectively. Both had low-frequency field modulation and were tuned for dispersion. The sample

	X band	K band
Microwave-frequency	9.2 GHz	23.3 GHz
Field modulation	$12.3~\mathrm{Hz}$	904 Hz
Tuning mode	dispersion	dispersion
Cavity	TE_{011}	TE_{011}
Q factor	43000	5000
Temperature	>7 K	4.5 K
Microwave power	-4010 dBm	-40 - +5 dBm
RF power (ENDOR)		+36 dBm
RF chopping		3.3 Hz

Table 5.1 Quantitative specifications of the EPR spectrometers.



Figure 5.3 Spectra of Si-NL52, as measured at the X-band (9.225718 GHz) spectrometer, for a magnetic field along the crystallographic directions <100>, <111> and <011>, respectively. The microwave power (P_{μ}) was -20 dBm and the sample temperature T = 7.7 K. The observed (integrated) intensity ratio of the (single) side and central lines is, at these conditions, 1:53.

was kept at temperatures close to ambient pressure liquid-helium temperature in the center of TE_{011} cylindrical, high-Q-factor cavities. Here it was exposed to low-power microwave radiation in the μ W range [1]. See table 5.1 for quantitative details of the spectrometers used.

5.2 Results

The sample preparations as described above resulted in the generation of the Si-NL52 spectrum, see Figure 5.3, where the spectra are shown for the magnetic field along the principal crystallographic directions $\langle 100 \rangle$, $\langle 111 \rangle$ and $\langle 011 \rangle$, as acquired at the X-band spectrometer. Comparison of the $\langle 100 \rangle$ spectrum to the K-band spectrum for the same field direction (see Figure 5.4) shows that the splitting of the outside lines is caused by a field-independent interaction, i.e., a hyperfine term in the Hamiltonian describing the interaction of the electron spin with a (magnetic field of a) nuclear spin. The same analysis also reveals that the splitting of the central line *is* (mostly) due to the anisotropy of such a field-dependent term: electronic Zeeman interaction $\mu_{\rm B}$ B·g·S.



Figure 5.4 Spectra of Si-NL52, as measured at the X-band (a) and K-band (b) spectrometers, for the magnetic field along the crystallographic direction <100>. This identifies the nature of the splitting as HF interaction and shows that the intensity ratio can change.

Another interesting feature which is revealed by the comparison of the X- and Kband spectra is the difference in (integrated single line) intensity ratio of the side and middle components. These ratios depend on the operating temperature, microwave frequency and power in an intricate way. Experimental values of 1:3 for high powers and low temperatures at our K-band spectrometer to ratios as high as 1:200 have been observed. The angular dependence of the Si-NL52 spectrum (see Figure 5.5) displays that the symmetry of the originating center must be trigonal (point group C_3 , S_3 , C_{3v} , D_3 or D_{3d}).





In addition to the EPR spectra, a limited ENDOR (electron nuclear double resonance) study was started on the defect. This revealed the presence of interacting hydrogen and silicon in the vicinity of the defect, although the interactions are rather small. All lines were in the neighborhood of the nuclear Zeeman frequencies (42.5759 MHz/T for ¹H and 8.458 MHz/T for ²⁹Si [3]). Figure 5.6 shows a hydrogen ENDOR scan for a magnetic field close to the <011> direction. The scan shows a symmetric



Figure 5.6 An ENDOR scan for the magnetic field (B=826.00 mT) 5° away from <011>. The scan is split at the nuclear Zeeman frequency of hydrogen $(\nu_Z = 35.168 \text{ MHz} \text{ for this field})$ and folded back. The symmetric pattern which results indicates that the lines are caused by hydrogen (see also Figure 5.7).

pattern around the nuclear Zeeman frequency of hydrogen, indicating that the source for the resonances is hyperfine interactions with hydrogen. Figure 5.7 shows the magnetic-field-dependence of a typical line of Figure 5.6. In this way the chemical identity of the involved nucleus can be determined: the position of the lines in Figure 5.6 follow the relation for a general ENDOR frequency caused by hyperfine interactions of the nucleus with the electron spin

$$\nu = |g_N \mu_N B \pm m_S A|/h. \tag{5.1}$$

In equation 5.1 the only field-dependent part is the first term; the nuclear Zeeman frequency. The field dependence shows the nuclear moment and the relative magnitude of the nuclear Zeeman and the hyperfine interaction:

$$\frac{d\nu}{dB} = \pm g_N \mu_N / h. \tag{5.2}$$

If the sign in equation 5.2 is negative, the hyperfine interaction is larger than the nuclear Zeeman interaction, otherwise it is smaller. In this way Figure 5.7 shows that the α line

in Figure 5.6 is caused by small hyperfine interactions with hydrogen. The magnitude of the interaction (A = 1.184 MHz) indicates a very low paramagnetic electron density (0.083%) on this site ¹ Large interactions were not found, neither for hydrogen, nor for silicon.



Figure 5.7 Position of the ENDOR line α of Figure 5.6 for magnetic fields of 824.81 mT (a), 824.50 mT (b) and 825.10 mT (c). This closely follows the dependency expected for hydrogen (42.5759 MHz/T [3]) as indicated by the heavy-dotted straight line in the right part of the figure.

5.3 Discussion

To understand the experimental data the most obvious explanation would be to ascribe the side and central lines to totally different spectra, possibly not even related to the same defect. This would readily account for the fluctuation in intensity ratio. However, this model can easily be put aside if one bears in mind that 1) the spectra have identical g tensors and 2) they show exactly the same electron nuclear double resonance (ENDOR), which can only be explained if we assume that the parts of the spectrum belong to the same defect.

There are still several possibilities for the nuclear spin configuration. The spectrum can be attributed to a combination of two spectra: one without hyperfine interaction because of the absence of nuclear spins in the defect (I=0) and one with ligand hyperfine

¹see appendix C for a derivation of the LCAO parameters for hydrogen

interaction with neighboring ²⁹Si atoms. Although there would be no problem with fitting of the parameters of such a model to the observed line *positions*, there is a problem with explaining the *intensity* ratio of the two spectra which is changing from 1:3 to a ratio as high as 1:200, as mentioned before. If one takes into account the fact that ²⁹Si has a natural abundance of 4.70% the expected intensity ratio is 2.46% (1:40.6) if there is one silicon atom in the interaction shell. The experimental data are contradicting this. Apart from this, a drifting intensity of a silicon ligand spectrum has never been observed before, which makes the assignment of the large HF splitting to silicon irrational. For Figure 5.3 the experimental conditions accidentally produce an intensity ratio close to the value expected for ²⁹Si. Figure 5.4 shows that the intensity ratios can be quite different.



Figure 5.8 Detail of the Si-NL52 spectrum as acquired at the K-band spectrometer. The scan shows the splitting of the HF structure at the <111> field direction due to HF interactions with atomic hydrogen.

The involvement of a guest atom other than hydrogen in the defect is even more unlikely, since the starting material was undoped. Further, the same arguments can be used against this model as for the case of silicon. This leaves the possibility of hydrogen as the source for the large HF splitting. One hydrogen atom is not enough because this would give rise to a spectrum of two patterns (hydrogen has a nearly 100% abundant isotope with I=1/2). Two atoms are needed to comply with the data. If one assumes a weak coupling between the two hydrogen atoms one would, in principle, expect 4 lines when the field is parallel to the <100> axis. But when the two atoms are exactly equivalent the middle two lines would coincide. The second-order effect (~ A^2) splitting (0.04 mT) of the central two lines is smaller than the linewidth. The intensity ratio of a side line ($m_{I_1} = m_{I_2}$) as compared to the middle lines ($m_{I_1} = -m_{I_2}$) would be 1:2 and stable. On the other hand, if we assume a strong coupling between the two atoms, as is normal for isolated hydrogen molecules [5], there will be two possible nuclear spin states, namely para-hydrogen with the nuclear spins anti-parallel (I=0) and ortho-hydrogen with the spins parallel (I=1). The observed spectrum can then be explained by assuming that it is a superposition of the triplet and the singlet spectra. Because the para state has lower energy than the ortho state, with a difference of approximately 180 K (for hydrogen in vacuum [5]), it will be (nearly) the only one occupied at low temperatures. The fluctuation of the intensity ratios can now be explained by a conversion from ortho- to para-hydrogen, and vice versa.

Closer inspection of the spectrum reveals an extra splitting of the spectrum, see for instance the detail of the spectrum taken at a magnetic field along the <111> direction (Figure 5.8). This may be caused by hyperfine interactions with two non-equivalent independent (non molecular) hydrogen atoms. The existence of such elaborate centers falls nicely into the model of hydrogen clustering as predicted by Zhang and Jackson [6], among others. The interaction seems to be <111>-axial which indicates that the hydrogen atoms are on the extension of the H₂ molecule bond axis.

We can now ascribe the spectrum to a Hamiltonian

$$\mathcal{H} = \mu_{\rm B} \vec{\rm B} \cdot \mathbf{g} \cdot \vec{\rm S} + \vec{\rm S} \cdot A_{\rm H_2} \cdot \vec{\rm I}_{\rm H_2} + \vec{\rm S} \cdot A_{\rm H}^1 \cdot \vec{\rm I}_{\rm H}^1 + \vec{\rm S} \cdot A_{\rm H}^2 \cdot \vec{\rm I}_{\rm H}^2, \qquad (5.3)$$

with S=1/2 and $I_{H_2}=1$ for the triplet spectrum and $I_{H_2}=0$ for the singlet spectrum. In both cases $I_{H}^{1} = I_{H}^{2} = 1/2$. The values of the parameters, obtained by fitting to the experimental data, are given in Table 5.2.

Table 5.2 Spin-Hamiltonian parameters for Si-NL52. <111>-axial symmetry.

	+		
term		\bot	unit
g	2.00069	2.00951	
A _{H2}	217.8	128.2	MHz
A_{H}^{1}	4.8	1.5	MHz
A ² H	12.1	-5.0	MHz

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Chapter 6

A possible new identification of the \mathbf{P}_b defect

6.1 Introduction

The increasing number of devices on an IC is made possible by the continuing scaling down of the structures. The ever decreasing dimensions make the two-dimensional structures relatively more important with regard to the three-dimensional ones. This explains the escalating interest in the physics of surfaces and interfaces of semiconductors. Since the dawning of the semiconductor age in the 1950's, SiO₂ has never lost its leading role of perfect material for isolation in silicon-based material. This is caused by the many advantages of silicon oxide over other materials; it is nontoxic, has high mechanical hardness and elasticity, has high stability under ambient conditions, has high heat conductance, is cheap, has practically unlimited resources, can withstand strong electrical fields of up to 8 MV/cm for years without being destroyed, and has excellent isolating features because of the very high energy gap of more than 9 eV. One can say that the properties of SiO_2 have finally tipped the scale over to silicon as starting material for semiconductors. Other types of semiconductor have lost terrain for the reason that they could not compete with the sublime qualities of the silicon technology, leaving only extreme-conditions areas of the semiconductor spectrum to more fancy materials like SiC and GaAs (see Chapters 2 and 3 of this thesis, respectively). It may serve as an example that germanium, another material of the early days of the semiconductor era, has a water-soluble oxide [1].

Defects in the oxide and Si/SiO_2 interface cause trapping of charges and thus formation of unwanted electrical fields, thereby influencing the carrier transport properties and degrading the overall performance of the device. This defect formation may eventually lead to a spontaneous occurrence of short-circuit in the insulating oxide and a breakdown of the device. Evidently, it is of utmost importance to know the exact nature of these defects, such as their formation kinetics and microscopic structure.

The most familiar intrinsic defect at the interface is the P_b center, which accounts for up to 100% of all electrical trapping [2]. Its electron paramagnetic resonance (EPR) spectrum was first detected by Nishi [3] and subsequently attributed by Poindexter *et al.* [4] to a silicon dangling bond stabilized normal to the <111> Si/SiO₂ interface. Later, the same spectrum was found in oxygen-implanted silicon (SIMOX), where a layer of silicon-oxide is created below the surface [5]. Also in the novel material porous silicon (po-Si) the same spectrum was revealed [6]. This brought new interest to the P_b center as part of the quest for the explanation of the luminescence in po-Si.

6.2 Comparison of the P_b and Si-NL52 spectra

In Chapter 5, an EPR spectrum with similar features as the P_b spectrum is described. This spectrum was observed in an entirely different type of silicon [7]. The spectrum, labeled Si-NL52, was detected in high-purity (FZ), undoped, bulk silicon, after a high-dose hydrogen implantation, followed by a short (20 min.), low-temperature heat treatment (250 °C). A comparison of the two spectra reveals that they must originate from basically the same microscopic structure.

When comparing the properties of the two spectra, one first notices that the spin Hamiltonians are similar. Both have trigonal g tensors and contain a trigonal hyperfine (HF) interaction term $S \cdot A \cdot I$, which combine into a total spin Hamiltonian $\mathcal{H} = \mu_B B \cdot \mathbf{g} \cdot S + S \cdot A \cdot I$, where μ_B is the Bohr magneton, \mathbf{g} the g tensor, A the hyperfine interaction tensor, and S and I the electron and nuclear spins, respectively.



Figure 6.1 Scatter plot of the parameters of trigonal centers. Out of the 59 listed in Ref. [8] 38 have their parameters in the small area defined by $|g_{iso} - 2.0023| < 0.012$ and $|g_{aniso}| <$ 0.006. The P_b (×) and Si-NL52 (+) are close together, but in a high-density region.



Figure 6.2 Angular dependencies of the electron paramagnetic resonance at $\nu = 23.2$ GHz, for a spin Hamiltonian as described in the text and with spin-Hamiltonian parameters as given in Table 6.1. The thick trace is Si-NL52, whereas the thin trace represents P_b . The place of the FSE scan of Figure 6.12 is indicated by a dashed line. The typical linewidth of Si-NL52 of 0.9 mT is indicated.

The g tensor is nearly equal for the Si-NL52 and P_b spectra. But this is not sufficient to prove their equivalence. Figure 6.1 shows that many trigonal centers have g tensors in this region. It is the first of a list of similarities of Si-NL52 and P_b . The magnitude of the anisotropic part of the electronic Zeeman interaction is slightly different for the two centers (see Table 6.1). One has to bear in mind here that the spread in g factors, as found in the P_b literature, is substantial. The value of g seems to depend strongly on the exact type of material studied [5]. Stesmans has shown that stress, present in the environment of the defect, influences the g_{\parallel} value significantly [9]. In the light of this, the deviating value for g_{aniso} as observed in the current study can be explained with the assumption that a different (e.g. oxygen-lean) environment is created by the ion implantation. Figure 6.2 illustrates the similarity of the spectra by showing simulations for the Hamiltonian with the parameters of Si-NL52 and P_b.

spectrum	term		\bot	error	unit	Ref.
Si-NL52	g	2.00069	2.00951	± 0.0002		[7]
	$A_{HF}(1)$	218	128	± 2	MHz	
P_b	g	2.0016	2.0090			[10]
	$A_{HF}(2)$	438	255		MHz	
	$A_{HF}(1)$	219	127		MHz	
\mathbf{P}_{b}	g	2.0012	2.0081			[11]
P _b	g	2.0014	2.0086			[9]
(1): Assuming $I=1$.						

 Table 6.1 Comparison of the spin-Hamiltonian

 parameters for the Si-NL52 and P_i spectra

(2): Assuming I=1/2.

The hyperfine interaction tensors (A) are remarkably close for the P_b and Si-NL52 spectra, when taking into account the nuclear spin used in the models (I=1/2 and)I=1, respectively). For further discussion, it is important to recall the actual reasoning behind the assignment of the hyperfine interaction for both spectra. In the case of the P_b spectrum, the ascription to ²⁹Si is essentially based on the observed intensity ratio of HF satellites (²⁹Si, I=1/2) to the central line (²⁸Si+³⁰Si, I=0). This should closely follow the natural abundance of 29 Si (4.67%) and should result in a HF line intensity of 2.45% (ratio 1:40.8), as compared to the central line ¹. This interpretation also has as an essential element that, in this model of a dangling bond connected to a single silicon atom, the number of "equivalent" silicon atoms in the largest HF interaction shell is one. The observed ratios sometimes do come close to this value (1:67 [10]), but also ratios as deviating as 1:100 are commonly reported in the literature [12, 9]. In Ref. [10] this mismatch is recognized, but attributed to a possible loss of signal due a poor signal-to-noise ratio, as well as line broadening of the hyperfine satellites. The lack of reasonable alternatives for the HF interaction (the mismatch for ¹⁷O or ¹³C would even be bigger) then led to the assignment to ²⁹Si.

¹See appendix B for a derivation of the hyperfine line intensities



Figure 6.3 Power dependence of the Zeeman (×) and HF (+) lines of the Si-NL52 spectrum. The integrated single HF line to Zeeman line ratio is indicated with \Box 's. This ratio is changing dramatically even outside the range of saturation ($P_{\mu} < -20$ dBm). The solid lines are fits using the equations in subsection 6.3.1.



Figure 6.4 Two scans of the Si-NL52 EPR spectrum for the magnetic field along <100>. The thick trace was taken at 5.2 K, while the thin trace was taken at a temperature of 11.4 K. A clear change of relative intensities is observed.

On the other hand, the assignment of the HF interaction lines to H_2 in the case of the Si-NL52 center is partly based on the observed variable intensity ratios [7]. The current study on this subject revealed that the observed ratio depends on temperature, microwave power and frequency in a complicated way. Ratios as high as 1:3 have been observed. In Figure 6.3 a power dependence of the intensity of the individual components of the Si-NL52 spectrum is shown, while in Figure 6.4 two scans, taken at different temperatures for the same microwave power, are depicted. This excludes the possibility of the HF lines as arising from silicon. In Ref. [7] the Si-NL52 spectrum is attributed to the superposition of the triplet and singlet spectra of the ortho- and para-form of a hydrogen molecule, respectively. The variation of the ratio of the two spectra is identified as a conversion between para- and ortho-hydrogen. In the present study alternative causes for a varying ratio have been studied exhaustively and will be discussed in section 6.3.

6.3 Intermezzo: Spectrum distortion

6.3.1 Saturation of the EPR lines

The most obvious reason for the distortion of the EPR spectrum would be high microwave power. Figure 6.3 shows that saturation cannot be the cause for the anomalous behavior of the line intensity ratio, since this is changing dramatically even before saturation sets in. Apart from this, all parts of the spectrum would be equally affected by the saturation. Normal EPR saturation cannot explain the non-uniform distortion as observed for Si-NL52. A non-uniform, asymmetric distortion is discussed in the next section. Upon closer inspection Figure 6.3 discloses some interesting details.

For homogeneously broadened lines, for low microwave powers the signal intensity is directly proportional to the amplitude of the applied microwave field (B_1) , thus proportional to the square root of the power. When saturation effects become important this dependence becomes [13]

$$y \propto \frac{s^2 B_1}{(1+s)^2},$$
 (6.1)

where s is the saturation parameter,

$$s = 1/(1 + B_1^2 \gamma^2 T_1 T_2), \tag{6.2}$$

with T_1 and T_2 the spin-lattice and spin-spin relaxation times respectively, and $\gamma = 2\pi g \mu_B / h$. For low powers s is approximately unity, and Equation 6.1 reduces to a form

where y is proportional to B_1 . For high powers the saturation parameter is inversely dependent on the power, $s \propto B_1^{-2}$, and the signal is therefore decreasing upon increasing power:

$$y \propto \begin{cases} B_1 & \text{for } B_1 \to 0, \\ B_1^{-3} & \text{for } B_1 \to \infty. \end{cases}$$
(6.3)

For inhomogeneously broadened lines, the low-range microwave power dependence is equal to that of homogeneously broadened lines. In the high-power range, the signal saturates to a constant value [14]. For this case

$$y \propto B_1 \sqrt{s},$$
 therefore (6.4)

$$y \propto \begin{cases} B_1 & \text{for } B_1 \to 0, \\ \text{constant for } B_1 \to \infty. \end{cases}$$
(6.5)

These two cases are drawn in Figure 6.5.



Figure 6.5 Power dependence of homogeneously and inhomogeneously broadened lines.

Figure 6.3 reveals that the hyperfine components of the Si-NL52 spectrum closely follow the power dependence as described above for homogeneously broadened lines. On the other hand, the Zeeman component for low powers is not proportional to B_1 , but instead to $\sqrt{B_1}$. In analogy of a two photon process, i.e., a transition from one level to another that requires two-photons instead of one, which has a linear power dependence $(y \propto B_1^2)$, or, in general, a multi-photon process where $y \propto B_1^n$, this can be called a half-photon process. The exact implications and underlying physics of such a statement are not clear at this moment.

Since, for low powers, the Zeeman line intensity is proportional to $\sqrt[4]{P}$ and the intensities of the hyperfine components are proportional to \sqrt{P} , the ratio of Zeeman:HF follows the dependence $r = 1/\sqrt[4]{P}$. For higher powers the ratio does not vanish. Instead it goes to a steady value r_{∞} :

$$r = r_1 / \sqrt[4]{P} + r_\infty. \tag{6.6}$$

Fitting of this dependence to the measured ratios gives the value $r_{\infty} = 2.04 \pm 0.1$. This value is close to what one would expect for two independent, equivalent hydrogen atoms (see previous chapter); namely a central line which is twice bigger in intensity than the HF lines. Apparently, the high microwave power decouples the two atoms in the hydrogen molecule. The power dependence for the Zeeman line does not follow equation 6.1, but instead

$$y_{Zeeman} \propto \frac{s^2}{(1+s)^2} (\sqrt{B_1} + 2B_1).$$
 (6.7)

For very low powers, the ratio is expected to deviate from the relation of equation 6.6. Instead of going to infinity this ratio is expected to reach the thermal equilibrium value of the para- to ortho-hydrogen ratio [15].

To summarize, saturation cannot account for the anomalous ratio changing, since this ratio already changes outside the range of saturation, while the exact microwave power dependence points to the involvement of two hydrogen atoms; for high powers the Zeeman:HF ratio approaches 2.0, as expected for $2 \times H$.

6.3.2 Nuclear core polarization

The intensities of the hyperfine satellites often lead to the identification of the nucleus involved, as is demonstrated in appendix A. On the other hand, the experimental conditions, such as illumination or saturation of the EPR signals may lead to deviations from these expected intensity ratios. Overhauser [16], Kittel [17] and Korringa [18] predicted a polarization of the nuclei caused by saturation of the EPR signal, which was observed by Carver and Slichter [19]. Feher [20] extended this theory to population inversions generated by illumination which was indeed observed by Konchits *et al.* [21]. In both cases the electron spin needs to be coupled to the nuclear spin through a hyperfine interaction contributing to a total Hamiltonian

$$\mathcal{H} = g\mu_{B}\vec{B}\cdot\vec{S} + A\vec{S}\cdot\vec{I} + g_{N}\mu_{N}\vec{B}\cdot\vec{I}.$$
(6.8)

For S=1/2 and I=1, the level diagram is drawn in Figure 6.6. At low temperatures (4 K) and nominal field strengths (800 mT), the spin systems preferably are in the lowest three levels (m_S =-1/2), with a negligible inhomogeneity in the distribution over the different nuclear states. The ratio of the occupancy of the lower levels and the higher levels is determined by the Boltzmann factor $x = e^{g\mu_B B/kT} \approx 1.3$. The most important relaxation for the electron spins is the cross-relaxation (λ_X) in which a simultaneous flip of the electron and nuclear spins occurs, thus obeying the spin conservation law. Apart from this relaxation also electronic (λ_E) and nuclear (λ_N) relaxations are to be considered, although they are of less importance.



Figure 6.6 Level diagram of the Hamiltonian as in the equation 6.8. The relaxation paths are indicated with λ_N , λ_E and λ_X for nuclear, electronic and cross-relaxations, respectively. Resonant (EPR) transitions are labeled with λ_R

The equations which discribe the time dependencies of the populations of the levels are

$$\begin{split} dN_{1}/dt &= \lambda_{N}(N_{2}-N_{1}) &+ \lambda_{E}(xN_{6}-N_{1}) &+ \lambda_{X}(xN_{5}-N_{1}), \\ dN_{2}/dt &= \lambda_{N}(N_{3}-N_{2}) - \lambda_{N}(N_{2}-N_{1}) &+ \lambda_{E}(xN_{5}-N_{2}) &+ \lambda_{X}(xN_{4}-N_{2}), \\ dN_{3}/dt &= -\lambda_{N}(N_{3}-N_{2}) &+ \lambda_{E}(xN_{4}-N_{3}), \\ dN_{4}/dt &= \lambda_{N}(N_{5}-N_{4}) &- \lambda_{E}(xN_{4}-N_{3}) &- \lambda_{X}(xN_{4}-N_{2}), \\ dN_{5}/dt &= \lambda_{N}(N_{6}-N_{5}) - \lambda_{N}(N_{5}-N_{4}) &- \lambda_{E}(xN_{5}-N_{2}) &- \lambda_{X}(xN_{5}-N_{1}), \\ dN_{6}/dt &= -\lambda_{N}(N_{6}-N_{5}) &- \lambda_{E}(xN_{6}-N_{1}). \end{split}$$
(6.9)

Without an external resonant (microwave) field, the steady-state solution of this coupled set of equations is the thermal equilibrium distribution, as described before:

 $N_1=N_2=N_3=xN/(3+3x)$ and $N_4=N_5=N_6=N/(3+3x)$, with N the total number of paramagnetic spin systems. When the external field is resonant, two extra terms are added. For example, the resonance $1\leftrightarrow 6$ gives an extra transition:

$$(dN_1/dt)' = dN_1/dt + \lambda_R(N_6 - N_1),$$

$$(dN_6/dt)' = dN_6/dt - \lambda_R(N_6 - N_1),$$

$$(6.10)$$

where λ_R is the quasi relaxation, depending on the power of the applied microwave field. The intensity of the EPR signal is linearly proportional to the number of resonant transitions:

$$I_{\text{EPR}} \sim \lambda_{\text{R}} (N_6 - N_1). \tag{6.11}$$





As an example, the numerical solution of the equations as described above, with values $x=4 \lambda_N=10^{-6}$, $\lambda_E=10^{-4}$, $\lambda_X=10^{-2}$, and $\lambda_R=0.1$, yields an EPR intensity ratio of 1.55:0.86:0.59. The saturation of the EPR lines distorts the normal ratio (1:1:1) in an asymmetrical way. In Figure 6.7 this distortion is depicted in comparison with the low-microwave-power spectrum, while Figure 6.8 draws the line intensities as a function of the stimulated-transition probability, which is a measure for the microwave power. Other parameters of the relaxation times λ_N , λ_E , and λ_X will give different ratios, but the asymmetry always remains.



Figure 6.8 Microwave-power dependence of the individual line intensities. The spectra, as expected for $\lambda_R = 0.1$ and 10^{-7} , are drawn in Figure 6.7.

The Si-NL52 spectrum does not show this asymmetrical spectrum distortion, therefore nuclear core polarization can be excluded as the source for the anomalous behavior of the hyperfine lines.

6.3.3 Defect band formation

Another source for spectrum distortion, which can be encountered for higher concentrations of the defect, is defect-conduction band formation. In that case, a single (isotropic) Zeeman resonance, with a different g value is expected for these conduction electrons [22]. As an example, Figure 6.9 shows the change of the signal of phosphorusdoped silicon with the increasing of the phosphorus concentration. The spectrum itself is independent of the applied microwave power when the individual parts, the phosphorus donor signal and the defect-band electron signal, have the same power dependence.

No defect band is formed in the samples used for studying Si-NL52. Here all components have the same, anisotropic, g factor, deviating from the free-electron value.

 Magnetic
 Magnetic

 7x1016.E
 Magnetic

 7x1016.E
 Magnetic

 Magnetic
 Magnetic

 7x1016.E
 Magnetic

 7x1016.E
 Magnetic

 7x1016.E
 Magnetic

 7x1016.P
 Magnetic

 7x1016.P
 Magnetic

 7x1017.P
 Magnetic

 4x1017.P
 Magnetic

 3x1016.P
 Magnetic



6.3.4 Motional averaging

A defect with a certain symmetry has, generally speaking, several possible ways to be embedded in the crystal. These possible realisations are called orientations and are, in the absence of external forces like uniaxial stress, etc., equally occuring in the crystal. Each orientation has its own dependence on the magnetic field angle, and thus a set of branches results in the angular dependence. A trigonal defect may serve as an example. This has a 3-fold axis, and since the silicon lattice has four such axes, there are four possible realisations in the crystal. An angular pattern with four branches results. For low temperatures, hopping between two orientations is not possible; the threshold of this process is too high. When the temperature is increased and the activation energy of the hopping is not too high (which especially is likely to be the case for interstitial defects), this might occur. If this hopping has a relaxation time shorter than the microwave period, effectively the symmetry of the defect is higher, because the interaction tensor (e.g. g) is averaged. In the spectra, this is visible by first an appearance of resonance between the distinct orientations and, for higher temperatures, the disappearance of the original spectrum and the presence of a spectrum with higher symmetry.

This is not observed for Si-NL52. First, the effect described above is independent of the applied microwave power, while the anomalous intensity behavior of Si-NL52 is strongly dependent on P_{μ} . Second, the central part of the Si-NL52, which is relatively increasing for higher temperatures and lower powers, has the same symmetry as the satellite components. Motional averaging can be excluded as a source for intensity-ratio changing.

6.4 Superhyperfine structure

Now that the large hyperfine interaction has extensively been discussed as arising from molecular hydrogen, a more detailed examination of the spectrum is worthwhile. A closer inspection of the P_b spectrum resolved extra superhyperfine (SHF) structure, arising from the interactions with ligand silicon atoms [12]. The axial SHF tensor, with a principal axis along <111>, has an isotropic part $A_{iso} = 1.6-1.8 \text{ mT}$ (45-50 MHz) [10, 23, 24]. The added intensity of these two SHF lines, as compared to the central line is approximately 10-15% (5-7.5% for a single line), "consistent with an assignment to two or three neighboring atoms" [12]. This SHF structure was then attributed to the shell of three next-nearest (or next-next-nearest [25]) neighbors in the model of trivalent silicon. A graphical presentation of the discussed models for P_b is given in Fig. 6.10. Indeed, in such a model one would expect three atoms in the second shell, but the symmetry of the resulting interaction would have been monoclinic, instead of the observed trigonal symmetry reported in Ref. [12]. Moreover, whereas the intensity ratio for the SHF structure is discussed at a considerable length and meaningful conclusions regarding the number of silicon atoms are drawn, the fact that at the same time the intensity ratio for the largest hyperfine structure, also related to ²⁹Si and simultaneously measured, is at least 2.5 times smaller than the value expected for the model, is not commented upon [12]. This inconsistency should not be overlooked since it might indicate a different nature for the two interactions.



Figure 6.10 The old (left) [25] and proposed new model (right) for the P_b center. The various shells of HF interaction are indicated. For simplicity the further environment (e.g. SiO_2) is not shown.

The complicated nature of the Si-NL52 EPR spectrum does not permit a similar analysis of the SHF interaction directly. This is due to the fact that in the Si-NL52 spectrum a fourfold splitting of the lines has been observed which is caused by moredistant hydrogen interactions [7]. Such a fourfold splitting increases the linewidth and inhibits the precise observation of small-intensity hyperfine satellites. Fortunately, the method of field-scanned ENDOR (FSE) [26] provides a way to decompose the EPR spectrum into parts where the SHF structure is resolved.



Figure 6.11 The principle of Field Scanned ENDOR (FSE) illustrated for S=1/2, I=3/2. By looking at the intensity of an ENDOR line (indicated with $\Delta m_1 = 1$), as a function of the magnetic field, that part of the EPR spectrum is reproduced that is connected to the ENDOR line.

6.4.1 Field-scanned ENDOR

In FSE the intensity of an ENDOR (electron-nuclear double resonance) line is monitored as a function of the magnetic field. The radio frequency (RF) is continuously varied with the changing magnetic field, in order to constantly fulfill the resonance (NMR) conditions. In this way only EPR signals which are connected to the particular ENDOR line contribute to the FSE spectrum. This is shown in Figure 6.11

The result of a measurement for Si-NL52 is illustrated in Figure 6.12, where EPR and FSE scans are shown together for an angle of 85° in Fig. 6.2. The advantage of using the FSE technique is immediately evident. First, part of the spectrum (between 826 and 829 mT) is removed, because it does not belong to the defect orientation connected to the particular ENDOR line. In addition to this, the line shape is significantly simplified and now pronounced ²⁹Si hyperfine structure is revealed. The outermost SHF satellites correspond to an effective hyperfine interaction of approximately 45 MHz, equal to the value obtained by Brower [10, 23], and in good agreement with Carlos [12] for the field in this specific direction. This again provides evidence for the equivalence of the Si-NL52 and P_b spectra. Due to the increased resolution, the intensity of a satellite can now be accurately measured and is found to be 5% of the central line. This indicates the presence of two equivalent silicon atoms in the shell, rather than three. This is inconsistent with the old P_b model. On the other hand, the intensity as well as the symmetry of the SHF structure can readily be understood in terms of the model which was originally used for the Si-NL52 center. Here the interstitial hydrogen molecule is oriented along a <111> direction, exhibiting D_{3d} symmetry. The SHF lines can then be attributed to the interaction of the electron spin with the two first-neighbor silicon atoms on the extended H-H bond axis (see Fig. 6.10). Such an interaction has trigonal symmetry, as indeed experimentally observed for P_b [12].

The FSE spectrum also reveals a second shell of SHF interactions. The intensity of these lines is more difficult to estimate, since they are positioned on undetermined backgrounds of the central line, and, as well, may interfere with possible other shells of nuclei with SHF interactions of comparable magnitudes. Therefore it is, at this moment, difficult to ascertain the true number of silicon atoms in this shell.

The last interesting feature of Figure 6.12 is the fact that a small peak is observed in the high-field range (\approx 829.6 mT), which coincides with the EPR line of the large ortho-hydrogen hyperfine interaction. The intensity of this line is exactly scaled to the corresponding EPR line. In other words, the FSE/EPR intensity ratio for the line around 825 mT is equal to FSE/EPR ratio for the line around 829.6 mT. This



is a direct proof that the central and side lines as indicated in Figure 6.2 are indeed connected; they belong to the same center, because they have the same ENDOR line.

Figure 6.12 Field Scanned ENDOR (thin trace) at 85° (see Figure 6.2) showing well-resolved ²⁹Si hyperfine interactions. The FSE technique has isolated a clean spectrum as compared to the EPR scan (thick trace). The ENDOR transition which was used in the FSE spectrum was a typical hydrogen line (35.78900 MHz) for a magnetic field of 824.93 mT at a microwave frequency of 23.202344 GHz. The correction for the constantly changing nuclear Zeeman frequency was 42.5758 MHz/T. During the FSE experiment, the temperature was kept at 12.4 K.

Summarizing, it has been shown that the Si-NL52 and P_b spectra can be described by the same spin Hamiltonian and have very similar g tensors as well as equal HF and SHF parameters. In addition to that, both the P_b and Si-NL52 spectra show the same anomalous varying intensity ratio of central-to-side-lines. This confirms that both spectra correspond to defects which have basically the same structure.

At the same time, new experimental evidence challenging the arguments behind the (present) identification of the P_b center as a silicon broken bond was presented; namely it was shown that the varying intensity ratio of the large hyperfine interaction components is a characteristic feature of the spectrum and cannot be attributed to spectroscopic or experimental peculiarities [10]. Further, by a precise measurement of the intensity of the biggest SHF interaction, whose line intensity behaves in the usual manner, we concluded that the nearest-neighbor shell contains only two silicon atoms. This result contradicts the current interpretation of the P_b center. On the other hand, the 2-atom shell is fully consistent with the model of a <111>-axial H₂ molecule occupying an interstitial site halfway between the two silicon atoms along the axis of the defect, as proposed for the Si-NL52 spectrum.

In view of the above, one is likely to conclude that, whereas some of the questions concerning the Si-NL52/P_b center are still unanswered - such as its hydrogen passivation - its identification as a trivalent bonded silicon atom cannot be sustained. As an alternative, the P_b center might be generated by paramagnetic H₂ molecules trapped at the Si/SiO₂ interface. Such an identification is also supported by reports of a prominent presence of hydrogen at such interfaces [27].

6.5 Critical remarks

While the above description can explain many aspects of the Si-NL52 spectrum and hence of the P_b center, many questions still remain unanswered and some data concerning the spectra are difficult to understand. Some of them will be mentioned here.

6.5.1 Oxygen in the defect structure

The most obvious difference of Si-NL52 and P_b is their production conditions. P_b is observed in oxygen-rich materials, such as Si/SiO₂ interfaces, or oxygen-implanted bulk silicon, or oxidized (porous) silicon, while Si-NL52 is observed in oxygen-lean, hydrogen-implanted, bulk silicon. The difference might be that in Si-NL52 (atomic) hydrogen has taken over the role of oxygen in P_b of trapping, stabilizing and activating

the (molecular) hydrogen. This could then also explain the small experimental dissimilarities such as the difference in line shape (fourfold splitting for Si-NL52) or the minute deviations of the g tensor.



Figure 6.13 Infrared absorption spectrum of the sample containing Si-NL52 (AA). For reference similar spectra of Czochralski and Float Zone silicon are shown. The 1106 cm⁻¹ absorption band, caused by a vibrational mode of an oxygen atom bound to two silicon atoms, can be used for the determination of the oxygen concentration.

On the other hand, it cannot be excluded that the oxygen is introduced into the crystal during the hydrogen implantation. Under normal conditions, oxygen has a very small diffusion coefficient $(D = 0.11 \exp\{-2.51 \text{eV}/kT\} \text{ cm}^2/\text{s})$, but it has been reported [28] that this can be greatly enhanced by the presence of hydrogen. Indeed, the first (FZ) sample which was used in this study contained a substantial amount of oxygen. Figure 6.13 shows the infrared absorption spectrum of the first sample. The oxygen concentration can be estimated from the absorption coefficient at the 1106 cm⁻¹ band at room temperature [29, 30]. The transmitted IR light (I) will follow the equation

$$I = I_0 e^{-\lambda d},\tag{6.12}$$

with d the sample thickness, λ the absorption coefficient, and I_0 the background transmittance. The measured values d = 0.085 cm, $I_0 = 13.9\%$, and I = 12.3% then produce
a value for λ

$$\lambda = \ln(\frac{I_0}{I})/d = 1.4 \text{ cm}^{-1}.$$
 (6.13)

This value can be correlated to a total oxygen concentration of approximately $[O] = 4 \cdot 10^{17} \text{ cm}^{-3}$ [30]. This is rather high for originally float-zone material, which should have an oxygen concentration in the range 10^{15} cm^{-3} . The validity of this measurement is doubtful, since for untreated high-quality float-zone silicon, the oxygen concentration estimated with this method was $[O]_{FZ} = 9 \cdot 10^{16}$.

6.5.2 LCAO analysis

Usually the hyperfine parameters can give information on the local density of the wavefunction of the paramagnetic electron at the nuclear site. The magnitude of the isotropic part of the hyperfine interaction $(\frac{1}{3}TrA)$ is proportional to the amount of electron in s-wavefunction, while the anistropic part represents density in higher orbitals $(p, d, f, \dots$). It can be calculated that a complete electron in an sorbit on a hydrogen atom would generate an isotropic HF interaction of 1423 MHz, while a complete p electron would result in an axial HF tensor with main-values 2b, b, b, with b=8.9 MHz (see Appendix C for a derivation of these values). The observed HF interaction parameters ($A_{iso} = 157, A_{aniso} = 30$ indicates 11.1% of an electron in an s-orbital and 340% in a p-orbital. These numbers have to be multiplied with two, because there are two atoms in the interaction shell. This yields extremely large values. The question rises if LCAO analysis can be applied when hydrogen is involved, since this can basically not even explain anisotropic HF interaction. Anisotropic interactions can only be the result of p-orbitals (or higher) and these states are much higher in energy compared to the not completely filled s-states of hydrogen. Though such interactions have been observed for hydrogen. To explain the anisotropic part of Si-AA9 94% of a p-electron is needed on the hydrogen core [31]. The case for Si-NL52/P_b is more extreme, but one also has to bear in mind here that the interacting species is molecular hydrogen, and it is not exactly clear what the molecular orbits on H₂ will produce in the LCAO model. On basis of the HF (H₂), SHF (²⁹Si), SSHF (H) magnitudes of Si-NL52, which, in the model all originate from interactions with nuclei on the <111> axis, a plot of the density of the wavefunction at the various sites on the <111> axis can be made. This is shown in Figure 6.14.



Figure 6.14 A plot of the s density of the wavefunction on the <111> axis. This shows the smooth decay in space. The percentages in the bottom of the picture are derived from the Hamiltonian parameters (H) or from the FSE scan (Si).

The HF parameters of Table 6.1 can also be used with the assumption that the interacting nucleus is ²⁹Si, as in the old P_b model. In that case the observed values $(A_{\parallel} = 438 \text{ MHz}, A_{\perp} = 255)$ correspond to 6.9% of an electron in an s-state around the silicon nucleus and 53.4% in p-state [32]. This fits well in the model of a dangling bond on a silicon atom where the paramagnetic electron resides (mainly) in the sp^3 hybridized state, which is for 75% p-wave function and 25% s-wave function.

6.5.3 Deuterium implantation

A direct proof for the involvement of molecular hydrogen in the structure can be obtained from a simple experiment. Instead of hydrogen, deuterium can be taken as implantation species. The nuclear spin of deuterium is different (I=1 for D, $I=\frac{1}{2}$ for H). Also the hyperfine interaction parameters are different. Since the nuclear g-factor (g_N) is 6.5 times smaller for deuterium, the expected distances between the HF lines are expected to be 6.5 times smaller, if the electronic wavefunction is unaltered. Together with the changing of the number of HF lines, a clear, predictable change of the spectrum is expected. In the current study a deuterium-implanted sample with a similar dose was examined. The scans showed many resonances. The most prominent ones belonged to the Si-NL52/P_b spectrum with unaltered HF structure, i.e., with identical HF line

distances. On the other hand, a changing of the lineshape is observed. The small fourfold splitting of the lines due to interactions with monatomic hydrogen in the case of Si-NL52 (see previous chapter), was changed into a much narrower line in accordance to the above-decribed theory.

Apart from the unaltered Si-NL52 spectrum, a spectrum with smaller intensity (approximately $10\times$) and with less distant HF lines was observed. This spectrum could be identified with a defect, identical to Si-NL52, but with the H₂ molecule replaced by an HD molecule. In this way, the expected intensity of the DD-molecule based spectrum is only about 1%. Since also the splitting is much less, causing it to be hidden by the Zeeman lines, no observation of the DD-molecule spectrum is expected. Indeed, none was observed.

	Н		D				
Ι	$\frac{1}{2}$		1				
$g_{_N}$	5.585	36	0.857386				
Zeeman	42.5759	MHz	6.53566	MHz	1		
HF:1s	1423	MHz	218	MHz	2		
	50.8	mΤ	7.78	mΤ	2		
HF:2p	8.9	MHz	1.36	MHz	2		

Table 6.2 Comparison of the hyperfine interaction parameters for H and D.

To explain the presence of the HH spectrum there are two possibilities. Either the hydrogen was already present in the crystal before implantation, and the implantation only activated it, or the deuterium atoms in the molecule are slowly replaced by hydrogen atoms. The latter seems most likely.

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Appendix

A Fundamental physical constants

$\mu_{\scriptscriptstyle N} = 5.0507866 \cdot 10^{-27}$	$\rm J~T^{-1}$						
$\mu_{\scriptscriptstyle B} = 9.2740154 \cdot 10^{-24}$	${ m J}{ m T}^{-1}$						
$\mu_{\rm o}=4\pi\cdot 10^{-7}$	$\rm N \ A^{-2}$						
$\mu_e = 9.2847901 \cdot 10^{-24}$	${\rm JT^{-1}}$						
$\mu_p = 1.41060761 \cdot 10^{-26}$	${ m J}{ m T}^{-1}$						
$g_e = 2.002319304$	*						
$h = 6.6260755 \cdot 10^{-34}$	J s						
$c = 2.99792458 \cdot 10^8$	${ m ms^{-1}}$						
$e = 1.60217733 \cdot 10^{-19}$	С						
$a_0 = 5.29177249 \cdot 10^{-11}$	m						
$m_e = 9.1093897 \cdot 10^{-31}$	kg						
$m_p = 1.6726231 \cdot 10^{-27}$	kg						
*: free electron $g_e = 2\mu_e/\mu_B$							

from "Symbols, Units, Nomenclature and Fundamental Constants in Physics", prepared by E.R. Cohen and P. Giacomo, 1987 revision.

B Hyperfine interactions with isotopes

In electron paramagnetic resonance studies often hyperfine interactions with nuclear spins are observed. These spins are connected to the nucleus of the atom. Not every isotope of this atom has the same nuclear spin. The distribution of spins, as set by the natural abundances of the isotopes, causes a characteristic pattern of the hyperfine lines. The analysis of this "fingerprint" often enables the determination of the nucleus (nuclei) involved, and the number of nuclei in the shell of the interaction under consideration.

The isotropic Zeeman interaction of the paramagnetic electron (S=1/2) with the external magnetic field (B) can be expressed in the spin Hamiltonian: $\mathcal{H}_{Zeeman} = g\mu_B B \cdot S$. This will give rise to a single line with (relative) intensity 1 ($C_0 = 1$). A nuclear spin (I) which interacts with the electron spin causes a splitting of the spectrum due to the added term in the spin Hamiltonian $\mathcal{H}_{hyperfine} = AS \cdot I$. The total intensity of the spectrum remains the same, therefore, each line of the multiplet gets an intensity 1/(2I+1). We can put this in operator form. The operator X working on the intensities vector \vec{C} , generating a new vector $\vec{C}^1 = X\vec{C}$, where

$$C_i^1 = \sum_{j=i-I}^{i+I} \frac{1}{2I+1} C_j,$$
(B.1)

where i and j can take even and odd values, though in the summation the step is 1. If the abundance of the isotope with nuclear spin I is taken into the calculation, then only this amount of the spectrum is spread, the rest is left unaffected. Assuming the abundance is a_I , this can be expressed as

$$C_i^1 = \sum_{j=i-I}^{i+I} \frac{a_I}{2I+1} C_j + (1-a_I) \delta_{ij} C_i.$$
(B.2)

If more than one atom is involved, then the operator X has to be iterated as many times as there are atoms in the interaction shell

$$\vec{C}^n = X^n \vec{C}.\tag{B.3}$$

The procedure is now to start with a seed vector $(C_i=0 \text{ for } i\neq 0 \text{ and } C_0=1)$ and generate the expected spectrum with equation B.3. For atoms with more than one isotope with $I\neq 0$, this can be calculated on the condition that the gyro-magnetic moments g_N of the isotopes are (nearly) equal, since the magnitude of the splitting is directly proportional to the size of the hyperfine tensor, which in turn linearly depends on g_N . In the Table these results of this calculations for a variety of selected atoms with a number of shell sizes are presented. The given line intesities are scaled to the strongest line (100%) and lines with half-integral spin are written in **bold**, while lines with integral m_I are shown in normal typeface.

nucleus	iso	topes		fingerprint spectra						
Н	I = 1/2	100%	1x	100:100						
Р			2x	50.0:100:50.0						
F			3x	33.3:100:100:33.3						
			4x	16.7:66.7:100:66.7:16.7						
			5x	10.00:50.0:100:50.0:10.00						
			6x	5.00:30.0:75.0:100:75.0:30.0:5.00						
D ⁽¹⁾	I=1	100%	1x	100:100:100						
N ⁽¹⁾			2x	33.3:66.7:100:66.7:33.3						
			3x	14.3:42.9:85.7:100:85.7:42.9:14.3						
			4x	5.26:21.1:52.6:84.2:100:84.2:52.6:21.1:5.26						
$H_2^{(2)}$	I=0	25%	1x	50.0:100:50.0						
	I=1	75%	2x	16.7:66.7:100:66.7:16.7						
			3x	5.00:30.0:75.0:100:75.0:30.0:5.00						
			4x	1.43:11.4:40.0:80.0:100:80.0:40.0:11.4:1.43						
С	I=0	98.892%	1x	0.560 : 100 : 0.560						
	I = 1/2	1.108%	2x	o:1.12:100:1.12:o						
			3x	o:o:1.68:100:1.68:o:o						
			4x	o: o: o: 2.24: 100: 2.24: oo: o: o						
			5x	o:o:o:o:2.80:100:2.80:o:o:o:o						
			6x	o:o:o:o:o:3.36:100:3.36:00:o:o:o:o:o						
Al	I = 5/2	100%	1x	100 : 100 : 100 : 100 : 100 : 100						
Mn			2x	16.7: 33.3: 50.0: 66.7: 83.3: 100: 83.3: 66.7: 50.0: 33.3: 16.7						
Si	I=0	95.3%	1x	2.47:100:2.47						
	I = 1/2	4.7%	2x	00: 4.93: 100: 4.93: 00						
			3x	o:0.182:7.38:100:7.38:0.182:o						
			4x	o: o: 0.362: 9.81: 100: 9.81: 0.362: o: o						
			5x	$\mathbf{o}: \mathbf{o}: \mathbf{oo}: 0.601: 12.2: 100: 12.2: 0.601: \mathbf{oo}: \mathbf{o}: \mathbf{o}$						
			6x	o: o: o: o: 0.898: 14.6: 100: 14.6: 0.898: oo: o: o: o						
As	I = 3/2	100%	1x	100:100:100:100						
Ga ⁽³⁾			2x	25.0:50.0:75.0:100:75.0:50.0:25.0						
			3x	8.33:25.0:50.0:83.3:100:100:83.3:50.0:25.0:8.33						
			4x	2.27:9.09:22.7:45.5:70.5:90.9:100:90.9:						

- less than 0.01% of main line. o :
- oo : $0.01\% < C_i < 0.1\%$ of main line.
- (1): Non natural abbundance.
- (2): Equilibrium abundances at $T=\infty$. (3): More than one isotope with I=3/2; equal g_N assumed.

C LCAO hyperfine interaction parameters for hydrogen

From the hyperfine interaction magnitude and anisotropy, normally the local electron density at the specific nucleus/nuclei can be calculated. In LCAO analysis, the paramagnetic wavefunction is described as a linear combination of atomic orbitals [1]

$$\Psi = \sum_{i} \eta_i \phi_i, \tag{C.4}$$

with

$$\phi_i = \alpha_i \psi_s^i + \beta_i \psi_p^i, \tag{C.5}$$

with ψ_s^i and ψ_p^i s and p electron wavefunctions respectively on the i-th nucleus. This will then result in hyperfine interaction tensors (A_i) with eigenvalues $a_i + 2b_i$, $a_i - b_i$ and $a_i - b_i$, where

$$a_{i} = \frac{2}{3} \mu_{o} g \mu_{B} g_{N} \mu_{N} \eta_{i}^{2} \alpha_{i}^{2} |\psi_{s}(0)|^{2}, \qquad (C.6)$$

$$b_i = \frac{2}{5} \frac{1}{4\pi} \mu_0 g \mu_B g_N \mu_N \eta_i^2 \beta_i^2 < r^{-3} >_p .$$
 (C.7)

If the type of the involved nucleus is known (see Appendix B), the appropriate value for $g_N \mu_N$ [2] can be substituted. The values for $|\psi_s(0)|^2$ and $\langle r^{-3} \rangle_p$ can be calculated. The 1s orbitals on a hydrogen atom has the form [3]

$$\psi_s(\bar{r}) = \sqrt{\frac{1}{\pi a_0^3}} e^{-r/a_0},\tag{C.8}$$

with a_0 the Bohr radius = $0.529177249 \cdot 10^{-10}$ m. Therefore

$$|\psi_s(0)|^2 = \frac{1}{\pi a_0^3} = 2.148061 \cdot 10^{30} \,\mathrm{m}^{-3}.$$
 (C.9)

Substituting this in C.6, together with the value of the nuclear g-factor for hydrogen $(g_N = 5.58536)$ and for the electronic g-factor the free-electron value (g = 2.002319304) gives a value for a_i :

$$\frac{a_i}{h} = 1422.7 \,\mathrm{MHz/electron.} \tag{C.10}$$

The 2p orbital on a hydrogen atom has the form [3]

$$\psi_p(\bar{r}) = \sqrt{\frac{1}{32\pi a_0^3}} \frac{r}{a_0} e^{-r/2a_0} \cos\theta, \qquad (C.11)$$

therefore

$$\langle r^{-3} \rangle = \int r^{-3} \psi_p^* \psi_p d\bar{r} \tag{C.12}$$

$$= \frac{1}{32\pi a_0^5} \int r^{-1} e^{-r/a_0} \cos^2\theta J dr d\theta d\phi, \qquad (C.13)$$

where J is the Jacobian of the transformation to spherical coordinates,

$$J = r^2 \sin\theta. \tag{C.14}$$

This will result in [4]

$$\langle r^{-3} \rangle = \frac{1}{24a_0^3} = 2.811805 \cdot 10^{29} \,\mathrm{m}^{-3},$$
 (C.15)

and equation C.7 becomes

$$\frac{b_i}{h} = 8.8920 \text{ MHz/electron.}$$
(C.16)

These values should be used with care, since the theory of LCAO can only be applied if the wavefunction is (close to) a superposition of atomic orbitals. For the case of hydrogen orbitals, the *p*-states are excited states and are not expected to be occupied. Therefore, anisotropic hyperfine interactions with hydrogen can not be explained within the framework of LCAO, although they are observed experimentaly [5].

The calculation of $|\psi_s(0)|^2$ and $\langle r^{-3} \rangle$ for other elements is not so straightforward, but the results are tabulated in the literature [6].

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Summary

"Investigation Of Selected Centers In Semiconductors"

The work described in this thesis is concerned with the study of defects in selected semiconductors. The first chapter gives an introduction to the application of group theory in solid state physics. It shows how, with a minimal of information, important conclusions can be drawn about the energy levels of the system. At the end of the chapter, a closer look is taken at the symmetry covering operations of a defect, and their implications to the magnetic resonance parameters. Here the restrictions to a tensor, as imposed by the symmetry operations, are calculated.

In chapter 2 EPR experiments on silicon carbide are described. In some hexagonal polytype SiC several new spectra were detected. A discussion is made of their spin-Hamiltonian parameters: 1) SiC-NL1, a rhombic II spectrum with high spin (S=3/2) and small crystal field interaction. 2) SiC-NL2, an isotropic spectrum. 3) SiC-NL3, a rhombic I spectrum with strong hyperfine interactions.

Chapter 3 discusses the study of the DX center in binary and ternary III-V semiconductors. The metastable character of the center was proved by detecting photopersistent EPR (PPE) and photo-enhanced persistent EPR in AlGaAs with various contaminants. With the determination of the strain-induced angular dependence of the DX signal in an epitaxial layer grown on a substrate, an estimation could be made of the magnitude of the valley-orbit splitting.

The last three chapters describe the extended study of hydrogen in silicon. Chapter 4 introduces the reader to some important aspects of this contaminant, like diffusion, solubility and stable lattice positions. The last part of this chapter reviews a study of a low-dose hydrogen-implanted float-zoned bulk single crystal. The EPR study revealed, apart from the well-known Si-B3 and Si-AA1 spectra, also a new spectrum (Si-NL51) which is ascribed to the excited state (S=1) of a <100>-oriented defect. The presence of hydrogen in the defect is expected, but could not be proved.

For higher concentrations, hydrogen is expected to cluster with as first stage diatomic hydrogen. In the next chapter (5) the theoretical models which predict the existence of a stable hydrogen molecule as most likely candidate for the diatomic species are discussed. A report is made of the observation of a spectrum (Si-NL52) related to such interstitial hydrogen molecules in high-dose hydrogen-implanted float-zone silicon. The spectrum is identified with H_2 on the basis of the anomalous intensity ratio variations of its individual parts. Whereas the intensities of the hyperfine components behave in a normal way - linear with microwave amplitude A_{μ} - the Zeeman lines show deviating behavior, namely proportional to the square root of A_{μ} . The variation is attributed to a conversion between ortho and para species of molecular hydrogen.

The last chapter (6) relates on the similarity of Si-NL52 with the P_b spectrum. It is shown that both spectra can be described with the same spin-Hamiltonian. Apart from this, it is argued that the current model used for the P_b center can no longer be sustained. This model of a dangling bond connected to a single silicon atom is replaced by the above described model of a hydrogen molecule. Sophisticated magnetic resonance techniques, like field-scanned ENDOR (FSE), are described in the chapter and are used to substantiate this model by determining the local environment of the defect.

Samenvatting

"Onderzoek Aan Enkele Paramagnetische Centra In Halfgeleiders"

Het werk beschreven in dit proefschrift is het onderzoek aan defecten in verscheidene halfgeleiders. Het eerste hoofdstuk geeft een inleiding in de toepassing van groepentheorie in de vastestoffysica. Het laat zien hoe, met een minimum aan informatie, belangrijke conclusies kunnen worden getrokken omtrent de energie niveaus van het systeem. Aan het eind van het hoofdstuk wordt een overzicht gegeven van de symmetrie operaties van kristallen en de gevolgen daarvan op de spinwisselwerkingstensors van de Hamiltoniaan.

In hoofdstuk 2 worden EPR experimenten aan silicium carbide beschreven. In een aantal SiC samples van hexagonale polytype werden drie nieuwe spectra ontdekt. De bijbehorende spin-Hamiltonianen worden besproken: 1) SiC-NL1, een rhombisch-II spectrum met hoge spin (S=3/2) en kleine kristalveldopsplitsing. 2) SiC-NL2, een isotroop spectrum. 3) SiC-NL3, een rhombisch-I spectrum met sterke hyperfijnwisselwerking.

Hoofdstuk 3 handelt over het onderzoek van het DX centrum in binaire en ternaire halfgeleiders. Het metastabiele karakter van het centrum werd bewezen door het waarnemen van lichtgeïduceerde, persistente EPR en persistent toegenomen EPR. Door de bepaling van de hoekafhankelijkheid van het DX signaal in een epitaxiale laag op een substraat kon een schatting worden gemaakt van de grootte van de vallei-baanopsplitsing.

De laatste drie hoofdstukken gaan over het uitgebreide onderzoek van waterstof in silicium. Hoofdstuk 4 geeft een inleiding voor de lezer in de belangrijke punten van deze verontreiniging, zoals diffusie, oplosbaarheid en stabiele roosterposities. Het laatste deel van het hoofdstuk bespreekt een onderzoek aan een eenkristal dat met een lage dosis waterstof is geïplanteerd. Het EPR onderzoek bracht, naast de bekende Si-B3 en Si-AA1 spectra, een nieuw spectrum (Si-NL51) aan het licht. Deze wordt toegeschreven aan de aangeslagen toestand (S=1) van een defect wijzend in de <100> richting. Terwijl de aanwezigheid van waterstof wordt vermoed, kon dit niet worden aangetoond.

Bij hogere concentraties zal waterstof gaan clusteren met als eerste stap diatomair waterstof. In het volgende hoofdstuk (5) worden de theoretische modellen besproken die het waterstof molecuul als meest waarschijnlijke vorm voorspellen. Een verslag wordt gedaan van een spectrum (Si-NL52), waargenomen in hoge dosis waterstof geïmplanteerd float-zone silicium, dat kon worden toegewezen aan zulke moleculen. De toeschrijving aan H₂ berust of de afwijkende veranderingen van de verhouding van de intensiteiten van de onderdelen van het spectrum. Terwijl de intensiteiten van de hyperfijn componenten zich op een normale manier gedragen, namelijk lineair afhankelijk van de microgolfamplitude A_{μ} , vertonen de Zeeman lijnen een afwijkende afhankelijkheid (rechtevenredig met de *wortel* van A_{μ}). De verandering van verhouding van de intensiteiten wordt toegeschreven aan een conversie van ortho- in para-waterstof en vice versa.

Het laatste hoofdstuk (6) bespreekt de overeenkomsten tussen Si-NL52 en het P_b spectrum. Aangetoond wordt dat beide spectra met een en dezelfde spin-Hamiltoniaan beschreven kan worden. Bovendien wordt beredeneert dat het huidige model voor P_b , een bengelende binding aan een enkel silicium atoom, niet langer stand kan houden. In plaats daarvan wordt een model zoals hierboven beschreven voorgesteld. Moderne resonantie technieken, zoals field-scanned-ENDOR, worden gebruikt om deze hypothese te onderbouwen, door de plaatselijke omgeving van het defect te bepalen.

Nawoord

Als afsluiting zou ik iedereen willen bedanken die heeft bijgedragen aan de totstandkoming van dit proefschrift. In de eerste plaats Rob Ammerlaan voor het creeren van de perfecte werkomstandigheden. Tom Gregorkiewicz heeft in zeer grote mate geholpen aan dit proefschrift en was grote steun op persoonlijk vlak. Zonder zijn hulp was dit werk nooit totstand gekomen.

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nucleus	iso	topes	1.00	HF fingerprint spectra							
Н	$I_{-1/2}$	100%	1 x	100 : 100							
Р			2x	50.0 : 100 : 50.0							
F			3x	33.3 : 100 : 100 : 33.3							
			4 x	16.7:66.7:100:66.7:16.7							
			5x	10.00:50.0:100:100:50.0:10.00							
			6x	5.00:30.0:75.0:100:75.0:30.0:5.00							
D	I =1	100%	lx	100 : 100 : 100							
N			2x	33.3:66.7:100:66.7:33.3							
			3x	14.3:42.9:85.7:100:85.7:42.9:14.3							
			4x	5.26:21.1:52.6:84.2:100:84.2:52.6:21.1:5.26							
H_2	0=1	25%	lx	50.0 : 100 : 50.0							
	I = 1	75%	$2\mathbf{x}$	16.7:66.7:100:66.7:16.7							
			$3\mathbf{x}$	5.00:30.0:75.0:100:75.0:30.0:5.00							
			$4\mathbf{x}$	1.43 : 11.4 : 40.0 : 80.0 : 100 : 80.0 : 40.0 : 11.4 : 1.43							
('	I=0	98.892%	1x	0.560 : 100 : 0.560							
	1 = 1/2	1.108%	2x	o:1.12:100:1.12:o							
			3x	o:o:1.68:100:1.68:o:o							
			-4 x	o: o: 0: 00: 2.24 : 100: 2.24 : 00: o: o							
			5x	o :o: o :oo: 2.80 :100: 2.80 :oo: o :o:o							
			6x	0:0:0:0:3.36:100:3.36:00:0:0:0							
Si	I=0	-95.3%	1 x	2.47 : 100 : 2.47							
	I = 1/2	4.7%	2x	00: 4.93 : 100: 4.93 : 00							
			3x	o:0.182:7.38:100:7.38:0.182:o							
			4x	o:o:0.362:9.81:100:9.81:0.362:o:o							
			5x	o :o: oo :0.601: 12.2 :100: 12.2 :0.601: oo :o: o							
			6x	0:0:0:00:00:0.898:14.6:100:14.6:0.898:00:0:0:0							

Spectral name	Point groups	Distinguishable orientations + (extra for B not in (011)-plane)											
Cubic	T, T_d	1											
Tetragonal	S_4, \tilde{D}_{2d}	1	3										
		2											
Trigonal	$C_3, S_3, C_{3v},$	l	2	4									
	D_3, D_{3d}	- 3											
Rhombic II	D_2	1	2	3									
		17	13	18									
Rhombic I	C_{2v}	1	2	3	4		<u> </u>						
		-5	6										
Monoclinic II	C_2	1	2	3	4	5	6						
		17	14	22	18	13	19						
Monoclinic I	C_{1h}, C_2, C_{2h}	1	2	3	4	5	6	7					
		11	9	12		8	10						
General	C_{1}, S_{1}	1	2	3	4	5	6	7	8	9	10	11	12
		20	15	22	18	13	19	24	17	21	14	16	23