ELECTRONIC STRUCTURE OF DEEP LEVELS IN SILICON
A Study of Gold, Magnesium, and Iron Centers in Silicon

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OF
SOLID STATE PHYSICS
UNIVERSITY OF LUND
SWEDEN
1994
Abstract

In this thesis, the electronic structure of gold, magnesium and iron related deep centers in silicon is investigated. Their deep and shallow levels are studied by means of Fourier transform spectroscopy, combined with uniaxial stress and Zeeman spectroscopy.

The neutral substitutional gold center in silicon is investigated and the center is paramagnetic, \( S = 1/2 \), with \( g_\| = 2.8 \) and \( g_\perp = 0 \), and has a static <100> distortion. Reorientation between different equivalent distortions is observed even at 1.9 K. A gold pair center in silicon is studied and several line series, with a zero-phonon line followed by several phonon replicas, are observed. Uniaxial stress and Zeeman results reveal a trigonal symmetry of the center, which together with the high dissociation energy of 1.7 eV suggests that the center consists of two nearest-neighbor substitutional gold atoms. A divacancy model is employed to explain the electronic properties of the center.

The interstitial magnesium double donor in silicon in its two charge states \( \text{Mg}^0 \) and \( \text{Mg}^+ \) is investigated. Deviations in the binding energies of the excited states from those calculated within the effective-mass theory (EMT) are found and explained by a perturbation in the central-cell region.

The quadratic Zeeman effect of shallow donors in silicon is analyzed within the framework of the EMT using a numerical approach. The wave functions are calculated on a discrete radial mesh and the Zeeman Hamiltonian has been evaluated for the lowest excited states for fields up to 6 T.

The neutral interstitial iron defect in silicon gives rise to two sets of line spectra. The first set arises when an electron is excited to a shallow donor like state where the electron is decoupled from the \( \text{Fe}^+ \) core which has a \( 4T_J \) ground state term. The second set arises when an excited electron of \( a_1 \) symmetry is coupled by exchange interaction to the core, yielding a \( 5T_J \) final state. Experiments determine the multiplet splitting of the \( 4T_J \) and \( 5T_J \) states due to spin-orbit interaction. Large deviations from the Landé interval rule are observed. Preliminary results strongly support a dynamical Jahn-Teller distortion to be the dominant mechanism responsible for the non-Landé behavior.

Key words: silicon, deep levels, shallow donor states, effective mass theory, EMT, Fourier transform spectroscopy, uniaxial stress, Zeeman spectroscopy, quadratic Zeeman effect, spin-orbit interaction, Jahn-Teller effect, Au, Mg, Fe.
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Cover Picture: A shallow donor $4f_0$ wave function in silicon, calculated for eleven values of the magnetic field, between 1 and 6 Tesla. For details, see section 2.3 in this thesis.
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1. Introduction

It has been said that "The engineers involved with microelectronics are doing their part to make many of the authors of science fiction look like prophets" (Colclaser 1980). This becomes obvious when we consider the fast development of micro-electronic devices, which started in the mid-1950's. During the last three decades the improvement in manufacturing techniques and the immense amount of research that has been carried out in the field of semiconductor technology, have resulted in a vast change in our everyday life. All of us come daily into contact with semiconductor devices, nicely hidden in, e.g., watches, hand-held calculators, television sets, cars, airplanes, medical apparatus, and of course personal computers. The list can be made long, and it will continue to grow in the future. The main reasons for this rapid development are the new techniques that make it possible to shrink the size of electronic devices, reduce costs, and simultaneously increase both performance and reliability.

What is a semiconductor and why is it so well suited for the manufacturing of electronic devices? In the following I will give a short summary of the most important properties of elemental semiconductors, which will be followed by an introduction to the field of defects in crystalline materials.

In a perfect crystalline semiconductor, the atoms are arranged in a regular periodic manner throughout the whole material. The most important elemental semiconductors are those made up of atoms from group IV of the periodic table, such as, e.g., silicon. These atoms have four valence electrons, and when they form a crystal, each of these four electrons will take part in a covalent bond to another atom, i.e., each atom binds four other atoms in a tetrahedral crystal structure, see Fig. 1. The valence electrons are tightly bound in their respective bond and occupy energy states within the valence band, which is completely filled with electrons at low temperatures. To make the material conductive, electrons have to be released from their respective covalent bonds. This corresponds to excitations of the electrons from the valence band, into the next empty energy band, called the conduction band. The conduction band is separated from the valence band by a forbidden band gap, $E_g$. The size of this band gap is different for different types of crystals, and for most semiconductors $E_g < 3$ eV. For silicon, studied in this thesis, $E_g = 1.12$ eV at room
temperature.

By doping the semiconductor crystal with foreign atoms, the conductivity of the material can be increased by several orders of magnitude. In general, impurity atoms can be situated either on substitutional lattice sites, i.e., on sites formerly occupied by a host atom, or on interstitial sites, i.e., in between lattice sites. The simplest example considers an impurity from group V of the periodic table, which have five electrons outside filled shells. When, the group V atom enters a substitutional lattice site, four of the valence electrons are needed in the covalent bonds to the surrounding silicon atoms, while the fifth electron is only weakly bound to the impurity core by Coulomb attraction. The energy needed to ionize the impurity, i.e., to transfer the electron to the conduction band of the semiconductor, can be hundred times smaller than the band gap energy. Thus the impurity introduces new energy levels in the band gap, situated closely beneath the conduction band edge. These levels are called shallow donor levels. The fifth electron, moving in the central field of the impurity core, can be bound not only in its ground state, but also in several excited states, in analogy with the hydrogen atom. The theory describing these shallow donor states is called effective mass theory (EMT), and is outlined in section 2 of this thesis.

Similarly, by introducing atoms from group III of the periodic table into the silicon lattice, on substitutional lattice sites, only three of the four covalent bonds surrounding the impurity will be complete. The incomplete bond can easily attract an electron from a neighboring bond, leaving behind a positively charged "hole" which can move in the crystal and contribute to a current. The new energy levels created by the impurity are positioned in the band gap, closely above the top of the valence band, and are called shallow acceptor states.

By a controlled doping of shallow donor and acceptor impurities in different areas of a semiconductor wafer, components like resistors, diodes, transistors and capacitors can be manufactured. However, other types of defects can enter the lattice in the fabrication process and, e.g., rare earth impurities, chalcogens, and transition metals can give rise to energy levels deep in the band gap. Such defects will modify the electronic properties of the crystal, although in a very different way compared to the shallow defects. The deep energy levels may act as recombination centers for electrons and holes, and shorten the life time of charge carriers. Therefore, such defects are needed in fast switching devices, while in, e.g., silicon solar cells, where long lifetimes are needed, their concentration has to be kept at a minimum.

Most theories of defects in crystals are based upon the assumption that the electrons belonging to the impurity atom can be divided into two parts. The first part are the core electrons, i.e., the electrons in the filled shells of the free atom, which are found deep in the valence bands when the atom is incorporated into the crystal. These electrons are considered as "inactive" and are usually not believed to affect the detailed energy level structure of the defect system. The second part are the valence electrons of the atom which can take part in the covalent bonds to neighboring atoms (when the defect is on a substitutional lattice site). Those valence electrons that do not participate in a bond, are the "active" electrons of the defect, and are usually believed to determine the electrical, optical and magnetic properties of the defect.
The defect systems studied in this thesis are gold, magnesium, and iron centers in silicon, and these defects can give rise to both shallow and deep energy levels in the band gap. All the experimental work is carried out by means of high resolution, Fourier transform infrared spectroscopy (FTIR). Optical absorption signals due to transitions from the ground state of the defect to different excited states are investigated. By applying a homogeneous stress field or a magnetic field to the crystal, valuable information on the electronic structure of both the initial and the final states of the studied transitions are obtained.

Gold in silicon has attracted a great deal of attention both experimentally and theoretically during the last 20 years. An acceptor and a donor level have been observed in gold doped samples, although it remained controversial whether these two levels derived from the same gold center or not. The position in the lattice was also a point of discussion, and since no EPR signal from isolated gold could be detected, many questions remained. In paper I of this thesis, the isolated substitutional gold center is investigated, and it is shown that both the donor and the acceptor levels are due to transitions at this center. In paper II, a gold-pair center is investigated where both gold atoms are assumed to be on nearest substitutional lattice sites.

Magnesium act as a double donor when it is situated on an interstitial lattice site in silicon. It can be described as a solid-state analog of the helium atom, and can exist in several charge states. The neutral charge state, Mg\(^0\), gives rise to a deep level in the band gap, and transitions to excited states, perfectly described by EMT, are studied. The positively charged state, Mg\(^+\), introduces an even deeper level in the band gap but the excited states can still be described within EMT. However, in this charge state, deviations from EMT were detected, and the cause of these deviations is studied in paper III.

A numerical calculation of the shallow donor wave functions and the corresponding binding energies in silicon are carried out to obtain an accurate description of how these donor states act when exposed to a magnetic field (paper IV). Due to the simple structure of the ground state of both Mg\(^0\) and Mg\(^+\), (studied in paper III), these systems are perfect for comparing our result from the calculation with experimental data.

Iron in silicon is an important transition metal impurity partly because it gives rise to several deep levels in the band gap, but also because it is always present in the fabrication of devices. During heat treatment, iron atoms easily diffuse into the crystal and form pairs with shallow acceptor impurities, form larger complexes, or, when the crystal is rapidly cooled, are found on isolated, interstitial lattice sites. In paper V, the electronic structure of neutral interstitial iron center is treated.

The following sections are given as a background to the enclosed five papers. In section 2, the shallow donor states will be discussed, with an emphasis on the Zeeman effect on these states. Section 3 deals with the energy level structure of deep centers in silicon, such as transition metal defects. The coupling between electronic states and vibrational modes in the lattice, i.e., the Jahn Teller effect, is treated in section 4.
Additional experimental results on the isolated gold center, not given in paper I, are presented in section 5, together with a brief background to the theoretical results obtained for the gold pair center in paper II.

1.1 List of Papers

I. "Structure of Gold in Silicon".

II. "The Trigonal Gold Pair Center in Silicon".

III. "The Interstitial Magnesium Double Donor in Silicon".
A. Thilderkvist, M. Kleverman, and H. G. Grimmeiss.

IV. "The Quadratic Zeeman Effect of Shallow Donors in Silicon".
A. Thilderkvist, M. Kleverman, G. Grossmann, and H. G. Grimmeiss.
(Accepted for publication in Phys. Rev. B.)

V. "The Electronic Structure of Interstitial Iron in Silicon".
A. Thilderkvist, G. Grossmann, M. Kleverman, and H. G. Grimmeiss.
(Manuscript 1994)

The following papers are not included in this thesis, since their content either overlaps that of the included papers, or because the subjects treated are outside the scope of this thesis.

VI. "The Electronic Structure of Interstitial Iron in Silicon".
A. Thilderkvist, G. Grossmann, M. Kleverman, and H. G. Grimmeiss.

VII. "The Neutral Interstitial Iron Center in Silicon".
A. Thilderkvist, M. Kleverman, G. Grossmann, and H. G. Grimmeiss.

VIII. "Spectroscopy on Transition-Metal Defects in Silicon".
IX. "The Gold Center in Silicon".

X. "The MnGa Acceptor Level in GaAs".
M. Kleverman, E. Janzén, A. Thilderkvist, M. Linnarsson, and B. Monemar

XI. "The Excited $^{5}T_{1}$ State of the Fe$^{5+}$ Center in Silicon".
A. Thilderkvist, G. Grossmann, M. Kleverman, and H. G. Grimmeiss.
2. SHALLOW DONOR STATES IN SILICON

2.1 The Effective Mass Theory

The effective mass theory (EMT) can be used to determine the shallow states of defects in semiconductors, where the electron is bound to the defect by a screened Coulomb potential, which give rise to a hydrogen-like energy spectrum. In the following, our attention will be focused on the EMT for shallow donor states in silicon (Kohn and Luttinger 1955, Kohn 1957).

The problem of a shallow donor in a semiconductor crystal can be related to that of the free hydrogen atom, whose electron moves in a central field, a Coulomb potential, \( e^2/4\pi\varepsilon_0 r \), around the positively charged hydrogen core. The possible energy levels of the electron are labeled by principal quantum number, \( n \), and orbital momentum, \( l \), of the electron, i.e., as 1s, 2s, 2p, 3s, 3p, 3d, etc., where states with the same value of \( n \) are degenerate. The ionization energy of the hydrogen atom and the Bohr radius of the ground state are determined by

\[
E = \frac{e^4 m}{2(4\pi\varepsilon_0\hbar)^2} = 13.6\text{eV} \quad a_o = \frac{4\pi\varepsilon_0\hbar^2}{e^2 m} = 0.53\text{Å}
\]

where \( m \) is the mass of the electron and the static dielectric constant \( \varepsilon \) is unity for vacuum. If the hydrogen atom were introduced into a semiconductor lattice, these values of energy and radius would be scaled due to the dielectric constant, \( \varepsilon \), of the surrounding material, (of the order of 10) and the effective mass, \( m_e \), of the electron, (most often \( m_e < m \)). The binding energy is scaled down by approximately \( 10^3 \), while the wave function of the ground state becomes much more delocalized, with a Bohr radius approximately \( 10^2 \) times larger than that of the free hydrogen atom. The electron orbits are thus large compared to the lattice spacing of the crystal (nearest-neighbor distances in a semiconductor crystal are usually around 1-3 Å). These results can be directly applied to the case of a shallow donor impurity. The electron may be weakly bound to the impurity by a Coulomb potential scaled down by the dielectric constant, and the local properties of the impurity core do not, in a first approximation, affect an electron moving in an extended orbit. This theory can describe several different shallow-donor like defects as long as the electron wave function is delocalized in space, but breaks down when the wave function has a non-negligible amplitude close to the impurity site. Such deviations from EMT are considered in section 2.2.

For shallow donor states in silicon the theory becomes more complicated than just a scaling of the hydrogen case since silicon has six anisotropic conduction band minima with cigar-like shapes, see Fig. 2. The effective masses, transverse and longitudinal, i.e., perpendicular and parallel to the conduction band valley axis, are \( m_t = 0.1905m \) and \( m_l = 0.9163m \), respectively. In a first approximation the problem is
solved for a single valley, i.e., no interactions between states corresponding to
different valleys are considered.

![Diagram of six conduction band minima](image)

*Fig. 2. The six conduction band minima along the <100> crystal axes of silicon.*

The wave function of a shallow donor state is constructed as a product of the
Bloch wave $\Psi(k, r)$ of the conduction band minimum under consideration and an
envelope function $F(r)$ which satisfies the Schrödinger equation $H_0 F(r) = E F(r)$ where

$$H_0 = \left[ -\frac{\hbar^2}{2m_t} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right) - \frac{\hbar^2}{2m_l} \left( \frac{\partial^2}{\partial z^2} \right) - \frac{Ze^2}{4\pi\varepsilon_0 r} \right]$$

and $E$ is an eigenvalue of $H_0$. The direction of the $z$-axis is chosen along the principal
axis of the conduction band minimum. In contrast to the Hamiltonian of atomic
hydrogen, the kinetic energy term has cylindrical symmetry. Therefore only the
projection of angular momentum along the principal axis of the conduction band
valley, $m_L$, and parity are good quantum numbers. The energy spectrum resulting
from Eq. (2.2) is shown in Fig. 3. The shallow donor states can be divided into several
series, classified by parity and $m_L$, and within each series the states are labeled
according to the hydrogen scheme, by principal quantum number, $n$, and orbital
angular momentum as

Even parity $m_L = 0$ s-like series: $1s, 2s, 3s, 3d_0, 4s, 4d_0, etc.$

Even parity $m_L = \pm 1$ d-like series: $3d, 4d, 5d_0, 5g, 6d, etc.$

Even parity $m_L = \pm 2$ f-like series: $3f, 4f, 5f, 6f_0, etc.$

Odd parity $m_L = 0$ p-like series: $2p, 3p, 4p_0, 4f_0, 5p_0, etc.$

Odd parity $m_L = \pm 1$ d-like series: $2d, 3d, 4d_0, 4g_0, 5d_0, etc.$

Odd parity $m_L = \pm 2$ f-like series: $2f_0, 3f_0, 4f_0, 5f_0, etc.$

The binding energy of each state is given by Janzén *et al.* (1984) and can be found in
Table II of paper IV. Two methods of calculating the energies are described in sections
2.1.1 and 2.1.2.

The effective mass approach can be used also for double donors, such as
interstitial group II impurities (e.g., magnesium), (Ho and Ramdas 1972 and paper III
of this thesis) or substitutional group VI impurities (chalcogens) in silicon
(Grimmeiss *et al.* 1982, Janzén *et al.* 1984, Wagner *et al.* 1984), which can be considered
as helium like systems, embedded in a dielectric medium. In these systems the
effective nuclear charge is two ($Z = 2$) instead of one as for the hydrogen like
defects. Experimentally, a hydrogen-like spectrum arises when one of the two 
electrons is excited, implying that the second electron together with the core electrons 
of the impurity screen the nuclear charge. The excited states can thus be described by 
EMT, and the agreement is expected to be good, especially for higher delocalized 
excited states. In the singly ionized system, the remaining donor electron is more 
tightly bound to the impurity, and the binding energies calculated within EMT must 
be multiplied by four \((Z^2 = 4)\). The electron orbits are subsequently decreased 
compared to those of the hydrogen-like defects.

---

**Fig. 3.** Energy levels of an electron bound to an impurity by a Coulomb potential in a silicon lattice. The 1s state with the largest binding energy (30.26 meV) is excluded from the picture and the lowest state shown is the 2p\(_o\) state which has a binding energy of 11.49 meV. Only states up to 4p\(_\pm\) are labeled in the figure. An infinite number of excited donor states exist between this state and the conduction band edge.

### 2.1.1 Variational Method

The commonly used method of calculating the shallow donor spectra is the variational method. Faulkner (1969) carried out the original calculation and the method is briefly outlined below. The Hamiltonian to be solved is

\[
H = -\frac{\hbar^2}{2m_e} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \gamma \frac{\partial^2}{\partial z^2} \right) - \frac{2}{r} 
\]

(2.3)

where \(\gamma = m_1/m_1\) and the units of energy and length were taken to be \(\hbar^24\pi\varepsilon_0/(m_e^2)\) and \(m_e^4/(2\hbar^24\pi\varepsilon_0^2)\), respectively. The Rayleigh-Ritz method was used to find the lowest eigenvalues of \(H\) by taking ellipsoidal hydrogenic wave functions as a basis set. The orthonormal functions used were

\[
\Phi_{n,L,m_L}(x,y,z) = \frac{1}{\gamma} E_{n,L,m_L}(x,y,\sqrt{\beta/\gamma}z) 
\]

with

\[
E_{n,L,m_L}(x,y,\sqrt{\beta/\gamma}z) = R_{n,L}(\alpha(L);r)Y_L^{m_L}(\theta,\phi) 
\]

(2.4)

where \(Y_L^{m_L}\) is a normalized spherical harmonic corresponding to orbital angular momentum, \(L\), and \(m_L\). The radial part \(R_{n,L}\) is given by
where $L$ is an associated Laguerre polynomial. The $\beta$ and $\alpha(L)$ are variational parameters. $\beta$ determines the "eccentricity" in the $z$-direction of the wave function and $\alpha(L)$ the degree of localization of the radial part. The eigenvalues to be determined are thus functions of these nonlinear variational parameters, which are varied to minimize the lowest eigenvalues of $\mathbf{H}$. The resulting energy values will be upper bounds to the true energy values. In Faulkner's work, the calculations were not carried out for a specific material, but instead for ten different values of $\gamma$. Binding energies of states in the $s$, $p_0$, and $p_{\pm}$-like series were determined by including three values of $L$ for each series, and for each $L$, six values of principal quantum number, $n$. This yields $18 \times 18$ matrices to be solved for each series of states. From comparison with experimental data on Si:P and Si:Li, the low temperature value of the dielectric constant of silicon was obtained to be $\varepsilon = 11.4 \pm 0.05$, which is the value used throughout this thesis.

The problem was later reconsidered by Janzén et al. (1984) to obtain a more accurate determination of the energies of the shallow donor states in silicon, since improved experimental spectra lead to a resolution of higher excited states. Faulkner's calculations were limited to the nine lowest states in each series, too few to explain the experimental features. In addition, the accuracy of the highest calculated excited states were low due to the small number of basis functions. Janzén et al. recalculated the shallow donor energies for the specific case of silicon which has $\gamma = 0.2079$. They included up to six values of $L$ in each series and for each $L$, up to 15 values of $n$, i.e., a secular problem of up to $90 \times 90$. Their results are listed in parenthesis in Table II of paper IV and will in the following be considered as the "exact" energies of the shallow donor states, with an accuracy of about 0.01 meV.

In the variational calculations a rather accurate determination of the energies can be obtained even if the corresponding wave functions do not perfectly describe the true ones. However, when studying the Zeeman effect of these shallow donor states, errors in the tail of the radial part of the wave functions will cause disagreements between theory and experiment. A different numerical approach, described in the next section, was therefore used for determining the wave functions.

2.1.2 Numerical Method

The main difference between the numerical approach and the variational method is that the form of the radial part is not specified a priori in the numerical method, but instead calculated on a radial mesh by the use of Lanczos recursion method (Pettifore and Weaire 1985). The procedure is described in detail in paper IV, and only the main features are given here. A plot of the radial parts of the wave functions, corresponding to the lowest donor states, is also given.
Fig. 4. The radial part $U_L(r)$ of the three lowest states in the s, $p_0$ and $p_\pm$ series. The length scale is given in units of the effective Bohr radius ($a_0$) for silicon (31.8 Å).

A coordinate transformation described by $x' = x$, $y' = y$, and $z' = z'/\sqrt{\gamma}$ is applied to Eq. (2.2), which transforms the kinetic energy term to one with spherical symmetry while the Coulomb term becomes distorted with a cylindrical symmetry. Introducing polar coordinates, the eigenfunctions $\Psi_{mL}(r, \theta, \phi)$ of the resulting Hamiltonian (Eq. 3 of paper IV) are expanded as a sum of radial functions multiplied by spherical harmonics $Y_{LM}$ of the same $m_L$.

$$\Psi_{mL}(r, \theta, \phi) = \sum_{L= L_0, L_0 + 2, \ldots}^\infty \frac{U_L(r)}{r} Y_{LM}(\theta, \phi).$$  \hspace{1cm} (2.6)

Since parity is a good quantum number, each shallow donor state only contains terms with either even or odd $L$ and our calculations showed that it was sufficient to
use L-values up to 12 for s-like states and 13 for p-like states in the expansion. The mesh used for describing $U_L(r)$ contained 512 points between $h = R_{\text{max}}/512$ and $R_{\text{max}}$, where a common $R_{\text{max}}$ was chosen for all states considered, large enough to ensure that the amplitude of the states was negligible for $R > 0.9R_{\text{max}}$. The Lanczos method was used in order to handle the large matrix problem. The full matrix (of dimension 512x7) was projected onto a limited number (20-50) of basis vectors $v_n$, resulting in a smaller matrix with eigenvalues that were good approximations to those of the full Hamiltonian. An iterative approach was used until convergence was reached.

The radial parts of the wave functions corresponding to the three lowest eigenvalues of each of the s, $p_0$ and $p_\pm$-series are shown in Fig. 4. By comparing the resulting energies with the "exact" ones (Table II, paper IV), clearly the accuracy of this calculation is lowest for the most localized wave functions, calculated at only a small number of mesh points. It is also clear that only the lowest states can be considered "pure", i.e., the donor 1s state has mainly hydrogenic-1s character, while for higher excited states the contributions from several different L-values become important. Therefore the labeling of the states according to "orbital angular momentum" is used merely for identification.

2.2 Deviations from EMT

The EMT breaks down when the electron wave function has a non-negligible amplitude (e.g. 1s) in the central cell region. Here it is affected by the short-range impurity potential, not accounted for in EMT. This short-range potential rises because the core of the impurity differs from that of the surrounding silicon atoms.

For highly localized states the one-valley approximation is not valid, and interactions between states corresponding to different conduction band minima have to be considered, i.e., valley-orbit interactions (Kohn and Luttinger 1955). The six-fold degeneracy of the EMT-like states is thus lifted, and the new states are linear combinations of the different valley states. The new states can be written as

$$\Psi_i = \sum_{j=1}^{6} \alpha_j(j)\psi_j$$

where $\psi_j = F_j(r)\Psi(k_j, r)$. The envelope function, $F_j(r)$, and the Bloch wave, $\Psi(k_j, r)$, are labeled by the number, $j$, of the conduction band minima, according to Fig. 2. The $\alpha_j$'s are determined so that the new states transform according to irreducible representations of the Td-point group. The ns and np$_0$ states transform as A$_1$+E+T$_2$ while np$_\pm$ states transform as 2T$_1$+2T$_2$. Deviations from EMT will give rise to a splitting of the six-fold degenerate ns and np$_0$ states into a singlet A$_1$, a doublet E, and a triplet T$_2$. Among the ns-states, the singlet state is the only state with non-vanishing amplitude at the origin, and this state is expected to have the largest shift from the ns-EMT value. For most shallow donor systems, the 1s(A$_1$) state is the ground state, which explains why the ionization energies of such systems are found to be larger.
than the predicted value of \( = 30 \text{ meV} \). Smaller deviations are expected for the states with \( E \) and \( T_2 \) symmetry. The schematic splitting due to valley-orbit interaction for the s, \( p_0 \), and \( p_\pm \)-like states is shown in Fig. 5. The magnitude of the splitting is determined by the short-range potential and the localization of the electron, and it is difficult to estimate absolute values. However, it can be shown that the relative splitting of the states scale as the probability of finding the electron at the origin. By approximating the envelope functions of the 1s, 2s and 3s-states with hydrogenic wave functions, the splittings were found to scale as \( 1: \frac{1}{8}: \frac{1}{27} \), i.e., as \( 1/n^3 \). p-like wave functions vanish at the origin which explains why deviations from EMT are so rarely observed for these relatively delocalized p-states. However, for the singly ionized Mg-double donor system, studied in paper III, such deviations are clearly observed in optical spectra, and an estimate of the relative splitting of the p-states is given.

\[
\begin{align*}
\text{s-states} & \quad \text{p}_0\text{-states} & \quad \text{p}_\pm\text{-states} \\
ns(E) & \quad np_o(E) & \quad np_\pm(T_1^{b}, T_2^{b}) \\
ns(T_2) & \quad np_0(T_2) & \quad np_\pm(T_1^{a}, T_2^{a}) \\
ns(A_1) & \quad np_0(A_1) & \quad \text{np}_\pm(A_1)
\end{align*}
\]

Fig. 5. A schematic picture showing the expected deviations from EMT for s, \( p_0 \), and \( p_\pm \)-like states. When \( 1s(A_1) \) is the initial state in the transition, only final states with \( T_2 \) symmetry can be reached. The positions of the \( np_\pm(T_1) \) states are assumed to be degenerate with the corresponding \( np_\pm(T_2) \) states, see paper III.

2.3 Zeeman Effect

2.3.1 General Aspects

When an electron moving in a central field is subject to an applied external magnetic field, the energy level of the electron will be split due to the interaction between the external field and the magnetic moment of the electron.

An electron possesses a spin magnetic moment \( \mathbf{\mu} = g_s (e/2m) \cdot \mathbf{s} \), where \( \mathbf{s} \) is the spin angular momentum \((\pm \hbar/2)\) and \( g_s \) is the electronic g-factor equal to 2.0023. When a magnetic field is applied, this magnetic moment interacts with the field and gives rise to an interaction energy \( E = -\mathbf{\mu} \cdot \mathbf{B} \). As a result, the components will shift by an amount \( \Delta E = (e\hbar/2m)g_s m_s B \) where \( m_s = \pm 1/2 \) (the quantization axis is chosen parallel to the applied field). If the electron also possesses orbital angular momentum, \( \mathbf{l} \), an additional splitting due to the magnetic moment \( \mathbf{\mu} = (e/2m) \cdot \mathbf{l} \) will occur. The total term, linear in \( \mathbf{B} \), that has to be added to the zero-field Hamiltonian of the electron is thus
For higher magnetic fields, however, linear terms in $B$ are not sufficient to describe the Zeeman behavior, and quadratic terms in $B$ become increasingly important. The procedure of deriving the total Zeeman contribution to the zero-field Hamiltonian in the general case is as follows (Garstang 1977):

The linear momentum $p$ in the kinetic energy term $(p^2/2m)$ of the zero-field Hamiltonian is replaced by $p + eA$ where $A$ is the vector potential of the field. $A$ is chosen as $A = -(r \times B)/2$, which satisfies $\nabla \times A = B$ and $\nabla \cdot A = 0$. The term replacing the kinetic energy term is now

$$\frac{1}{2m}(p + eA)^2 = \frac{p^2}{2m} + \frac{e}{2m}(p \cdot A + A \cdot p) + \frac{e^2 A^2}{2m}$$

(2.9)

Since the chosen $A$ satisfies $p \cdot A = A \cdot p$, the second term of Eq (2.9) becomes

$$\frac{e}{m}(p \cdot A) = -\frac{e}{2m}p \cdot (r \times B) = \frac{e}{2m}B \cdot (r \times p) = \frac{e}{2m}B \cdot l$$

(2.10)

where the orbital angular momentum is $l = r \times p$. It is obvious that this term is identical to the orbital part of Eq. (2.8) which together with the spin part describes the paramagnetic contribution to the Hamiltonian. The diamagnetic contribution is described by the last term of Eq. (2.9) which is quadratic in $B$:

$$H_{\text{Zeem}}^{\text{quad}} = \frac{e^2}{8m}(r \times B)^2$$

(2.11)

In most cases, this term is small compared to other terms in the Hamiltonian and can be neglected. For the free hydrogen atom, quadratic effects do not become important for the lowest states ($n < 10$) until the field reaches values far above 100 T. However, the effect increases rapidly as the principal quantum number $n$ of the occupied state increases, approximately as $n^4$ (Garstang 1977). Much effort has been devoted to solve the Zeeman problem for hydrogen for all magnetic field strengths, and in spite of the seemingly simple problem, no complete description has been obtained. Under terrestrial conditions it is difficult to achieve the high magnetic fields needed to study the quadratic effects experimentally for hydrogen.

These high field features can, however, be observed at considerably lower fields by studying the motion of bound electrons in solids. Due to the small effective mass of the electron, and the high dielectric constant of the solid, the magnetic interaction energy will be large compared to other terms (e.g., the Coulomb term) in the Hamiltonian. For shallow donors in silicon it is possible to experimentally study the quadratic Zeeman effect already at fields of about 2 - 3 T (Pajot et al. 1972, Mu et al. 1993 and paper III-V).
2.3.2 Shallow Donors in Silicon

Due to the anisotropy of the conduction band minima in silicon, only parity and \( m_L \) are good quantum numbers, as discussed above. Therefore, states with different \( \{|m_L|\} \) are separated in energy already at zero-field. An applied magnetic field will lift the degeneracy between \( m_L \) and \(-m_L\) if the field has a component in the direction of the principal axis of the conduction band valley, here chosen as the \( z \)-axis, see Fig. 6. The splitting due to the electron spin will not be considered here, since this spin splitting is identical in the initial and final state of the transitions for most shallow donors. If this is not the case, the spin splitting is easily superimposed on the orbital splitting which is described in detail below.

Fig. 6. One single conduction band valley of silicon, together with the coordinate system used in the calculations. The magnetic field direction is chosen to lie in the \( xz \)-plane.

The shift of the shallow states will in a first approximation depend only on the transverse mass, \( m_t \), of the electron and according to Eq. (2.8), the split \( \Delta E \) will be equal to

\[
\Delta E = \frac{eB}{2m_t}m_LB_z
\]  

Field components perpendicular to the valley axis will in this approximation not have any effect on the valley states. However, if the energy difference between states with different \( m_L \)-values is sufficiently small, these states will interact via \( B_x \) and \( B_y \) components of the magnetic field.

To obtain the full Zeeman Hamiltonian including quadratic effects, the coordinate transformation described in section 2.1.2. has to be applied to Eq. (2.9). This results in an equivalent problem where an electron, characterized by an isotropic effective mass \( m_t \), moves in a distorted Coulomb field and a transformed effective magnetic field. The resulting Hamiltonian then contains two parts, one linear in \( B \), and one quadratic in \( B \). Each part consists of several terms, labeled by the transformation properties of the electronic operators involved, which correspond to the irreducible representations of the \( D_{6h} \) symmetry group (see paper IV for details). In the following, the primed Cartesian coordinates and the polar coordinates refer to the transformed coordinate system, whereas the magnetic field components are, for convenience, given in the original coordinate system.

The dominant linear term in the Hamiltonian is identical to Eq. (2.12), and causes a linear splitting of all states with \( |m_L| > 0 \). The effect is exemplified by the \( 2p_\pm \), \( 3p_0 \) and \( 3p_\pm \) state in Fig. 7a (dashed lines) for \( B \) along the valley axis:
The second linear term
\[ H_1(\Sigma_g) = \frac{e}{2m_t} L_x B_z \tag{2.13a} \]

will only contribute when the field has a component perpendicular to the valley axis, and then it causes an interaction between states that differ in \( m_L \) by \( \Delta m_L = \pm 1 \), as shown in Fig. 7b for the 2p\(_\pm\) and 3p\(_0\) states. This term will also cause the somewhat unexpected negative shift of the lowest p-state, 2p\(_0\), due to the interaction between this state and all np\(_\pm\) states higher in energy.

The quadratic terms are dominated by the term
\[ H_2(\Sigma_g^+) = \frac{e^2 r^2}{8m_t} \left\{ \left(1 - \cos^2(\theta)\right) B_z^2 + \frac{\gamma}{2} \left(1 + \cos^2(\theta)\right) \left(B_x^2 + B_y^2\right) \right\} \tag{2.13c} \]

which causes all states to shift to higher energies for increasing field. The effect gets larger for increasing n-values, as expected from comparison with the hydrogen case. The shift caused by Eq. (2.13c) is shown as full lines in Fig. 7a. It does not mix states from different m\(_L\)-series, but will reduce the extension of the electronic states, i.e., the radial part of the wave function will shrink for higher fields. This effect gets increasingly larger the more delocalized the state is at zero-field.

The second quadratic term
\[ H_2(\Pi_g) = -\frac{e^2 r^2 \gamma}{4m_t} \cos(\theta)\sin(\theta) \left\{ \sin(\varphi)B_yB_z + \cos(\varphi)B_xB_z \right\} \]  
(2.13d)

has a similar effect as \( H_1(\Pi_g) \), i.e., it mixes states with \( \Delta m_L = \pm 1 \), but its matrix elements are found to be of less importance than those of \( H_1(\Pi_g) \). \( H_2(\Pi_g) \) is identically zero when \( B \) is either parallel or perpendicular to the valley axis.

The last quadratic term

\[ H_2(\Delta_g) = -\frac{e^2 r^2 \gamma}{16m_t} \sin^2(\theta) \left\{ \cos(2\varphi)\left( B_x^2 - B_y^2 \right) + 2\sin(2\varphi)B_xB_y \right\} \]  
(2.13e)

has the selection rule \( \Delta m_L = \pm 2 \) which causes an interaction for example between the \( np_+ \) and \( np_- \) states. This term becomes zero for \( B \) along the valley axis, but contribute with a small splitting of, e.g., the \( 2p_+ \) state when \( B \) is perpendicular to the valley axis. This splitting is however small compared to the superimposed splitting due to the linear interaction between \( 2p_+ \) and \( 3p_0 \) via \( H_1(\Pi_g) \), see Fig. 7c.

The Zeeman behavior of a single valley is simplest for the case when \( B_z = B \) and \( B_x = B_y = 0 \), since only \( H_1(\Sigma_g^+) \) and \( H_2(\Sigma_g^+) \) are different from zero. As soon as the field has a component perpendicular to the valley axis, the pattern becomes complicated due to the interaction between different \( m_L \)-series. In Fig. 8, an attempt to visualize all these possible interactions is made. Thus in order to describe the Zeeman behavior of states up to \( 4p_+ \), several higher states have to be included in the calculation, and values of \( m_L \) up to \( \pm 5 \) are used in our calculation.

The lowest states (\( 1s, 2s, 2p_0, 2p_\pm, 3p_0 \)) can be described by treating the full Zeeman Hamiltonian as a perturbation in a basis of zero-field states for magnetic fields up to 7 T. However, for the higher states, a limited number of zero-field wave functions can not accurately describe the true wave functions, which will become more localized due to the quadratic terms at higher magnetic fields. Therefore, new basis states were calculated for each value of the field by adding \( H_2(\Sigma_g^+) \) to the zero-field Hamiltonian. The residual terms were then treated as a perturbation in this new field-dependent basis. The shrinkage of the radial part of the wave functions is shown...
in Fig. 9 for the $2p_{\pm}$ and $3p_{\pm}$ states, at 0, 2, 4, and 6 T. For clarity, only the dominant L-terms in the expansion are shown ($L = 1, 3, and 5$).

As seen in Fig. 9, the effect of localization is negligible for the $2p_{\pm}$ state, and therefore the zero-field wave function is sufficient to describe the Zeeman pattern up to 6 T, whereas for $3p_{\pm}$, the wave function shows a large delocalization for higher fields. This effect increases further for the higher excited states and has to be accounted for in the calculations.

Experimentally, the Zeeman behavior of course gets more complex because we have to consider all six valleys simultaneously. When, e.g., $\mathbf{B}$ is applied along a [001] crystal direction, only the valleys 1 and 2 (see Fig. 2) will be parallel to the field, while valleys number 3, 4, 5, and 6 lie perpendicular to the field. An optical spectrum is therefore a superimposition of spectra corresponding to the six different valleys.

### 2.3.3 Double Donors in Silicon

The Zeeman analysis carried out above, can also be applied to singly ionized double donor systems. However, since the separation in energy between the excited states is four times larger than for a neutral donor, the interactions between different states decrease. At the same time, the quadratic effects are diminished due to the higher localization of the electron wave function. Therefore, for the lowest excited states and low fields, the splitting is well described by using only the linear term, Eq (2.13a). To accurately describe also the higher states, (> $4p_{\pm}$), although rarely observed in optical spectra, all terms have to be considered, and also the shrinkage of the wave functions due to the magnetic field has to be taken into account.
2.4 Uniaxial Stress

A uniaxial stress perturbation of the silicon crystal changes the symmetry of the crystal and destroys the equivalence of the six conduction band valleys. The shift in energy of a valley is described by the deformation potential approximation (DPA) (Wilson and Feher 1961), and the shallow donor states will shift exactly as their corresponding valley. The theory is briefly outlined in paper III and V. The resulting split for the EMT like shallow donor states will follow the pattern given in Fig. 10.

Fig. 10. The expected splitting of effective mass like donor state in silicon, as a function of applied uniaxial stress in the [001], [110], and [111] directions. The splittings are given in the figure, where $\Delta = \Xi_u (s_{11}-s_{12})/3$ and $\Xi_u$ is the deformation potential for pure shear and $s_{11}$ and $s_{12}$ are stiffness coefficients. $F$ is the magnitude of the uniaxial stress and defined to be negative for compression.

For states split by valley-orbit interaction, the stress field can cause an interaction between states of different symmetry, resulting in a more complex stress behavior. For stress values which give rise to an energy splitting much larger than the zero-field valley-orbit splitting, the stress pattern approaches that of the effective mass like states in Fig. 10. Stress experiments can thus serve as a way of verifying the donor character of an excited state investigated by optical methods.
3. DEEP LEVELS IN SILICON

3.1 Introduction

In addition to the shallow defect states, discussed so far, impurities in silicon can also give rise to deep levels in the band gap. In the following, we will focus on isolated transition-metal (TM) impurities (For a review on experimental results, see Weber 1983). These impurities are known to exist in several different charge states and then usually on interstitial lattice sites. The most frequently used models explaining the electronic structure of isolated interstitial and substitutional TM-defects will be given. The substitutional impurities from group IB, such as Au, will also be included in the discussion. Many particle effects, spin-orbit interaction and the effect of a magnetic field will be discussed, together with a model describing a trigonal transition-metal pair.

3.2 Transition Metal Impurities in Silicon

3.2.1 Ionic Model

The early paramagnetic resonance work of Ludwig and Woodbury (L-W) in 1960 on 3d-transition metals (TM) in silicon resulted in a simple model of these defects which satisfactorily described their experimental results. The model can still be applied for a qualitative understanding of the transition metal defects, although the vast amount of both experimental and theoretical work carried out since then has shown that it has to be modified.

The 3d-TM's have an atomic configuration corresponding to \([\text{Ar}]^{3d^n4s^m}\) where \(N = n + m\) is the total number of valence electrons. When the impurity is incorporated into the crystal, the 4s electrons are transferred to the d-shell, resulting in a \(d^N\) configuration for interstitial defects, and a \(d^{N-4}\) configuration for substitutional defects (four electrons are needed to complete the covalent bonds). The atomic d-state (\(l = 2\), with five-fold degeneracy) will be split into two components by the tetrahedral crystal field. The orbitals of these components transform according to the irreducible representations \(e\) (doublet) and \(t_2\) (triplet) of the \(T_d\) point group, as shown in Fig. 11. The angular dependencies of the states are given in the figure, and \(\Delta_{CF}\) labels the crystal field splitting. The crystal field totally quenches the orbital angular momentum for an electron in the \(e\) state, whereas an effective orbital momentum \(l' = 1\) can be associated with the electrons in the \(t_2\) state. The relative ordering of the two levels is determined by the microscopic configuration of the two nearest-neighbor shells, and for interstitial defects the \(t_2\) state is found below the \(e\) state, while substitutional defects have an inverted level ordering. In the model by L-W, these two levels are
populated by the electrons so that maximum possible spin $S$ is obtained, according to what is expected for a free atom (Hund’s rule). This implies that the exchange interaction, which splits the $e$ and $t_2$ levels into spin-up ($e^+$ and $t_2^+$) and spin-down levels ($e^-$ and $t_2^-$), causes an additional splitting, $\Delta_{ex}$, which is large compared to $\Delta_{CF}$. The relative level ordering then becomes $t_2^+ < e^+ < t_2^- < e^-$, as illustrated in Fig. 11, where neutral iron (3$d^8$ configuration) is used as an example.

This is referred to as the high-spin level ordering, and this model successfully described all 3$d$-TM impurities for which experimental data existed at the time of the model. The results of L-W are summarized in Table I, where $S$ is the total spin, $L'$ the effective orbital angular momentum and $J'$ is the effective total angular momentum.

![Fig. 11. The effect of a crystal field of $T_d$ symmetry on an atomic d-state. The d-state is split into e and $t_2$ one-particle levels. The additional splitting due to exchange interaction is shown for the case when Hund's rule is valid. The level occupation for Fe$^0$ (3$d^8$) is given.](image)

<table>
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<th>ion⇒</th>
<th>V$^{2+}$</th>
<th>Cr$^+$</th>
<th>Cr$^{2+}$</th>
<th>Mn$^{2+}$</th>
<th>Mn$^+$</th>
<th>Fe$^+$</th>
<th>Fe$^0$</th>
<th>Ni$^+$</th>
<th>Cr$^0$</th>
<th>Cr$^{2+}$</th>
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<td>d$^6$</td>
<td>d$^7$</td>
<td>d$^8$</td>
<td>d$^9$</td>
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<td>e$^{2t_2^3}$</td>
<td>d$^2$</td>
<td>d$^5$</td>
<td>e$^{2t_2^0}$</td>
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<td>3/2</td>
<td>1</td>
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<td>1</td>
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<td>0</td>
<td>1</td>
<td>5/2</td>
<td>1</td>
<td>5/2</td>
</tr>
<tr>
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<td>5/2</td>
<td>1, 2, 3</td>
<td>1/2, 3/2</td>
<td>1</td>
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</tbody>
</table>

Table I. The ground state configuration of some interstitial and substitutional 3$d$-TM’s in silicon, as deduced from EPR measurements (Ludwig and Woodbury 1960 and 1962)

3.2.2 Recent Theoretical Results

Theoretical investigations of 3$d$-TM ions have shown that the success of the model by L-W was more or less accidental, and evidence for a breakdown of Hund’s rule were found for the heavy interstitial and light substitutional TM-impurities (Beeler et al. 1985). One method, frequently applied in defect calculations, is the defect-molecule method (Hemstreet 1977, DeLeo et al. 1981 and 1982). This model makes use of a finite cluster in which only the host atoms close to the defect are included and the cluster is terminated by hydrogen atoms. A more accurate, but also more complicated
description is obtained by theoretical investigations based on a self-consistent Green's-function technique (see, e.g., Zunger and Lindefelt 1982 & 1983, Sankey and Dow 1983, Zunger 1987). In this method, the defect is embedded in the infinite perfect crystal. The results of the calculations of TM-defects in silicon are summarized in the following.

**Interstitial TM-Defects**

Theoretical calculations of *interstitial* TM-defects (DeLeo *et al.* 1981 & 1982) in silicon verified the assumption of L-W that t<sub>2</sub> and e-levels should be found in the band gap, with the t<sub>2</sub> state below the e state. However, the impurity de and dt<sub>2</sub> states were actually predicted to fall deep in the valence band to interact with p-like crystal states of e and t<sub>2</sub> symmetry situated near the top of the valence band. These crystal states will by the interaction be pushed into the band gap, and give rise to antibonding states, while the bonding states remain as resonances in the valence band, see Fig. 12. As a result, the band gap states are not purely d-like as predicted by L-W, but also contain a p-like component.

Going backwards through the 3d-series (decreasing Z-value), passing Cu, Ni, Co, Fe, Mn, Cr, V, Ti and Sc, the bonding resonances will rise to higher energies and become more and more delocalized. The antibonding e and t<sub>2</sub> states in the band gap are at the same time pushed to higher energies, becoming more localized. When the gap levels approach the conduction band edge, they interact with t<sub>2</sub> and e conduction-band states, leading to an anticrossing behavior. The additional exchange splitting, not shown in Fig. 12, has been calculated by Beeler *et al.* (1990). The calculations verified the high-spin ground states for those defects investigated by L-W, whereas a low spin ground state was predicted for some early interstitials, such as Ti and V.

**Substitutional TM and Group 1B Defects**

The properties of *substitutional* TM and group 1B defects, show some similarities to those of the interstitial defects. The impurity states act as compact, filled
d-shells, and fall into the valence band, where they interact with crystal states of the same symmetry. The most common theoretical approach is to apply the vacancy model (Hemstreet 1977, Watkins 1983). First a Si atom is removed from the lattice, i.e., a silicon vacancy is created, and then the impurity atom is placed on this vacant lattice site. The total impurity system can then be treated as an interaction between the impurity states and the states induced by the vacancy. A short summary of the lattice vacancy in silicon is given in Fig. 13 (Watkins 1983, Lannoo 1984). The dangling sp$^3$ hybrids originating from the four nearest-vacancy neighbors are labeled a, b, c, and d. One-particle states are formed according to a LCAO molecular orbital model. A non-degenerate state with $a_1$ symmetry falls just below the top of the valence band, while the triply degenerate $t_2$ state is found in the forbidden band gap. The eigenfunctions of the one-particle states are given in the figure. Lattice distortions are neglected for the time being.

$$ \text{It}_{2,x} = \frac{1}{2} (-a+b+c-d) $$
$$ \text{It}_{2,y} = \frac{1}{2} (a+b-c-d) $$
$$ \text{It}_{2,z} = \frac{1}{2} (a-b+c-d) $$
$$ |a_1> = \frac{1}{2} (a+b+c+d) $$

Fig. 13. The silicon vacancy with its four dangling bonds, labeled a, b, c, and d. The molecular model predicts an $a_1$ resonance in the valence band and a triply degenerate gap state of $t_2$ symmetry. The linear combinations of the vacancy orbitals, corresponding to the eigenfunctions of the two states, are given.

When the impurity is introduced on the vacant lattice site, the main interaction takes place between the impurity $dt_2$ state and the $t_2$ vacancy state. Bonding resonances are formed in the valence band and antibonding bound states in or close to the band gap, see Fig. 14. As $Z$ decreases, the energy of the impurity $d$ and $dt_2$ states increases, and the interaction with the vacancy $t_2$ state becomes stronger. The vacancy $t_2$ state is thus pushed towards higher energies in the band gap, and finally enters the conduction band.

Fig. 14. The interaction between the atomic $dt_2$ state and the vacancy $t_2$ state as a function of decreasing atomic number (Watkins 1983).
For the heavier 3d impurities, the $t_2$ gap state will be mainly dangling-bond like, implying that the impurity d-levels do not interact with the neighboring silicon atoms, but remain atomic like with a compact 3d shell. If the antibonding $t_2$ states in the band gap only has a small amount of d-character, the defects are referred to as "vacancy-like". This vacancy model can with success be applied also to some substitutional ions in the heavy side of the 4d and 5d TM-series. Theoretical and experimental investigations of substitutional transition metal ions (Delerue 1989) and group 1B defects have shown that, e.g., Ni, Pd, Pt, and Au are vacancy like (Fazzio et al. 1985, Williams et al. 1992, Anderson et al. 1991, 1992b & 1992c). However, in order to describe their detailed electronic structure, Jahn-Teller distortions have to be taken into account, as described in sections 4 and 5.

**Divacancy Model**

Since the vacancy model has been shown to describe some substitutional TM-defects appropriately, it is tempting to extend this model also to pairs of TM-impurities on nearest-neighbor substitutional sites, i.e., to use the divacancy model. The same approach as for the isolated vacancy is used in order to find the eigenstates made up of linear combinations of the six vacancy sp$_3$ orbitals (Watkins and Corbett 1965, Talwar and Ting 1982, Humphreys et al. 1983, Gomes et al. 1985). The undistorted divacancy is illustrated in Fig. 15, where the dangling bonds are labeled a, b, d, and a', b', d'. The corresponding eigenstates now transform according to the irreducible representations of the D$_{3d}$ group.

![Fig. 15. The divacancy in silicon with its six dangling bonds. The linear combinations of the sp$_3$ orbitals are given for the resulting eigenfunctions in D$_{3d}$ symmetry. The predicted energy level structure is shown, neglecting Jahn-Teller distortions.](image)

Experimental results on the divacancy show a reformation of bonds, correlated to a Jahn-Teller distortion. However, in the case of the substitutional gold-pair studied in paper II, other effects such as the spin-orbit coupling are assumed to stabilize the system against such distortions. A trigonal symmetry was found from stress experiments, justifying the use of the undistorted one-particle level structure in Fig. 16 as a starting point for the calculations.
Hybridization Effects

It is obvious that in the case of transition metal defects, the wave functions of the bound states in the band gap must be described as consisting of one d-like part and one p-like part. The $t_2$ gap state can be written as

$$|t_2, \mu\rangle_{\text{tot}} = \alpha|dt_2, \mu\rangle + \beta|pt_2, \mu\rangle$$  \hspace{1cm} (3.1)

where $\alpha$ and $\beta$ determine the relative proportions of d- and p-like components, where the $|pt_2 m\rangle$ state transforms as an atomic $l = 1$ orbital, and $\alpha^2 + \beta^2 = 1$. The $dt_2$ state, which is derived from an atomic d-orbital with $l = 2$, can be expressed in the $|l, m_L\rangle$ basis as

$$|dt_2, +1\rangle = |2, -1\rangle \quad \rightarrow |pt_2, 1\rangle$$
$$|dt_2, 0\rangle = \frac{1}{\sqrt{2}} (|2, -1\rangle - |2, +1\rangle) \quad \rightarrow |pt_2, 0\rangle$$
$$|dt_2, -1\rangle = |2, +1\rangle \quad \rightarrow |pt_2, -1\rangle$$ \hspace{1cm} (3.2)

These three $dt_2$ orbitals can then be related to the three atomic p-orbitals by a p-isomorphism (Griffith 1961) as given by the arrows in Eq. (3.2). Matrix elements involving the orbital angular momentum operator, $I$, within the $dt_2$ and $pt_2$ states are then related by

$$\langle dt_2, \mu|I_{\mu''}^n|dt_2, \mu'\rangle = -\langle pt_2, \mu|I_{\mu''}^n|pt_2, \mu'\rangle$$ \hspace{1cm} (3.3)

The total effect of the p and d-mixture in the wave functions thus results in a reduction of matrix elements involving the orbital angular momentum, which has consequences when evaluating the effects of, e.g., spin-orbit and Zeeman interactions, (see below). The relation between the matrix elements calculated by using the effective orbital angular momentum $l' = 1$, and the real value of the matrix element, can be described by a proportionality factor, $g_L$, so that

$$\langle t_2 | 1 | t_2 \rangle = g_L \langle pt_2 | 1' | pt_2 \rangle.$$ \hspace{1cm} (3.4)

For a pure p-state in the lattice, $g_L = +1$, but for states with some d-character, the $g_L$-value decreases, and becomes -1 for a pure d-state. For 3d-transition metals in silicon the $g_L$-value has been shown to be close to zero. It has however been argued that this quenching is too large to be explained by covalency effects alone. A dynamical Jahn-Teller distortion of the center has been shown to cause similar reduction factors as will be described in section 4.
3.3 Many-Particle Effects

3.3.1 Electrostatic Interaction

Up to now, only one-particle energy levels were considered. To find the final energy level structure we consider the different possible \( t_2^m e^n \) configurations. When the electron-electron interaction is large compared to other interactions, (e.g., spin-orbit, Zeeman, and Jahn-Teller interactions), we first find the possible \( 2S+1\Gamma \) terms of the \( t_2^m \) and \( e^n \) configurations separately, and then couple these terms in all possible ways. \( S \) is here the total spin and \( \Gamma \) labels the symmetry of the orbital part of the wave function. This is easiest shown by the simple example of neutral interstitial iron, Fe\(^0\), in a tetrahedral crystal field, which has the configuration \( t_2^6 e^2 \). Coupling of the six electrons in the filled \( t_2 \)-shell results in only one allowed term with \( S = 0 \) and orbital symmetry \( A_1 \), i.e. an \( ^3A_2 \)-term. If the two \( e \)-electrons were inequivalent, i.e., were found in different \( e \)-levels, the resulting terms would be \( ^3A_2, ^1A_2, ^3A_1, ^1A_1, ^3E \) and \( ^1E \). However, since the electrons belong to the same \( e \)-level, the Pauli exclusion principle will exclude three of these terms, and only \( ^3A_2, ^1A_1 \), and \( ^1E \) are allowed. These are then coupled to the \( ^1A_1 \)-term of the \( t_2^6 \) state, and the \( ^3A_2 \) term is lowest in energy according to Hund's rule. In order to calculate the term energies explicitly, matrix elements of the electrostatic energy \( e^2/\rho_{12} \), in the form of two-electron integrals have to be known (see Griffith 1961). Cluster calculations on several interstitial 3d-TM impurities have been carried out (DeLeo et al. 1982), where the electron-electron interaction is included as a perturbation, and their result for Fe\(^0\) is given in Fig. 16. The three different configurations within \( d^8 \) are included in the calculations. From this calculation, a \( ^3A_2 \) ground-state level is predicted, in agreement with EPR experiments (Ludwig and Woodbury 1960) and the relatively simple group theoretical treatment above. Similar calculations were carried out for the Fe\(^+\) ion, also given in Fig. 16. In this case, when many-electron effects were not included, the low spin configuration \( t_2^6 e^1 \) was predicted to be the ground state. When the electronic Coulomb interaction was included, the effect on this state was only a minor shift to lower energies, while the \( t_2^5 e^2 \) configuration split into several terms with a large negative shift of the \( ^4T_1 \) term. This term crosses the \( t_2^6 e^1 \) level and becomes the ground state, in agreement with experimental data (paper V).

3.3.2 Spin-Orbit Effects

When the effective orbital angular momentum, \( l \), of an electron is different from zero, it will couple to the spin, \( s \), of the electron, and the state will split into components characterized by an effective total angular momentum \( j \) (Abragam and Bleaney 1986).
For an electron bound to an impurity ion in a crystal, the one-particle spin-orbit operator is written

$$H_{so} = g_L \xi \mathbf l \cdot \mathbf s$$  \hspace{1cm} (3.5)

where $\xi$ is the spin-orbit parameter of the free ion. The orbital g-value, $g_L$, is a measure of the reduction of the matrix elements which involve $l$, see Eq. (3.4).

For a many-particle system, the spin-orbit Hamiltonian is generalized to

$$H_{so} = g_L \sum_i \xi_i l_i \cdot s$$  \hspace{1cm} (3.6)

where the sum is taken over all electrons involved. When all of the orbital contribution is due to electrons belonging to a single level, the spin-orbit parameters $\xi_i$ of the different electrons have the same value $\xi$. If the energy splitting due to spin-orbit interaction can be considered small compared to the term splitting discussed in the previous section, Eq. (3.6) within a given term can be written as

$$H_{so} = g_L \lambda \mathbf l' \cdot \mathbf s$$  \hspace{1cm} (3.7)

Here $\mathbf l'$ is the total effective orbital momentum $\sum l_i'$, $\mathbf s$ is the total spin $\sum s_i$, and $\lambda$ is an effective spin-orbit parameter. If the ground term obey Hund's rule, $\lambda = \pm \xi / (2S)$ (Abragam and Bleaney 1986), where the plus and minus signs are used for less than or more than half-filled electron shells respectively.

3.3.3 Zeeman Effects

When a magnetic field is applied, the electronic levels will split in accordance with Eq. (2.8), which for a many-particle system in a crystal is written
Here $g_s$ is the spin $g$-value equal to 2.0023 and $g_L$ is the same reduced orbital $g$-value as used in Eq. (3.5) to (3.7). When the Zeeman splitting is much smaller than the spin-orbit splitting, this is generalized to

$$H_{\text{zeeman}} = \mu_B B \sum_i (g_{L} l_i + g_s s_i)$$

(3.8)

The effective total angular momentum is $J' = L' + S$ and the split is determined by $\Delta E = \Delta m_i g_J \mu_B B$. The $g_J$-value can then be deduced from

$$g_J = \frac{1}{2J'(J'+1)} \left( (g_L + g_s)J'(J'+1) + (g_L - g_s)(L'(L'+1) - S(S+1)) \right)$$

(3.10)
4. JAHN-TELLER EFFECTS

4.1 Introduction

In 1936, Jahn and Teller discovered that a non-linear complex (such as a molecule or a crystal) which has an electronically degenerate state when in a symmetric nuclear configuration, will lower its energy by an asymmetric nuclear distortion which removes the electronic degeneracy. The only exception is Kramer's degeneracy, which can not be lifted by any distortion. The theorem is illustrated in Fig. 17 (Ham 1972) for an electronic state which is doubly degenerate in its unstable, undistorted configuration. A distortion, represented symbolically by Q, lifts the degeneracy and the system lowers its energy by the Jahn-Teller stabilization energy, $E_{JT}$, where the stable configuration corresponds to the distortion $Q_s$. The existence of a stable configuration comes about by including the elastic energy of the lattice, which increases quadratically in Q.

![Fig. 17. Illustration describing the Jahn-Teller theorem (Ham 1972). The two-fold degeneracy of the electronic state in the unstable symmetric configuration ($Q_o$) is lifted by a distortion to a stable asymmetric configuration ($Q_s$). The energy of the system is lowered by $E_{JT}$.

The electronic energy states of the system will couple to the nuclear displacements, and when treating the Jahn-Teller (JT) effect of defects in crystals, the whole lattice contributes to the nuclear motion. This results in a coupled motion of the electrons and the lattice vibrational modes. If the coupling is strong enough, the distorted configuration is stable and the local symmetry of the system becomes lower than the point symmetry of the lattice. This is referred to as the static JT-effect. The degeneracy of the electronic state is thus lifted. However, since the distortion itself is degenerate, i.e., there are several equilibrium configurations which are energetically equivalent, the electronic degeneracy is merely replaced by a "vibronic" degeneracy. In the case of a weaker coupling, i.e., the dynamic JT-effect, the system is able to reorient rapidly between the equivalent distortions, and no effective lowering of the symmetry occurs. In this case, the electronic and vibrational parts of the wave functions are intricately mixed and the electronic energy levels are strongly modified compared to the case with no coupling.
4.2 Jahn-Teller Effects in Td Symmetry

4.2.1 Molecular Model and the Hamiltonian

When the coupling involves an infinite number of lattice phonons, as in the case of crystal defects, the treatment becomes complicated. However, in a first approximation only the motions of the defect itself and its nearest neighbors will be considered, i.e., a molecular model is used. The vibrational coordinates of the lattice are represented by $Q$, the appropriate modes of distortions of the molecule. The possible modes of vibration for a defect in a tetrahedral environment can be described by the XY$_4$ molecule, shown in Fig. 18 (Sturge 1967, Berzucker and Polinger 1989). The nuclear displacements are classified by the irreducible representations of the Td point group, and the modes of $a_1$, $e_g$, and $e_u$ symmetry are illustrated in the figure. The collective coordinates for the respective modes are also given.

$$Q_{a_1} = \frac{1}{2}(z_1 + z_2 + z_3 + z_4)$$

$$Q_{e_g} = \frac{1}{2}(x_1 - x_2 - x_3 + x_4)$$

$$Q_{e_u} = \frac{1}{2}(y_1 - y_2 - y_3 + y_4)$$

Fig. 18. The displacements of the atoms in the XY$_4$ molecule, corresponding to $a_1$, $e_g$, and $e_u$ modes in a Td crystal (Sturge 1967). The collective coordinates, $Q$, are given for each mode, expressed according to the Cartesian coordinate systems defined in the left figure.
When treating the Jahn-Teller problem, we will only consider the simplest case of vibronic coupling and disregard other effects such as, e.g., spin-orbit coupling. We consider a single electronic level which is degenerate when the molecule has a symmetric nuclear configuration. The nuclear vibrations we take to be simple harmonic oscillators with a Hamiltonian consisting of the kinetic energy of the nuclei and the elastic energy as

$$H_{\text{nuc}} = \frac{1}{2} \sum_k \left( \frac{P_k^2}{M_k} + M_k \omega_k^2 Q_k^2 \right)$$  \hspace{1cm} (4.1)$$

$P_k$ is the momentum operator conjugate to $Q_k$, $M_k$ is the effective mass of the ions, and $\omega_k$ is the angular frequency of the $k$'th normal mode. The vibronic coupling, where we only consider the terms linear in the vibronic coordinates $Q$, can be written in the general form

$$H_{\text{vib}} = \sum_{\Gamma, \mu} V_{\Gamma} U_{\mu}(\Gamma) Q_{\mu}(\Gamma)$$  \hspace{1cm} (4.2)$$

where $V$ is the coupling strength and $U$ is an electronic operator transforming as the $\mu$'th partner of the irreducible representation $\Gamma$, and $Q$ is the collective coordinates describing the distortion of the lattice, see Fig. 18. Only vibrational modes which transform according to an irreducible representation contained in the direct product $\Gamma_e \otimes \Gamma_e$, where $\Gamma_e$ is the irreducible representation of the electronic state under consideration, can give rise to non-zero matrix elements.

4.2.2 $e \otimes E$ case

For the doublet electronic $E$ state, the only possible modes of vibration are those of $a_1$, $a_2$, and $e$ symmetry, out of which only the $e$-modes can cause a splitting of an electronic $E$ state. The vibrational part of the Hamiltonian can thus be written as

$$H_{\text{vib}} = V_E [U_{\theta} Q_\theta + U_e Q_e],$$

where $V_E$ is the linear coupling strength between an $e$-vibrational mode and an electronic $E$ state, neglecting non-linear terms. The $U_\theta$ and $U_e$ are the electronic operators which take the matrix form

$$U_\theta = \begin{pmatrix} -1 & 0 \\ 0 & +1 \end{pmatrix}, \quad U_e = \begin{pmatrix} 0 & +1 \\ +1 & 0 \end{pmatrix}$$  \hspace{1cm} (4.4)$$

in the basis of the electronic states $\psi_\theta$ and $\psi_e$.

The resulting energy surfaces obtained by adding the eigenvalues of $H_{\text{vib}}$ to the elastic energy of the nuclei, is generally referred to as the "mexican hat" and is obtained by rotating the energy curves of Fig. 17 around the energy axis. This rotational symmetry results in an infinite number of equivalent configurations with minimum energy along the bottom of the trough. This cylindrical symmetry will however be destroyed if higher order coupling terms is included, and three configurations of stable equilibrium will remain. The strength of this additional
coupling will determine whether the JT-effect is static or dynamic.

4.2.3 $e \otimes T_2$ case

An orbital triplet electronic state with $T_2$ symmetry can couple to modes with $a_1$, $a_2$, $e$, $t_1$ and $t_2$ symmetry, but only $e$ vibrational modes will be considered here. The coupling is given by $H_{vib} = V_T [U_0 Q_0 + U_e Q_e]$, where the $U_0$ and $U_e$ now take the matrix form

$$
U_0 = \frac{1}{2} \begin{pmatrix}
+1 & 0 & 0 \\
0 & +1 & 0 \\
0 & 0 & -2
\end{pmatrix}, \quad U_e = \frac{1}{2 \sqrt{3}} \begin{pmatrix}
-1 & 0 & 0 \\
0 & +1 & 0 \\
0 & 0 & 0
\end{pmatrix}
$$

in the basis of the electronic states $\psi_\xi$, $\psi_\eta$ and $\psi_\zeta$. The resulting energy surfaces is shown in Fig. 19, and consist of three displaced paraboloids, corresponding to the three electronic functions $\psi_i$ with $i = \xi, \eta, \zeta$. The total wave function in each paraboloid is a product of the electronic function $\psi_i$ and a two-dimensional harmonic oscillator function which is centered at the equilibrium position in the paraboloid.

![Fig. 19. The three paraboloids describing the energy surfaces of a $t_2$ electronic state coupled to a pair of $e$-vibrational modes, $Q_0$ and $Q_e$, from Ham (1972).](image)

For increasing JT-coupling, the separation of the paraboloids increases, and the overlap between the wave functions, corresponding to different paraboloids, decrease. Matrix elements of the orbital angular momentum operator, $l$, which only has off-diagonal matrix elements in the $\psi_l$-basis, will thus be reduced due to the JT-interaction, and in the limit of a static distortion, the matrix elements of $l$ are totally quenched. A partially quenching of the orbital angular momentum takes place in the dynamical JT regime, and this problem was treated in detail by Ham in 1965. He calculated the effect of this quenching on the energy splittings caused by spin-orbit and Zeeman interaction, and based his evaluation on the assumption that the JT-effect could be considered large compared to both these effects. The quenching effect was found to be similar to the effect of covalent bonding, and gave rise to a further reduction of the orbital $g$-value, in addition to that due to covalency (section 3). This was confirmed by EPR experiments on TM defects in silicon where the orbital $g$-value was found to be much smaller than predicted from considerations of covalent bonding alone. However, the estimated effect of the hybridization effects on the $g$-
value in those days were wrong. Katayama-Yoshida and Zunger (1985) showed that the quenching of orbital angular momentum is satisfactorily accounted for by hybridization effects. Nevertheless, a dynamic JT-effect could alter the spin-orbit splitting and the relative intensities of the split components (Manson and Sturge 1980, Ulrici 1984), without affecting the g-value of the ground state. In the case of the interstitial iron defect in silicon (paper V), we find anomalies in the spin-orbit splitting of the Fe+ core which most probably are due to a dynamic JT-effect.

### 4.3 Jahn-Teller Distortions at the Lattice Vacancy in Silicon

The lattice vacancy, V, was briefly described in section 3, and the energy level structure of the undistorted configuration is given in Fig. 13. The vacancy can exist in several different charge states which give rise to energy levels in the bandgap (Lannoo and Bourgoin 1981 & Bourgoin and Lannoo 1983, and review article by Watkins 1986). In the one-electron picture, these charge states are obtained by successively occupying the a1 resonance in the valence band and the triply degenerate t2 state in the band gap, see Fig. 20.

![Diagram of Jahn-Teller Distortions at the Lattice Vacancy in Silicon](image)

Fig. 20. Splitting of the t2 manifold for the silicon lattice vacancy in its V++, V+, V0, V- and V- charge states.

EPR studies have shown (Watkins 1986) that in the positive charge state, V+, the vacancy is distorted in a <100> direction, corresponding to a tetragonal, static JT-distortion of e-symmetry. In this charge state, the degeneracy of the t2 state is lifted, and three equivalent stable configurations, corresponding to the three paraboloids in Fig. 19, exist. For V0, two electrons occupy the t2 level, and the JT-energy is increased. In the negative charge state, the higher doubly degenerate level is occupied by one electron. This leads to an additional distortion with trigonal symmetry, which lifts the degeneracy of this state. It is worth noting that, for this charge state, the sum of the one-electron energies are the same, irrespective of the sign of the JT-distortions. For V-, the splitting due to the tetragonal distortion is much larger than that of the trigonal, and the singlet t2, ζ state is found to be lower in energy than the doublet t2, ξ>, and t2, π>. Calculations including many-particle effects (Lannoo et al. 1981) have shown that these are quenched by the large JT-effect and that the one-particle
level structure shown in Fig. 20 sufficiently accounts for the observed experimental properties of the lattice vacancy. The model of the negative lattice vacancy (Anderson et al. 1992a) is applied to the isolated substitutional gold center, described in the next section. An inverted level ordering, with the doublet lowest in energy, is assumed for this center.
5. GOLD DOPED SILICON

5.1 The Neutral Substitutional Gold Center, Au$_s^0$

5.1.1 Introduction

The Au$_s^0$ center in silicon is treated in paper I. Additional unpublished results will be given here, after a short summary of the main properties of the center.

The electronic configuration of Au$_s^0$ outside filled shells is 5$d^{10}6$s$^1$ and the center is assumed to be described within the vacancy model, i.e., an Au$^+$ atom with a 5$d^{10}$ configuration, occupying a negatively charged lattice vacancy, V$. The same model successfully describes the Pt$^+$ center (Anderson et al. 1991, 1992c) which is isoelectronic with Au$^0$. The Pt$^+$ center has been studied in detail by EPR (Anderson et al. 1992b), and was found to have spin $S = 1/2$ and a C$_{2v}$ symmetry, assumed to result from a static <100> tetragonal Jahn-Teller distortion followed by an additional trigonal distortion. However, the one-particle level-ordering of Pt$^+$ was found to be inverted compared to that of the negative lattice vacancy in Fig. 20. The g-values parallel and perpendicular to the defect axis were found to be $g_∥=2.1$ and $g_⊥=1.4$, respectively. Similar properties were later observed for the vacancy-like Pd$^+$ and Ni$^+$ centers in silicon (Williams et al. 1992). Pt$^+$, Pd$^+$ and Ni$^+$ in silicon all show a preferential alignment under uniaxial stress, i.e., all centers in the crystal align parallel to the stress field, already at temperatures below 4 K.

**Fig. 21. Schematic picture of the assumed level structure of the isolated substitutional gold center in silicon. A tetragonal distortion lowers the symmetry to $D_{2d}$, and spin-orbit interaction lifts the degeneracy of the orbital doublet.**
The fact that no EPR signal has been detected for Au$_s^0$, has unfortunately complicated both an identification of the center and an investigation of its electronic structure. Optical measurements on gold doped samples, however, have resulted in sharp line spectra at 611 and 793 meV. These were identified as excitations to shallow acceptor and donor states, respectively, from the same isolated gold center Au$_s^0$ (Petersen and Nielsen 1990 and paper I). By studying the Zeeman splitting of these spectral lines, it was established that also the Au$_s^0$ center is paramagnetic with $S = 1/2$ and undergoes a static <100> tetragonal distortion, but now with a larger $g$-anisotropy than the Pt$^{+}$ center, $g_{||} = 2.8$ and $g_{\perp} = 0$ (Fig. 2, paper I). The fact that $g_{\perp} = 0$ explains the failure to detect this center with EPR, and also implies that spin-orbit interaction splits the doublet and stabilizes the center against a trigonal distortion. In Fig. 21 a schematic picture describing the assumed level structure of Au$_s^0$ is given. Reorientation between the different equivalent <100> was observed at 2 K when a magnetic field was applied. The centers aligned parallel to the magnetic field direction.

5.1.2 Uniaxial Stress

The uniaxial stress splitting of the donor lines at 793 meV were investigated and the results are presented in Fig. 22 for FlII[001], [110], and [111]. For FlII[001] and [110] a very complex pattern is observed for stress values below 50 MPa. This is believed to be due to reorientation effects at the Au$_s^0$ center, which for higher stress values result in a preferential alignment. For FlII[111] a common shift of the lines is observed, in accordance with the tetragonal model, since all defects have the same angle to the stress axis. For higher stress values and all three directions of the stress, the splitting pattern is typical for that of the shallow donor states in silicon. We believe that the observed lines are due to transitions to a valley-orbit split 1s donor state, which is further split due to spin-orbit and Jahn-Teller interactions. The uniaxial stress results solely could not provide information on the preferred direction of the stress alignment.

Fig. 22. The uniaxial stress behavior of the spectral lines which are due to transitions from the Au$_s^0$ center to s-like shallow donor states, see text for details.
5.1.3 Combined Stress and Zeeman Experiments

In order to gain conclusive information on the stress alignment for the Au$_{\text{s}^0}$ center, the donor lines in Fig. 22 were studied by simultaneously applying both stress and a magnetic field. If a preferential alignment occurs when a uniaxial stress field is applied, it should be reflected in the ground state g-value, which equals $g = g_0 \cos \theta$, where $\theta$ is the angle between the distortion and the applied magnetic field. Four different combinations of the orientation of the magnetic field and the stress field were studied, as pictured in Fig. 23a. For each configuration, a constant stress field was applied, and then the splitting pattern were recorded for increasing values of the magnetic field. The experimental results are shown in Fig. 23b for the high energy components of the stress-split donor states. The observed split of the lines are due to the spin splitting of the final donor states, i.e., $\Delta E = g_\perp \mu_B B$ with $g_\perp = 2$, while the center of gravity shift of the split components originates from the shift of the ground state. When no such shift is observed, the centers must have aligned perpendicular to the applied magnetic field, since $g_\perp = 0$. From the experimental data presented here, it is clear that all centers align parallel to the stress direction. This is in agreement with the behavior of the Pr$^+$, Pd$^-$ and Ni$^-$ centers, and also with the observations of the negative vacancy, however with opposite sign of the alignment compared to V$^-$. 

![Diagram showing stress alignment of the Au$_{\text{s}^0}$ center with different magnetic and stress field orientations](image)

Fig. 23. Stress alignment of the Au$_{\text{s}^0}$ center. In the top of the figure, a to d show the four different orientations of the magnetic field, relative to the three equivalent orientations of the center. In the lower part, the experimental Zeeman splitting of the donor lines are shown for each case a to d.
5.2 The Trigonal Substitutional Gold-Pair Center, Au$_{2s}$

The gold pair center, with the two gold atoms on nearest-neighbor substitutional lattice sites, are investigated in paper II. Four sharp line series, labeled A, C, E, and F, and a number of additional weaker series, are observed in gold diffused, originally p-doped and weakly n-doped, silicon (Fig. 1, paper II). All series consist of an intense zero-phonon line and several phonon replicas, and with a phonon energy $\hbar \omega \approx 120$ cm$^{-1}$. All series are believed to arise due to transitions from the same ground state but to several different final excited states. The gold pair is found to have trigonal symmetry, D$_{3d}$, and a high dissociation energy, which favors our assignment of this center to consist of two nearest-neighbor substitutional gold atoms.

The calculations carried out in paper II is based upon the doubly, negatively charged, undistorted lattice divacancy, described in section III. The fact that gold atoms are placed on the empty lattice sites, causes the $e_u$ and $e_g$ band gap states to not only have p-character as in the case of the divacancy, but also some impurity d-character in accordance with the gap states of the isolated transition metal impurities. The crystal field splitting $\Delta_{CF}$ of the band gap e-states for the divacancy is assumed to be approximately 0.8 eV (Humphreys et al. 1983). This large splitting for the divacancy lead us to assume that the ground state of the gold-pair has a $e_u^4e_g^0$ configuration, resulting in a $^1A_{1g}$ term. The states are labeled according to the irreducible representations of the D$_{3d}$ group. The excited states arise from the $e_u^3e_g^1$ configuration, which is split due to electron-electron, spin-orbit, and probably also affected by a Jahn-Teller interaction. Since the free gold atom has a large spin-orbit parameter compared to that of Si, the spin-orbit interaction is assumed to be much larger than the other effects. The one-particle states are then split according to Fig. 24a, where $\lambda_u$ and $\lambda_g$ label the effective spin-orbit parameter of the hole in the $e_u$ state and the electron in the $e_g$ state, respectively.

Four different ways of populating these states exist, and the respective energies of the final states can be evaluated:

\[
\begin{align*}
\Psi_1 &= |\pm 1/2\rangle_u |\pm 3/2\rangle_g, \quad E_1 = \Delta_{CF} + \frac{1}{2}\lambda_u - \frac{3}{2}\lambda_g \\
\Psi_2 &= |\pm 1/2\rangle_u |\pm 1/2\rangle_g, \quad E_2 = \Delta_{CF} + \frac{1}{2}\lambda_u + \frac{1}{2}\lambda_g \\
\Psi_3 &= |\pm 3/2\rangle_u |\pm 3/2\rangle_g, \quad E_3 = \Delta_{CF} - \frac{3}{2}\lambda_u + \frac{3}{2}\lambda_g \\
\Psi_4 &= |\pm 3/2\rangle_u |\pm 1/2\rangle_g, \quad E_4 = \Delta_{CF} - \frac{3}{2}\lambda_u - \frac{1}{2}\lambda_g
\end{align*}
\]  
(5.1)

By assuming the spin-orbit parameters to be negative, the four states is associated with the A, C, E, and F series, respectively, and from the experimentally observed transition energies for these series, $\lambda_u$ and $\lambda_g$ were evaluated to be approximately equal and $\approx -600$ cm$^{-1}$ and $\Delta_{CF} = 6500$ cm$^{-1}$. In Fig. 24b, the final level structure is given, using the results from Eq. 5.1. A weak electron-electron interaction can split these four levels further, but calculations show that transitions are allowed only to
one component in each of the energy groups. The fact that we observe weaker line series in addition to the A, C, E, and F series, could be due to a static Jahn-Teller interaction of e-symmetry, which lowers the symmetry, and can transfer dipole strength to formerly forbidden transitions.

Fig. 24. In a) the one-particle level structure of the substitutional gold pair in silicon is given. The \( e_u^3e_g^1 \) configuration can be treated as a hole in the \( e_u \) state and an electron in the \( e_g \) state. These one-particle states split by spin-orbit interaction into four levels. These can be populated in four different ways, resulting in four final excited states, shown in b), where \( \lambda_e \) and \( \lambda_g \) have been assumed to be negative and approximately equal, \( |\lambda_u| > |\lambda_g| \).
6. EXPERIMENTAL TECHNIQUES

6.1 Fourier Transform Spectroscopy

The analyses of the different centers studied in this thesis, are based upon an investigation of the absorption signal which arise when a defect is optically excited from its ground state to several possible excited final states. The method used is Fourier transform spectroscopy (FTS) (Bell 1974) and has the advantage of providing spectra with high resolution and a high signal-to-noise ratio (SNR). The transition energy can thus be determined with a very high accuracy, and small energy splittings of the involved electronic states, induced by external fields, can be resolved. The high SNR makes it possible to investigate also defect systems which give rise to small absorption signals, e.g., due to low defect concentrations. The principle of Fourier transform spectroscopy will be outlined very briefly, and some advantages and limitations will be discussed.

![Diagram](image)

**Fig. 25.** Schematic illustration showing the main components and the function of the Bomem DA3.02 Fourier transform spectrometer, used for all spectroscopic experiments in this thesis (Olajos 1989).

After passing a circular aperture, a parallel light beam from a broad-band light source is directed towards a Michelson interferometer, see Fig. 25. In the interferometer, the light beam is divided into two equally intense beams, labeled A and B, by a beamsplitter. The beams travel along two different paths with optical path lengths $x_A$ and $x_B$, respectively, where $x_A$ is constant, while $x_B$ is determined by the position of a movable mirror. After passing the beamsplitter once more, the two beams recombine and give rise to an intensity modulated signal, $I(x_A-x_B)$, which varies as a function of the path difference between the two beams. The light passes the sample and the resulting interferogram registered by the detector is described by

$$I(\Delta x) = \int I(\sigma)(1 + \cos(4\pi\Delta x\sigma))d\sigma$$

(6.1)
Here $\sigma$ is the wavenumber (cm$^{-1}$) of the light, and $I(\sigma)d\sigma$ is the intensity in the spectral element $[\sigma,\sigma+d\sigma]$. $\Delta x$ is the displacement of the movable mirror from the position corresponding to zero path difference (ZPD), i.e., $\Delta x = (x_A - x_B)/2$. By performing an inverse Fourier transform of the interferogram, the transmitted intensity as a function of wavenumber, $I(\sigma)$, is obtained.

There are several advantages with FTS compared to, e.g., grating monochromators. The most important advantage is that the resolution of FTS is determined mainly by the total scan length, $\Delta x_{\text{max}}$, of the movable mirror and not by the intensity passing the entrance aperture. In FTS, which has a circular aperture and transmits all frequencies simultaneously, it is thus possible to have a high intensity at the source, which increases the SNR by several orders of magnitude compared to a grating monochromator. With FTS we can gain information on the whole spectral range in a very short time period (one scan in ~1-5 sec, dependent on the resolution of the recorded spectra), and instead spend the time to add several interferograms, which increases the SNR further. The SNR is approximately proportional to the square root of the number of added scans.

As mentioned above the resolution of the spectra in an FTS is limited by the scan length, $\Delta x_{\text{max}}$, of the moving mirror. The resolution is approximately $1/\Delta x_{\text{max}}$ but the abrupt truncation of the interferogram can cause "ringings" around sharp spectral lines. On the expense of resolution, however, these "ringings" can be effectively reduced by a multiplication of the interferogram with a function which minimizes the discontinuities at $-\Delta x_{\text{max}}$ and $\Delta x_{\text{max}}$. This procedure is referred to as apodization.

6.2 Perturbation Techniques

6.2.1 Uniaxial Stress

The samples used for the uniaxial stress measurements are cut in the three main crystal directions <100>, <110>, and <111>, and have the approximate dimensions 2x2x10 mm$^3$. The sample is mounted in a stress rig, where stress is applied via a push rod made of stainless steel. The pressure on the rod is exerted by a pneumatic cylinder. The magnitude of the stress was varied by externally changing the gas pressure in the cylinder.

For defect systems which are highly sensitive to stress fields, it is important to have a perfectly homogeneous stress field throughout the whole sample. Inhomogeneous stress will broaden the lines, and complicate an accurate determination of the stress splittings. To achieve homogeneous stress, the sample must be accurately oriented and mounted perfectly parallel to the applied field. This can be accomplished by a parallel lapping of the end surfaces and placing a sheet of indium metal at one end of the sample. This minimizes edge effects and the effects of misalignment of the sample. A more accurate method was however needed when
studying the gold donor in silicon: The sample ends were lapped into a pyramidal shape, see Fig. 26a. A stress rig were constructed in which cylindrical, pointed, brass parts, with a small central hole, could be mounted on both sides of the sample, see Fig. 26b. The points of the sample were placed in the holes, and the sample was automatically aligned. The softness of the brass caused the points of the samples to slowly merge into the brass parts without breaking or tilting.

6.2.2 Zeeman Measurements

In the Zeeman experiments, the sample is placed in an Oxford superconducting split-coil magnet used in the Voigt configuration, i.e., the magnetic field direction is perpendicular to the direction of the incoming light. The sample is kept at a temperature below the λ-point by placing the sample in a helium bath and pumping the compartment above the helium surface. Magnetic field values of up to 6.5 Tesla were used.
7. ACKNOWLEDGMENTS

This thesis could not have been completed without the generous help from several members of the department of Solid State Physics in Lund, and the encouragement from my friends and my family.

First I would like to express my gratitude to my supervisor Dr. Mats Kleverman, who with great enthusiasm introduced me to the field of defects in semiconductors, and initiated the projects which led to this thesis. I am grateful for his expert advice and for sharing his great knowledge in science.

All the scientific advice from Dr. Günter Grossmann as well as the constructive discussions, detailed but still with respect to the totality, are highly appreciated, in addition to practical computer help, when time and memory suddenly ran short.

I am indebted to Prof. Hermann Grimmeiss for not only creating an excellent scientific environment, but also for support and advice.

I wish to thank Prof. George Watkins, Lehigh University, for a fruitful collaboration during his stay in Lund in 1990.

Finally, I am sincerely grateful to my very good friend and collaborator Sara Ghatnekar-Nilsson for the invaluable help and encouragement at all stages in this work and for critically reading all versions of the introductory part of my thesis.
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