Defects in Semiconductors - Edited by H. J. von Bardeleben.
Materials Science Forum Volumes 10-12 (1986), pp. 729-734.

ELECTRONS OF 3d TRANSITION METALS IN SILICON

E. G. Sieverts, D. A. van Wezep, R. van Kemp
and C. A. J. Ammerlaan
Natuurkundig Laboratorium der Universiteit van Amsterdam
Valckenierstraat 65
1018 XE Amsterdam
THE NETHERLANDS

Hyperfine interaction constants for ^{29}Si neighbours of interstitial transition metal impurities in silicon have been determined with electron nuclear double resonance. In order to convert these results into a picture of the wave functions of the unpaired electrons of the transition ions, an LCAO analysis has been developed which takes full account of the spin multiplicity and the symmetry of the neighbour sites. Resulting data on spin delocalisation of titanium (Si:Ti$^+$), iron (Si:Fe^0), and chromium (Si:Cr$^+$) are compared with recent theoretical calculations.

1. INTRODUCTION

The extensive magnetic resonance studies on transition metal impurities in silicon by Ludwig and Woodbury date back to more than 25 years ago [1]. A renewed interest in their properties grew only in recent years, when it was realised that transition metals are often present as unwanted impurities in silicon. As a result many experimental and theoretical studies have been done in the last couple of years, also on very fundamental aspects.

One intriguing problem which the transition metal impurities pose is the duality between localisation and delocalisation of the impurity wave functions [2,3]. Experimentally, the observed isotropic contact hyperfine interactions with the transition ion nuclei are much smaller than in most other host crystals and than for free ions. As they are generally ascribed to exchange polarisation of paired shells of core and valence s-electrons, this is considered as an indication of delocalisation of the polarising unpaired d electrons. Complexes of transition metal ions with other impurities or defects have lower than cubic symmetry, which allows the impurity hyperfine interactions to be anisotropic. These anisotropies directly reflect the distribution of the impurity d-electrons. Also here the observed values show a marked reduction with respect to free ion values [4,5]. These observations suggest an important delocalisation of the impurity d-electrons, probably by covalent hybridisation with silicon neighbour ligand orbitals. On the other hand, the same electron paramagnetic resonance (EPR) studies which gave these impurity hyperfine interactions showed that hyperfine interactions with silicon nuclei were hardly or not resolved [1,6]. This seemed to indicate that admixture of silicon ligand orbitals could not account for any degree of spin delocalisation. Moreover, the successful model of Ludwig and Woodbury relied on the applicability of Hund's rule and on the coupling of total electron spin and total effective orbital momentum for the d electrons. This is only justified for localised d electrons for which the spin-spin interaction is larger than crystal fields. Also the high diffusion coefficients of the interstitial transition metals suggest that these ions hardly interact with the silicon lattice.

In order to obtain more information on the ^{29}Si hyperfine interactions, electron nuclear double resonance (ENDOR) measurements on a number of transition metals have been performed [7-11]. The analysis of hyperfine interactions in terms of electron wave functions is mostly performed by taking linear combinations of atomic orbitals (LCAO). The usual one-electron approach is not appropriate for these systems with multiple unpaired electrons which couple to spins higher than S=1/2. Therefore a more-electron approach is applied. Results for the orbital singlet ground states $3d^3$ (Ti^+ [8]), $3d^5$ (Cr^+ [10]) and $3d^8$ (Fe^o [7,9]) will be discussed. Fe^+ with an orbitally degenerate $3d^7$ ground state requires a too complicated analysis to be discussed here [11].

2. ANALYSIS OF MORE-ELECTRON ENDOR DATA

In the usual analysis of hyperfine interaction tensors, they are decomposed into an isotropic and an anisotropic part: $\overleftrightarrow{A} = a\overleftrightarrow{1} + \overleftrightarrow{B}$. In the silicon lattice a single electron LCAO wave function is taken which contains atomic s and p orbitals. The isotropic part of the interaction with a certain nucleus gives the amount of admixed s orbital at that site, the anisotropic part the amount of admixed p orbital. The anisotropic part must be axially symmetric in the direction of the p orbital [4,12].

If more unpaired electrons are involved in the total spin of a paramagnetic centre, the analysis is less straightforward. For each of the unpaired electrons again an LCAO wave function can be taken. In the case of transition metal impurities in silicon the unpaired electrons are thought to originate primarily from the impurity d orbitals. Wave functions for the individual electrons can then be written

$$\Psi = \alpha d_{TM} + \sum_i \eta_i (\beta_i s_{Si} + \gamma_i \sigma_{Si} + \delta_i \pi_{x,Si} + \epsilon_i \pi_{y,Si}) \ . \qquad (1)$$

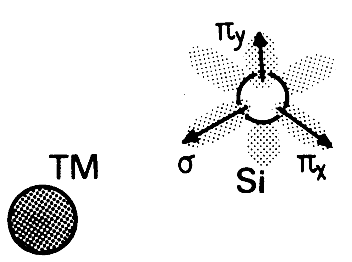

Figure 1. Directions of σ and π atomic silicon p-orbitals with respect to the central transition ion (TM).

In this notation σ denotes a silicon p orbital pointing towards the central ion, π_x and π_y are p orbitals in two perpendicular directions, as illustrated in figure 1. The interactions from the various unpaired electrons must be added.

In the tetrahedral environment of interstitial transition ions in silicon, the fivefold orbitally degenerate level of the d electrons is split into a t_2 triplet state below an e doublet state. In a group-theoretical treatment which takes into account the symmetry of the various d orbitals and the symmetry of the different kinds of neighbour sites, it can be determined which silicon atomic s and p orbitals are allowed to admix. The results from such analyses [8-10] are summarised in Table I. The three most important types of lattice sites are included. T denotes sites in octahedral coordination as the next-nearest neighbours (002), "3" sites in tetrahedral coordination like the nearest neighbours (111), and M sites in the {110} mirrorplanes of the silicon lattice such as position (113).

Table I. Symmetry allowed admixture of silicon ligand orbitals to interstitial transition ion d-orbitals. T, "3", and M indicate three types of silicon neighbours. Ligand orbitals are as defined in figure 1 and Ref. [8,9].

orb.		T (00k)	"3" (kkk)	M (kkl)
t_2	d_{xy}	s σ – –	s σ $(\pi_x-\sqrt{3}\pi_y)/2$	s – σ – – – π_y
	d_{yz}	– – π_x π_y	s σ $(\pi_x+\sqrt{3}\pi_y)/2$	– s – σ π_x π_y –
	d_{zx}	– – π_y π_x	s σ $-\pi_x$	– s – σ π_x π_y –
e	$d_{3z^2-r^2}$	s σ – –	– – $(\pi_x-\sqrt{3}\pi_y)/2$	s σ – π_y
	$d_{x^2-y^2}$	– – – –	– – $(\pi_y+\sqrt{3}\pi_x)/2$	– – π_x –

The columns in table I contain ligand orbitals which admix with equal coefficients. If two perpendicular π orbitals are equally admixed to different d orbitals their (anisotropic) hyperfine interactions add up to an interaction which is axially symmetric along the σ direction, but with opposite sign. This can be understood as it can also be described as a situation where some spin in a σ orbital is lacking from a cubic orbital environment with zero anisotropy. In a $3d^3$ state with three unpaired t_2 electrons and allowed admixture of σ and π orbitals, this means that contributions may partly cancel and that even the sign of the resulting hyperfine interaction depends completely on the relative strengths of the independent admixtures. As a result, the actual amount of admixed ligand electron can be larger than the hyperfine interaction seems to indicate. Thus for Ti^+ with three unpaired t_2 electrons and for Cr^+ with two unpaired e and three unpaired t_2 electrons as well, only a lower limit of ligand admixture can be derived from the observed hyperfine interactions. For Fe^0 with two unpaired e electrons the actual admixtures can be calculated.

3. EXPERIMENTAL DATA

Principal values of experimental hyperfine interaction tensors can conveniently be decomposed as $A_1 = a + 2b$, $A_2 = a - b + c$, and $A_3 = a - b - c$, where a is the isotropic part, b is the axially symmetric part, and c is the deviation from axial symmetry. From the earlier discussion it is clear that the anisotropic interaction needs not always to give a negative axial hyperfine parameter b as in the one-electron case, but can be of either sign. Therefore it is important to determine also the absolute signs of hyperfine interactions.

Mostly ENDOR measurements can be described with a spin hamiltonian with zeeman interactions and hyperfine interaction

$$\mathcal{H} = \mu_B \vec{B}\cdot\overleftrightarrow{g}\cdot\vec{S} + \sum_i(-g_n\mu_n\vec{B}\cdot\vec{I}_i + \vec{S}\cdot\overleftrightarrow{A}_i\cdot\vec{I}_i). \qquad (2)$$

ENDOR transitions are those for which the nuclear spin changes; in first order:

$$h\nu = |\, g_N\mu_N B - m_S A_{eff} \,|, \qquad (3)$$

where m_S is the electron spin quantum number. This means that ENDOR spectra are in principle symmetric with respect to the zeeman frequency of the nuclear spin. In practice this is not always true, however, as ENDOR is the observation of nuclear transitions through a change in the intensity of an EPR signal. This means that only ENDOR transitions are observed for those m_S values which belong to the pertinent EPR line. For systems with low electron spin in cubic symmetry all EPR transitions coincide, so that all ENDOR transitions are observed in a single scan. Because of the symmetry with respect to the nuclear zeeman frequency, the absolute sign of the hyperfine interaction can not be determined in that case. For the S=5/2 system of Cr^+ the various EPR transitions are split by a cubic field splitting term. That means that ENDOR can be done on one EPR line at a time, between only two adjacent m_S values. Here it was first realised that this allowed the experimental determination of signs by choosing for instance the $m_S = +1/2 \rightarrow +3/2$ transition [10]. For the S=1 and S=3/2 systems of Fe^0 and Ti^+ the EPR lines for the various $\Delta m_S = 1$ transitions are normally not split. In these cases splitting can be achieved by the application of uniaxial stress. For the hyperfine interactions of Fe^o as first measured by Greulich-Weber et al. [7], the signs could be determined in this way [9]. Because of a poor signal-to-noise ratio under uniaxial stress, signs for Ti^+ could not yet be ascertained.

Experimental values of a and b for these three systems and restricted to only the six nearest neighbour shells with together 42 atoms, are given in Table II. In this table all signs for Fe^o and Cr^+ are as determined; for Ti^+ only the relative signs between a and b are known. All interactions are approximately axially symmetric. Unless otherwise indicated, the axes deviate only little from the direction towards the central ion.

Table II. Hyperfine parameters (kHz) for the six nearest shells of silicon atoms for interstitial Fe^o, Ti^+, and Cr^+. Shell numbers refer to Fig. 2. Dipole-dipole interaction b_{d-d} is calculated for 100% localised d orbitals.

shell	no	Fe^o		Ti^+		Cr^+		b_{d-d}
		a	b	a	b	a	b	
3(111)	1	+158	+1402	-8124	-442	-5067	-728	-1250
$3(\underline{2}\underline{2}\underline{2})$	4	+777	-196	-1417	+678	-3269	-332	-156
$3(\bar{2}\bar{2}\bar{2})$	5	+3245	-157	-749	-12	+217	-110	-156
T(200)	2	-4642	-799	-852	-3116*	+668	-1352*	-811
M(113)	3	-3870	-434#	-2246	-160	-2359	-202	-178
M(331)	6	-381	-85#	-2858	-162	-1388	-145	-78

* axis ∥ [110]   # axis ~∥ [111]

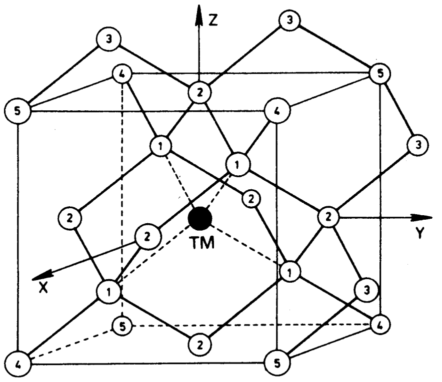

Figure 2. Silicon lattice with the first five shells of neighbours of an interstitial transition ion.

4. DISCUSSION

We will now review and compare results for the three types of neighbour sites. When comparing them, we should realise that the relation between hyperfine interaction and LCAO wave functions contains a factor 1/2S [8,9]. Thus a same admixture results in 2/5 smaller interactions in Cr^+ than in Fe^o. A first contribution to the observed anisotropic hyperfine interactions always comes from the dipolar interaction between the electron spins at the central ion and the ^{29}Si nuclei. For a completely localised point charge the calculated values of the resulting axially symmetric interactions are also given in table II. For this interaction the factor 1/2S is exactly compensated by the number of unpaired electrons on the ion which is 2S. If there is spin transfer from the ion to the silicon ligands, values are proportionally smaller.

For tetrahedrally coordinated <111>-axial neighbours (shells 1, 4, and 5) of Fe^o $(3d^8,e^2)$ only admixture of π orbitals is allowed. This gives a positive contribution to b. For the nearest neighbours this contribution far outweighs the dipolar effect and indicates a large spin transfer. No s admixture is allowed. If it were, it should always contribute a negative a. The sometimes large positive values should thus originate from other sources. Generally they are ascribed to exchange polarisation of silicon core and valence s states. In this case an other, more probable source is polarisation of the completely filled t_2 level where s admixture is allowed. This conclusion is also drawn from theoretical calculations [2,3,13]. Also the too large negative b for shells 4 and 5 will probably originate from this effect. For neighbours of this symmetry of Ti^+ ($3d^3,t_2^3$) all admixtures are allowed, so that no prediction as to the sign can be made. Only a lower limit of the spin transfer can be derived. For Cr^+ ($3d^5,t_2^3e^2$) the same applies. As there are no paired d levels the positive a for one of the shells can only be explained by the ordinary Si core and valence s-electron polarisation. It seems probable that this is the same neighbour shell which also gives the large $a=+3245$ kHz in Fe^0.

The octahedrally coordinated next-nearest neighbours (shell 2) of Fe^0 allow only s and σ admixture, which is observed indeed. Complete hyperfine data for this shell show an off-diagonal element of ~ 500 kHz which should be zero by symmetry [9]. Exchange polarisation of filled t_2 states is again a good explanation, as for Ti^+, where this tensor element is allowed, it is about 15 times as large. For Ti^+ this element causes [110]-axiality of the interaction which indicates equal admixture of the allowed π_x and π_y in d_{yz} and d_{zx}. Although in the silicon lattice s and σ orbitals are formally also allowed for this shell, they are forbidden for a purely octahedral AB_6 complex. From experiment we may thus conclude that this interdiction is still largely obeyed. For Cr^+ the e states may admix s and σ orbitals. Yet, the shell 2 interaction is [110]-axial as well and much more resembles Ti^+ than Fe^0. The isotropic a is even positive. Again, exchange polarisation should probably account for it. This indicates at any rate the almost complete absence of s admixture.

For the mirrorplane neighbours (shells 3 and 6) of Fe^0 all admixtures are allowed in independent proportions. In practice axiality is observed which deviates only little (up to 10°) from <111> lattice bond directions. This might suggest the occurrence of Si valence bond polarisation. Although in this symmetry all admixtures are allowed for Ti^+ as well, a sound identification of all eight experimental M shells (six more than shown here) could be made by assuming that their axial directions point towards the central ion [8]. This indicates the prominence of s and σ admixture, even somewhat enhanced by the central dipole-dipole interaction. The large negative a values support this view. Results for Cr^+ are very similar to Ti^+ for the three observed M shells, although the deviations from the central axial directions are somewhat larger.

From the complete analysis of the hyperfine interactions, for Fe^0 a total delocalisation to silicon ligands of 25 % was found, with 16 % on shell 1 [9]. Thus the d electrons in the e state seem to hybridise preferentially into <111> directions. For Ti^+ a lower limit of 40 % was found, with most on shell 2 [8]. This means that the t_2 d-electrons hybridise stronger and rather into <100> directions. A preliminary analysis for Cr^+ gives a very similar result, with a minimum transferred spin of also about 40 %. This is not surprising in view of the similarities which we noted already for the various types of neighbour sites. In this $3d^5$ state the amounts of spin delocalisation from the e and from the t_2 states need certainly not be the same. The similarity with Ti^+ indicates that they are not the same, indeed. Even if the factor 1/2S between the Fe^0 and Cr^+ hyperfine interactions is taken into account, one must conclude that the kind of admixtures as found in Fe^0 is largely missing. Although it is formally not possible to divide the observed hyperfine interactions in parts from e and from t_2 states, comparison with the Fe^0 and Ti^+ data shows that the t_2 are much more delocalised than the e states, even while present simultaneously. Consequently the average Cr^+ delocalisation of at least 40 % may very well be constituted from, for instance, 50 % t_2 and 25 % e.

5. COMPARISON WITH THEORETICAL DATA AND CONCLUSIONS

The delocalisation or spin transfer discussed in the previous section is actually the parameter η^2 from Eq.(1). Detailed theoretical data on individual neighbours are mostly missing (except [13]). Instead, one rather determines the localisation α^2. Yet, a comparison is possible as $\alpha^2 + \Sigma\eta_i{}^2 = 1$. Calculations of the amount of magnetic moment or spin within some impurity volume have been performed by Beeler et al. [14] and Katayama-Yoshida and Zunger [15].

Although they do not calculate the magnetic moment over exactly the same impurity space, results from both are given in Table III.

Another measure for the localisation/delocalisation of the unpaired electrons has already been discussed in the introduction. This central impurity-ion hyperfine interaction measures the s-electron core-polarisation. As mentioned, the experimental values [1] show a marked reduction with respect to the free ion values [16], $a_{TM,Si} = \lambda \cdot a_{TM,free}$. Core polarisation is generally a good measure for the amount of polarising d electrons. Unfortunately "covalency effects", as the present spin transfer is sometimes called as well, seem to complicate this proportionality [2,3]. Although λ and α^2 are thus not exactly the same, they are both related to the localisation. Experimental and theoretical values are also given in Table III.

Table III. Experimental and theoretical values of spin transfer ($\Sigma\eta^2 = 1 - \alpha^2$) and reduction of central ion hyperfine interaction (λ).

	$\Sigma\eta^2$	$1 - \alpha^2$		λ	
	(exp.)	[14]	[15]	(exp.)	[15]
Fe^0	0.25	0.12	0.29	0.46	0.34
Ti^+	$>$0.40	0.58	0.34	0.25	0.22
Cr^+	$>$0.40	0.34	0.25	0.46	0.47

The present analysis of the experimental hyperfine data indicates that the actual spin transfer from transition metal ions to silicon ligand orbitals is much larger than suggested by the absence of well resolved hyperfine structure in EPR. The experimental aspect of the localised/delocalised paradox is thus resolved. On the other hand a marked difference is found between the e and t_2 d-orbitals of the transition metals, the e-type orbitals being more localised. This is in agreement with some of the theoretical results [14] in Table III.

REFERENCES

[1] Ludwig, G.W. and Woodbury, H.H., in Solid State Physics, edited by F. Seitz and D. Turnbull (Academic, New York, 1962), Vol. 13, p. 223 ff.

[2] Katayama-Yoshida, H. and Zunger, A., Phys. Rev. Letters **53**, 1256 (1984); Phys. Rev. B **31**, 7877 (1985)

[3] Zunger, A., in Solid State Physics, edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1986), Vol. 39, p. 275 ff.

[4] Sieverts, E.G., Muller, S.H., Ammerlaan, C.A.J., Kleinhenz, R.L., and Corbett, J.W., Phys. Status Solidi (b) **109**, 83 (1982)

[5] Muller, S.H., Tuynman, G.M., Sieverts, E.G., and Ammerlaan, C.A.J., Phys. Rev. B **25**, 25 (1982)

[6] Sieverts, E.G., Muller, S.H., Ammerlaan, C.A.J., and Weber, E.R., Solid State Commun. **47**, 631 (1983)

[7] Greulich-Weber, S., Niklas, J.R., Weber, E.R., and Spaeth, J.M., Phys. Rev. B **30**, 6292 (1984)

[8] van Wezep, D.A., van Kemp, R., Sieverts, E.G., and Ammerlaan, C.A.J., Phys. Rev. B **32**, 7129 (1985)

[9] van Wezep, D.A., Gregorkiewicz, T., Sieverts, E.G., and Ammerlaan, C.A.J., Phys. Rev. B **34** (1986, in press)

[10] van Kemp, R., Sieverts, E.G., and Ammerlaan, C.A.J., to be published

[11] van Kooten, J.J. and Ammerlaan, C.A.J., to be published

[12] van Kemp, R., Sieverts, E.G., and Ammerlaan, C.A.J., this conference

[13] Katayama-Yoshida, H. submitted to Phys. Rev. Letters

[14] Beeler, F., Anderson, O.K., and Scheffler, M., Phys. Rev. Letters **55**, 1498 (1985)

[15] Katayama-Yoshida, H. and Zunger, A., Phys. Rev. B **31**, 8317 (1985)

[16] Watson, R.E. and Freeman, A.J., in Hyperfine Interactions, edited by A.J. Freeman and R.B. Frankel (Academic, New York, 1967) p. 53 ff.