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HYPERFINE INTERACTIONS FROM EPR OF IRON IN SILICON

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At high microwave power very well resolved EPR spectra from isolated neutral interstitial iron atoms in silicon can be observed. From these spectra hyperfine interactions with at least three shells of neighbouring lattice sites, containing 18 or 22 atoms, can be determined. The localization of the unpaired electron on these sites is only small. On nearest neighbour sites it is found to be even smaller than on next nearest sites.

1. INTRODUCTION

AROUND 1960 EXTENSIVE electron paramagnetic resonance (EPR) experiments on a series of substitutional and interstitial transition metal impurities in silicon have been performed by Ludwig and Woodbury [1, 2]. They also proposed a highly successful model for an explanation of the various observed EPR spectra. Only rather recently, there is a renewed general interest in transition metal impurities, both from an applied and fundamental point of view. Especially iron received much attention as it was found to be a prominent thermal defect in silicon [3, 4]. Using EPR, also the interaction of isolated interstitial iron with other impurities and with lattice defects was studied [5, 6]. From these recent experimental results, as well as from the earlier work by Ludwig and Woodbury, it followed that the atomic wavefunction parameters as derived from the observed hyperfine interactions were considerably reduced with respect to the free atom values [7]. This reduction could not be accounted for in the elegant but simplified model of Ludwig and Woodbury. Recently this model has been given a more solid background by theoretical calculations by DeLeo *et al.* [8]. In their self-consistent scattered wave $X\alpha$ cluster method also many-electron effects could be incorporated. For a series of $3d$-transition metal impurities, they found states in the bandgap which originated from collective band states and which got a considerable fraction of d-like localization on the impurity atom. In view of these calculations, it is interesting to present some experimental information on the defect electron as derived from hyperfine interactions.

Isolated iron atoms are found to occupy tetrahedral interstitial sites in the silicon lattice. They are present in high concentration after a rapid quench from 1200°C. The model of Ludwig and Woodbury [2] predicts that their neutral charge state has a $3d^8$ electron configuration. This fits with the observation that they give rise to paramagnetic centers with a spin $S = 1$. Their EPR spectrum can be described with an isotropic g-value $g = 2.070$. In full tetrahedral symmetry the $m_s = +1 \leftrightarrow 0$ and $m_s = 0 \leftrightarrow -1$ transitions coincide, as the zero-field splitting of this $S = 1$ center vanishes. By the application of uniaxial stress this degeneracy is lifted [9]. The inevitable presence of small random internal stresses gives rise to inhomogeneous broadening of the EPR line. Typically a minimum linewidth of 0.25 mT can be achieved [9]. As already observed by Woodbury and Ludwig [1], this effect can be circumvented when performing EPR experiments at high microwave power. Later this was explained by the occurrence of two-quantum transitions $m_s = +1 \leftrightarrow -1$ which prevail in high microwave fields [10]. In this case stress effects cancel and a narrow EPR line with a very pronounced structure can be observed. As already suggested in references [1] and [10], this structure can be ascribed to hyperfine interactions with ^{29}Si nuclei. In this paper these hyperfine interactions are further analysed. Hyperfine interactions with the central iron atom can easily be observed in ^{57}Fe enriched samples [1, 2, 6].

2. OBSERVED HYPERFINE INTERACTIONS

Under conditions of high microwave power (about 5 mW), in dispersion mode, and with the external magnetic field **B** in the [100] direction, a spectrum of at least seven equidistant lines is observed (Fig. 1). The

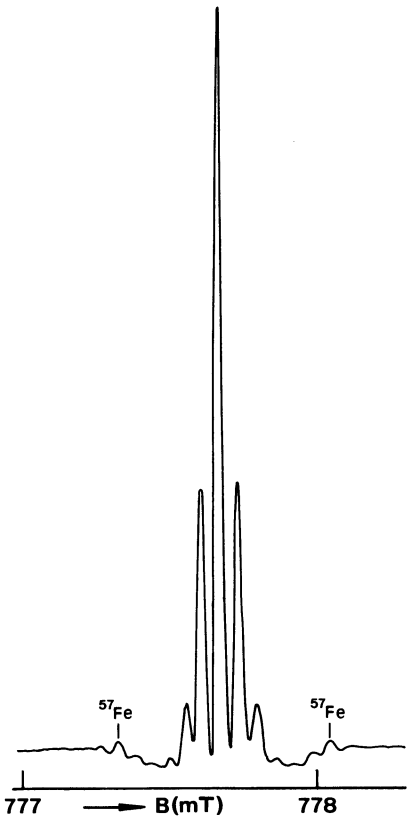

Fig. 1. EPR spectrum of Fe_i^0 in silicon at K-band, in dispersion mode, at $T \simeq 8$ K, for **B** || [100], at high microwave power.

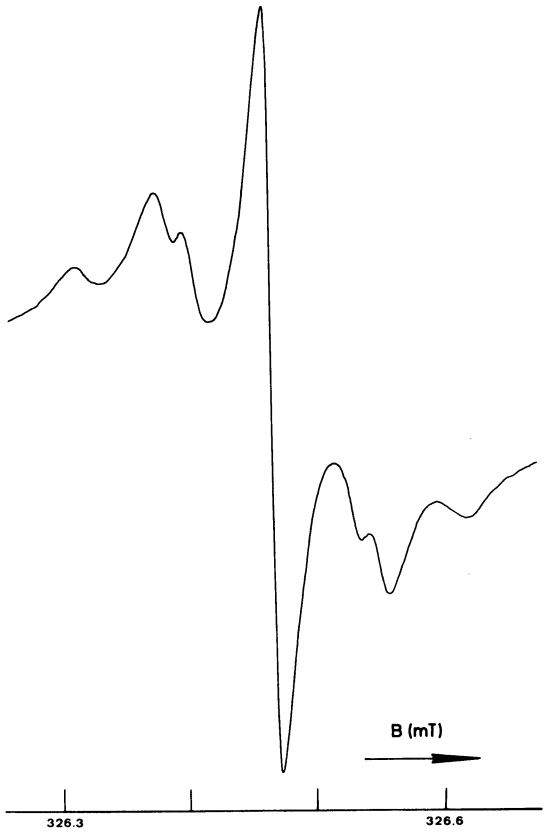

Fig. 2. EPR spectrum of Fe_i^0 in silicon at X-band, in absorption mode, at $T \simeq 25$ K, for **B** || [111], at high microwave power.

Table 1. Intensities of hyperfine satellites as observed, and as calculated for 16 and for 18 neighbour sites

Number of satellite	Intensity		
	Observed	16 neighbours	18 neighbours
0	100	100	100
1	37	36	40
2	8	6	8
3	1	0.7	1
4	–	0.05	0.1

Table 2. Shells of lattice sites around a tetrahedral interstitial site

Position	Number of sites	Symmetry type	Distance (Å)
[111]	4	trigonal	2.35
[200]	6	rhombic I	2.7
[311]	12	monoclinic I	4.5
[222]	4	trigonal	4.7
[$\bar{2}\bar{2}\bar{2}$]	4	trigonal	4.7

strong central line has a linewidth at half height of about 0.025 mT. For the satellite lines the width gradually increases till 0.035 mT for the weakest lines. The observed intensity ratio is about 1:8:37:100:37:8:1. Eventual more remote satellite lines are obscured by other weak hyperfine lines due to the presence of ^{57}Fe, which are centered at about 0.35 mT from the central line. The exact magnitude of this hyperfine interaction has been determined in ^{57}Fe enriched samples [1, 6].

The observed central structure can be explained by the occurrence of nearly equal hyperfine interactions with ^{29}Si nuclei (4.7% abundant) in several shells of neighbouring lattice sites. First satellites arise primarily from centers with only one ^{29}Si nucleus in all those shells, second ones primarily from those with two, etc. A superposition of the structures for centers with zero, one, two, three (and so on) ^{29}Si nuclei on a total of 16 or 18 approximately equivalent neighbour sites gives the values in Table 1.

It is very unlikely that the hyperfine interactions on so many sites are actually identical. That this is not the case indeed, can be seen from the increasing linewidth of the further satellites. Moreover the interactions are not isotropic either, as seen from a gradual

Table 3. Hyperfine parameters of Fe_i^0 *in silicon*

Pattern	Shell	Nuclei	a (MHz)	b (MHz)	c (MHz)	$\|\psi^2\|$ (Å^{-3})	$\langle r^{-3}\rangle$ (Å^{-3})
	[000]	1 ^{57}Fe	20.9 ± 0.1	0	0	0.95	–
B, C	[200]	6 ^{29}Si	4.6 ± 0.2	0.7 ± 0.2	<0.2	0.035	0.11
A	[111]	4 ^{29}Si	3.4 ± 0.4	<0.4	0	0.026	<0.06
A	[222] + [$\bar{2}\bar{2}\bar{2}$] or [311]	8 ^{29}Si 12 ^{29}Si	3.4 ± 0.4	<0.4	–	0.026	<0.06

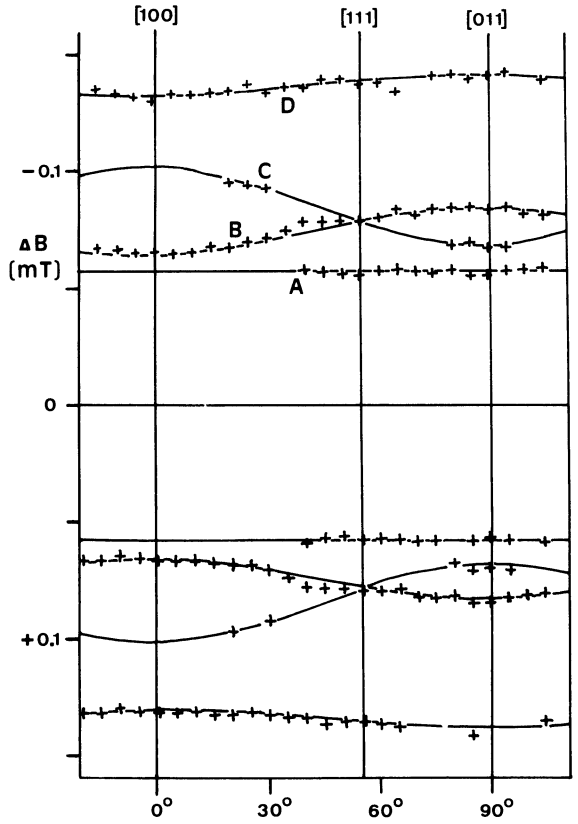

Fig. 3. Angular dependence of the line structure of the EPR spectrum of Fe_i^0 in silicon, for magnetic field directions in the $\{0\bar{1}1\}$ plane. Results from X-band experiment in absorption mode, at $T \simeq 25$ K, at high microwave power (after Berke [11]).

smearing out of the original pronounced structure, if the magnetic field is turned out of the [100] direction. This means that actual intensities will become smaller than those calculated, so that it is well possible that even more than 18 sites are involved.

For a comparison of EPR line intensities, dispersion spectra are very appropriate. Small anisotropies and line splittings however, are sometimes better observed in absorption mode. Unpublished work by Berke gave additional information in this case [11]. A representative absorption spectrum is shown in Fig. 2. Fig. 3 shows the observed anisotropy of the satellite lines. Pattern A has no resolved anisotropy. For some magnetic field directions the lines of this pattern are obscured by other lines. The lines B and C together form a pattern of approximate [100] axial (tetragonal) symmetry. For this symmetry B should have twice the intensity of C. Pattern D, finally, does hardly have any resolved anisotropy. For $\mathbf{B} \parallel [100]$ A and B nearly coincide giving rise to the first satellite in the dispersion spectrum of Fig. 1. Pattern D is at their double distance, forming the second satellite. C cannot be observed in between, as it can be calculated that its intensity should be even smaller than D.

Defining a shell as a set of lattice sites which are equivalent under those symmetry transformations which leave invariant the silicon lattice with a tetrahedral interstitial impurity, the nearest five shells are given in Table 2. As shell [200] is the only candidate to produce the pattern B–C, it should actually be of lower, rhombic symmetry, although it is not further resolved in EPR. The unresolved nearly isotropic pattern A will arise from a superposition of the hyperfine interactions of either shells [111], [222], and [$\bar{2}\bar{2}\bar{2}$], or [111] and [311]. The unresolved pattern D is at close to twice the distance of the weighted average of A and B for magnetic field directions between [100] and [111], of A, B, and C for directions between [111] and [011]. In order to discriminate between the two above mentioned possibilities for pattern A, a computer simulation of the dispersion spectrum has been made to fit both intensity and lineshape for several angular settings of the magnetic field direction. From a slow scan of the central line an empirical basic lineshape was deduced. It was found to be in between a Gaussian and a Lorentzian lineshape. When superimposing the spectra for various distributions of ^{29}Si nuclei a best fit was obtained for the hyperfine parameters in Table 3. No decision could be made however, in favour of one of the two possibilities for pattern A. We can conclude, however, that the largest hyperfine interactions do not arise from only 16 lattice sites, but from 18 or even 22.

In the discussion of the dispersion spectrum along the [100] direction this possibility was already considered.

3. DISCUSSION

The hyperfine parameters in Table 3 are determined assuming a nearly axially symmetric hyperfine tensor. In this approach, a is the isotropic part, b the anisotropic part, and c the deviation from axial anisotropy, so that the three principal values of the hyperfine tensor are $a+2b, a-b+c$, and $a-b-c$. The parameters a and b are related with the wavefunction of the unpaired electron. The parameter a, the Fermi contact interaction, is proportional to the probability density of the electron on the nucleus: $a_i = (8/3)\,\pi g\mu_B g_N \mu_N\, |\psi(0_i)^2|$. For simple atomic p-orbitals, b enters through the dipole–dipole interaction: $b = (2/5)\, g\mu_B g_N \mu_N \langle r^{-3}\rangle_p$, where $\langle r^{-3}\rangle_p$ is the expectation value of r^{-3} over a p-orbital. Using these formulas, wavefunction parameters can be derived for the various shells of atom sites. They are also given in Table 3.

When adopting the model of Ludwig and Woodbury, the isotropic interaction on the iron nucleus should arise from core polarization. If so, the unpaired electron density is much smaller than for free iron atoms [7]. The wavefunction parameters on the silicon sites should be compared with the values for free atomic orbitals: $|\psi_{3s}(0)^2| = 31.5$ Å^{-3} and $\langle r^{-3}\rangle_{3p} = 16.1$ Å^{-3}. From this we conclude that only a small fraction of less than 1% of the unpaired electron is localized on each of the 18 or 22 neighbouring lattice sites.

In the above treatment, hyperfine interactions were assigned to the two shells of nearest and next nearest neighbours of the interstitial iron atom. It is noteworthy that the largest interaction is not with the nearest but with the next nearest neighbours. In other impurity systems like the substitutional shallow donors P, As, and Sb even stronger oscillations of the hyperfine interaction and hence of the wavefunction as a function of distance have been observed. In that case the effect arises from the strong conduction-band character of the shallow level electrons. For a deep center like iron, where the unpaired electron is primarily located in a d-like orbital on the transition metal ion, such effects are not to be expected. Therefore it was decided that in this case the largest hyperfine interactions had indeed to be identified with the nearest shells of lattice sites. Only symmetry considerations forced us to slightly diverge from a purely monotonic decreasing wavefunction [12]. The presence of d-orbital lobes in the [100] directions may account for this effect.

Calculations by DeLeo *et al.* [8] have been performed on small clusters of only 10 silicon atoms. This number is much smaller than the 18 or 22 silicon sites which have been found experimentally to have largest and roughly equal hyperfine interactions. Therefore their calculations cannot give very reliable results for the wavefunction on neighbouring lattice sites. It would nevertheless be interesting if they compared their results with the present experimental values. For more detailed experimental data, also on further shells of silicon atoms, ENDOR measurements have to be awaited.

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