

Atomic and electronic structure of hydrogen-passivated double donors in silicon

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Hydrogen is known for its propensity to interact with shallow and deep dopants in silicon terminating their electrical activity. A particular interesting case is given by the partial passivation of double donors leading to the formation of complexes with single donor character. In the neutral charge state the hydrogen–double-donor complexes are expected to be observable in magnetic resonance. In this paper double-donor–hydrogen complexes were studied by electron paramagnetic resonance (EPR) and electron-nuclear double resonance. For sulphur in silicon two complexes each consisting of one sulphur atom and one hydrogen atom in a trigonal configuration were identified; their EPR spectra are labelled Si-NL54 and Si-NL55. They are thermally stable up to temperatures of about 600 °C. Thermal donors are double donors with a core of oxygen atoms. Their partial passivation renders them more shallow with even more extended electronic wave function. The EPR spectrum Si-NL10 is associated with this partially passivated centre of triclinic symmetry.

1. Hydrogen in silicon

Hydrogen passivation of electronic centres is an important topic of current interest in the materials science of semiconductors. It is a manifestation of impurity reactions changing the electronic properties, such as conductivities and free-carrier lifetimes, of crystalline or amorphous semiconductors.

Upon interaction with atomic hydrogen the electrical activity of all kinds of impurities can be terminated. This passivation process was first reported by Pankove *et al.* [1] for shallow acceptors in silicon. For shallow impurities passivation was found to be particularly effective in the case of acceptors. For donors the passivation process proceeds more slowly and is never very effective. A most important finding was that upon exposure to atomic hydrogen a decrease of electron density is always accompanied by a simultaneous rise of the mobility [2]. On this basis it was concluded that the interaction process involves a close binding of the hydrogen atom to the electrically active impurity resulting in passivation rather than compensation. Theoretical calculations have established that in the case of substitutional shallow acceptors the hydrogen atom takes a bond-centred position between the acceptor atom and a nearest-neighbour silicon atom. In the case of the shallow group-V donors the lowest-energy configuration was found for the hydrogen antibonded to a nearest-neighbour silicon atom. The antibonding position on the donor atom itself was found to be a local minimum energy configuration, with an analogous passivation action.

Single donors in silicon are paramagnetic in their neutral charge state, with electron spin $S=1/2$, and magnetic resonance, electron spin resonance (EPR) and electron nuclear double resonance (ENDOR), has been applied with great success to reveal their electronic structures. However, by passivation of the single donors their paramagnetism is lost. For double donors the situation is more promising as it may be expected that passivation can either be partial by binding one hydrogen atom, or complete when two hydrogen atoms attach. The partially passivated double donor is expected to be paramagnetic in its unionised state, allowing the magnetic resonance technique to be applied.

The present paper reports on studies by magnetic resonance on two double donors in silicon which represent quite different kinds of electronic centres. Sulphur, as an example from the group-VI chalcogen impurities, is a well-studied substitutional point defect. Oxygen-related thermal donors have an extended size of their cores of which the structure is still not finally established.

The magnetic resonance experiments were carried out in a superheterodyne spectrometer operated near 23 GHz (K band) tuned to observe dispersion signals. Sample temperatures were near 9 K for most of the measurements.

2. Passivation of sulphur

Substitutional chalcogen atoms represent a classical example of double-donor impurities in silicon. In the past these centres have been subjected to intensive experimental and theoretical investigations. As a result their properties are well understood. The chalcogen impurities and several of their homo- and hetero-nuclear complexes have been identified by magnetic resonance and deep-level transient spectroscopies (DLTS). In particular Pensl *et al.* [3] reported on a variety of double-donor levels related to isolated chalcogens and their complexes. Upon exposure to hydrogen plasma passivation of the electrical activity of chalcogens has been observed. For sulphur the most important findings [4] can be summarized as follows: (a) both double donor levels are passivated in one step, (b) all sulphur-related centres are passivated regardless of their original mutual concentration, (c) upon passivation of the double-donor levels no new sulphur-related levels can be detected in the gap, (d) the electrical activity of the passivated centres can be fully recovered by a 10-minutes heat treatment at 500 °C. One should note here that the above listed conclusions do not necessarily imply that two hydrogen atoms take part in the passivation process. To decide on this issue the kinetics of the process were studied; this was shown to involve a single step mechanism, being thus consistent with the participation of a single hydrogen atom. A simultaneous generation of new single-donor levels in the gap was not detected.

Theoretical treatment of the sulphur passivation process has been attempted by Yapsir *et al.* [5], who have examined various configurations of S-H and S-H₂ complexes. For the S-H defect the lowest-energy configuration was found with the hydrogen atom in a distorted bond-centred position of monoclinic symmetry. Local minima were also found for both antibonding positions of hydrogen on sulphur and nearest-neighbour silicon atoms. Further, from thermodynamic considerations, it was concluded that whereas S-H and S-H₂ complexes were stable in an environment with an excess of sulphur the sulphur-hydrogen pair would be preferentially created. In this way the first-order kinetics could be explained.

More recently the hydrogenation of sulphur donors was also investigated in infrared absorption spectroscopy by Peale *et al.* [6]. They have observed electronic transitions of new sulphur-hydrogen complexes of a single effective-mass donor character; these were apparently created upon hydrogen passivation of sulphur-related double donors. The newly found centres were identified as singly passivated species and were further suggested to be paramagnetic in their neutral charge state.

In the present study we have used n-type, phosphorus-doped silicon of float-zoned (FZ) and Czochralski-grown (Cz) types. The samples, of typically $1.4 \times 1.4 \times 10 \text{ mm}^3$ size, were first diffused with sulphur at 1370 °C for 48 hours and subsequently with hydrogen or deuterium at 1250 °C during 0.5 hours. Following the diffusion step the samples were quenched to room temperature.

The EPR measurements on thus prepared samples revealed the presence of two new spectra [7]. These, labelled further Si-NL54 and Si-NL55, were partly overlapping and were not resolved sufficiently in the regular EPR spectrum, as shown in Fig. 1(a). Applying the higher resolution of ENDOR two separate trigonal patterns were observed close to and symmetric with respect to the Zeeman frequency of the hydrogen nucleus. The result for the angular dependence of ENDOR frequencies is given in Fig. 2(a). Locking on these frequencies and scanning the magnetic field the ENDOR signal revealed the underlying EPR spectra. With this so-called field-scanned ENDOR (FSE) method the two components of the EPR spectrum, as also indicated in Fig. 1(a), were separated. Both spectra also have the $\langle 111 \rangle$ axial symmetry in their fine structure, again with a somewhat different degree of anisotropy. The corresponding g-tensor values are summarized in Table I. The observed EPR pattern indicated splitting into two components being consistent with the hyperfine interaction with a 100% abundant nucleus with nuclear spin $I=1/2$. The involvement of a single hydrogen atom in each of the newly reported centres was further confirmed by EPR and ENDOR measurements on samples doped with deuterium. As expected, due to the higher nuclear spin and lower g_N value, the hyperfine structure could not be resolved for these samples in the EPR. Figures 1(b) and 2(b) illustrate the deuterium results.

In order to conclusively establish the participation of sulphur in the Si-NL54 and Si-NL55 centres samples doped with isotopically enriched sulphur (25% ³³S, $I=3/2$) were prepared. The EPR spectra recorded for these samples displayed a clearly resolved hyperfine interaction

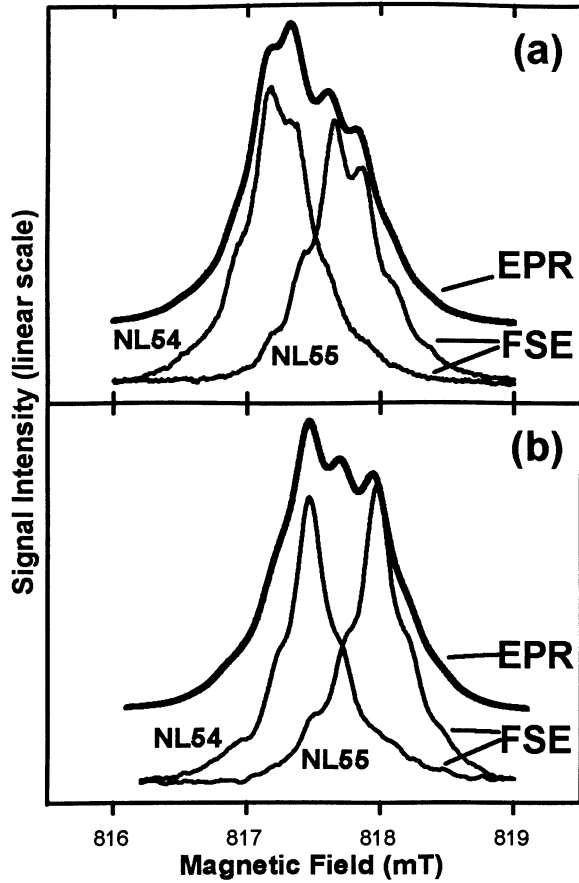


Figure 1. The EPR and FSE spectra of Si-NL54 and Si-NL55 centres for magnetic field B parallel $\langle 100 \rangle$, recorded at a temperature $T=9$ K. (a) Spectra of the sample diffused with hydrogen and natural sulphur, microwave frequency $\nu=22.8809$ GHz. (b) Spectra of the sample diffused with deuterium and natural sulphur, $\nu=22.8851$ GHz.

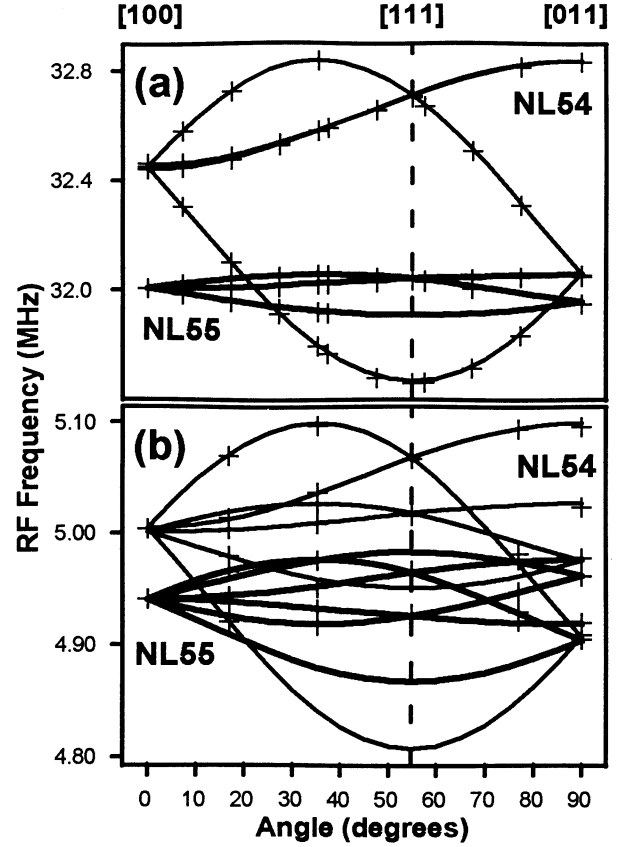


Figure 2. (a) Angular dependence of the hydrogen-ENDOR spectra of Si-NL54 and Si-NL55 observed in the sample diffused with hydrogen and natural sulphur, and (b) the similar result for a deuterium diffused sample. + symbols represent the experimental data; solid lines correspond to a simulation with the spin-Hamiltonian parameters as given in Table I.

with one sulphur nucleus. The fact that identical centres were generated regardless of the isotopic composition of sulphur could be fully confirmed by hydrogen ENDOR which was found to be identical in both cases. The EPR- and FSE-recorded spectra are compared in Fig. 3. They could be fitted with the spin-Hamiltonian

$$\mathcal{H}_S = \mu_B \mathbf{B} \cdot \mathbf{g} \cdot \mathbf{S} - g_N \mu_N \mathbf{B} \cdot \mathbf{I} + \mathbf{S} \cdot \mathbf{A} \cdot \mathbf{I} + \mathbf{I} \cdot \mathbf{Q} \cdot \mathbf{I},$$

where \mathbf{A} and \mathbf{Q} represent the hyperfine and the quadrupole interactions with the sulphur nucleus, and the electron spin is $S=1/2$. The values of the tensors resulting from fitting are included in Table I.

Based on the above presented experimental data the Si-NL54 and Si-NL55 centres are identified as two configurations of sulphur–hydrogen pairs, i.e., a substitutional sulphur double donor passivated by one hydrogen atom. Consistent with the $S=1/2$ spin value the spectra are assigned to the neutral charge state of such complexes. For the sulphur atom in the complex the substitutional position of the isolated sulphur donor is assumed. Following the trigonal symmetry of the centre the position of the hydrogen atom has to be along a $\langle 111 \rangle$ direction with respect to sulphur. This leaves three possibilities: bond-centred (BC), and two antibonding (AB) sites on S and nearest-neighbour Si, respectively. We note here that our results do not support the conclusions of Yapsir *et al.* [5] who predicted a distorted BC site for hydrogen in the S–H complex. On the other hand they are certainly consistent with the first-order kinetics of sulphur donor passivation, as concluded from the DLTS studies [4].

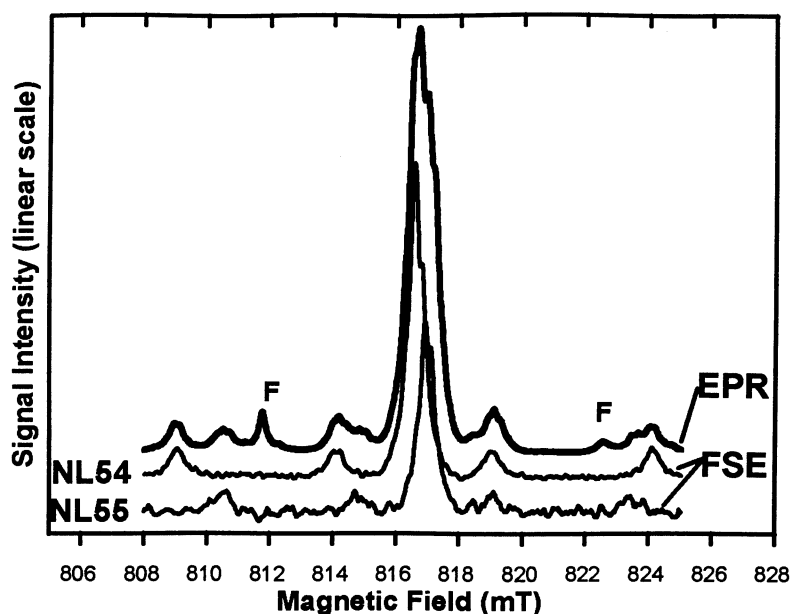


Figure 3. The EPR and FSE spectra of Si-NL54 and Si-NL55 centres for magnetic field B parallel to $\langle 100 \rangle$ in the sample diffused with hydrogen and isotopically enriched sulphur. To each central line ($I=0$) belongs a four-fold spectrum ($I=3/2$) showing the involvement of a single ^{33}S nucleus (the lines labelled F belong to a different spectrum). The spectra were recorded at a microwave frequency of $\nu=22.8637$ GHz and at a temperature of 9 K.

Table I. Spin-Hamiltonian parameters for Si-NL54 and Si-NL55 spectra, as obtained from computer fits of the FSE angular dependencies. Electron spin is $S=1/2$. Hyperfine and quadrupole tensor parameters correspond to interactions with the ^{33}S sulphur nucleus.

	Si-NL54		Si-NL55		unit
g_{\parallel}	1.99886	$\pm 4 \times 10^{-5}$	1.99823	$\pm 4 \times 10^{-5}$	
g_{\perp}	2.00126	$\pm 4 \times 10^{-5}$	1.99974	$\pm 4 \times 10^{-5}$	
A_{\parallel}	143.1	± 2.7	124.0	± 2.6	MHz
A_{\perp}	137.7	± 2.7	117.9	± 2.6	MHz
Q_{\parallel}	6.6	± 2.7	5.0	± 2.6	MHz
Q_{\perp}	-3.3	± 2.7	-2.5	± 2.6	MHz

3. Passivation of thermal donors

Thermal donors (TD's) are among the most complicated defect centres in silicon; an undisputed model for their microscopic structure is still missing. Among many other experimental techniques also magnetic resonance spectroscopy has been used to study these centres. As a result two EPR spectra, Si-NL8 and Si-NL10, both of orthorhombic-I symmetry are now associated with the TD's. One of them, Si-NL8, has been identified as a singly ionized state TD^+ ; the identification of the second one still poses a problem, although some suggestions have been put forward [8]. Soon after the passivating effect of hydrogen was discovered also passivation of TD's has been reported [9]. The passivation degree was found to be around 70% which is somewhat less than for shallow acceptors but much more than for shallow donors. It has been concluded that both electrical levels of the TD's are passivated, but the actual number of H atoms taking part in the process, one or two, was not established. In the same study some effort has been made in order to relate the hydrogenation mechanism to the microscopic structure of thermal donors; it has been suggested that the earlier TD's, which are generally believed to have a more simple structure, were more readily passivated.

In a sample with a strong Si-NL10 signal but otherwise not intentionally doped with hydrogen new ENDOR lines were indeed detected [10]. The spectrum appeared to be symmetric with respect to the Zeeman frequency of a free proton. By recording the ENDOR spectra for different resonance field values and monitoring the frequency shift the value of the proportionality constant was found to be 42.61 MHz/T, equal, within experimental accuracy, to the nuclear Zeeman frequency of a proton. This result, illustrated in Fig. 4(b),

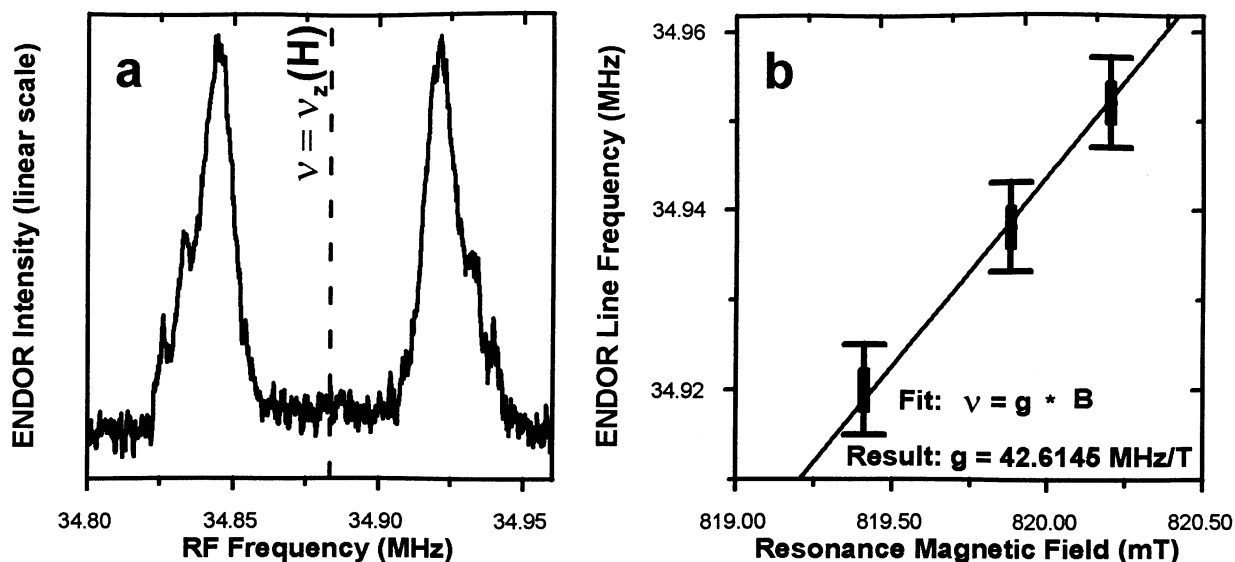


Figure 4. The hydrogen ENDOR spectrum observed in Cz-Si:Al sample after 470 °C, 55 hours heat treatment. (a) Spectrum recorded with B parallel $\langle 110 \rangle$ direction, $B = 819.324 \text{ mT}$. (b) displacement of the ENDOR line as a function of the magnetic field shift fitted with linear function.

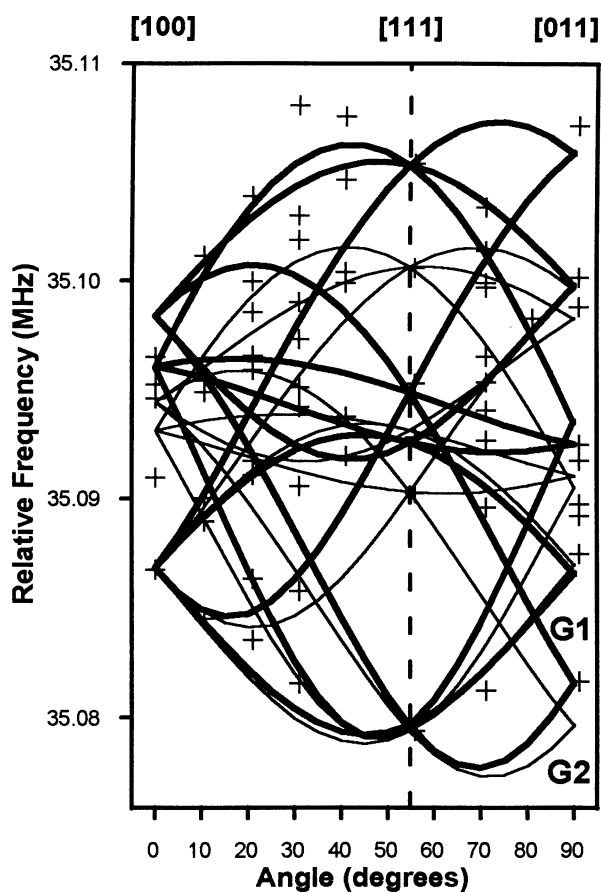


Figure 5. Angular dependence of the hydrogen ENDOR spectra observed for a Cz-Si:P sample after 470 °C heat treatment for 64 hours. + symbols represent experimental points, bold and thin lines represent simulations for two different tensors, G1 and G2, corresponding to individual Si-NL10 species.

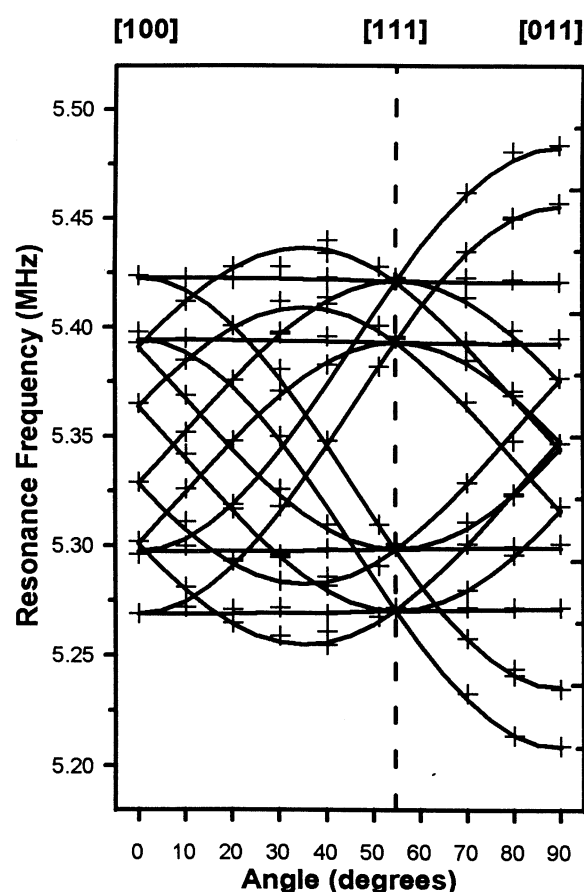


Figure 6. Angular dependence of the deuterium ENDOR line positions observed on the Si-NL10 spectrum in a Cz-Si:In sample, treated 0.5 hour at 1250 °C in a D_2O atmosphere and annealed 42 hours at 470 °C. + symbols represent experimental data points; solid lines are from computer simulation by one tensor of orthorhombic symmetry.

identifies hydrogen as responsible for the detected hyperfine interaction. Having established that, a series of samples was intentionally doped with hydrogen. These samples were prepared from commercially available high-grade Czochralski silicon. Hydrogen was introduced by sealing a sample in a quartz ampoule with a few milligrams of water and exposing it to a short high-temperature heat treatment (1250 °C, 0.5 hours) followed by a quench to room temperature. Subsequently, a TD generation heat treatment at 470 °C was performed. In all thus prepared samples a hydrogen ENDOR spectrum similar to that depicted in Fig. 4(a) was observed. Once recognized, traces of the same spectrum could also be detected in nearly all the samples which did not undergo the hydrogen diffusion. This result confirms the wide-spread hydrogen contamination of commercially available high-grade silicon crystals.

The hydrogen ENDOR spectrum was found to be a superposition of independent tensors. By the FSE technique it could be shown that each of them was related to a different Si-NL10 species. In this way the multispecies character of the Si-NL10 centres, established before on the basis of the oxygen and aluminium ENDOR studies [11], has been confirmed. The angular dependence of the hydrogen ENDOR was studied in a hydrogen-doped Cz-Si:P sample; results are presented in Fig. 5. Preliminary analysis revealed in this case the presence of two similar hyperfine tensors, labelled G1 and G2, which could be assigned to two different Si-NL10 species. The symmetry of both tensors was established as triclinic. The hyperfine interaction was found to be very small explaining that its presence could not be noticed in an EPR experiment. The spin localization on the hydrogen nucleus, estimated at $\approx 0.006\%$ in the framework of an LCAO analysis, is minute. A similar experiment was performed after deuterium diffusion. The angular dependence of ENDOR frequencies as illustrated in Fig. 6 is rather different for the deuterons compared to the protons. In the case of deuterons, with nuclear spin $I=1$, the quadrupole interaction dominates the angular variation.

The current findings allow us to propose a microscopic identification of the Si-NL10 centre as a neutral charge state of a singly passivated thermal donor. Such an identification is consistent with the characteristic features of the Si-NL10 structure and its similarities with the Si-NL8 [8]. At the same time it accounts for the more shallow character with respect to Si-NL8.

4. Conclusions

We have observed that high-temperature heat treatment in water vapour of monocrystalline silicon samples leads to an effective passivation of double donors present as bulk impurities in the samples. The passivation process involves the formation of double-donor–hydrogen pairs which have single donor character and are paramagnetic in their neutral charge state. Two examples of such complexes, S–H and TD–H pairs, were detected and studied by magnetic resonance spectroscopy (EPR, ENDOR and FSE). We note that both complexes must differ significantly in the detailed bonding configuration of hydrogen. This is evidenced by the structural information and is supported by different formation/dissociation characteristics. Theoretical models providing full explanation of the presented experimental results are still to be developed.

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