MAGNETIC RESONANCE INVESTIGATIONS OF THERMAL DONORS IN SILICON

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Abstract

Heat treatment of oxygen-rich silicon in the temperature range 450-500°C for times ranging from minutes to several hundreds of hours produces centers with donor activity. By the method of electron paramagnetic resonance (EPR) two prominent spectra, labelled Si-NL8 and Si-NL10, respectively, were observed and were associated to paramagnetic states of these centers. On the basis of angular dependent resonance patterns the centers were described with g tensors of orthorhombic-I symmetry. Introducing the ^{17}O oxygen isotope and applying electron nuclear double resonance (ENDOR) the presence of oxygen atoms in both centers was established; the oxygen atoms are located on one of the mirror planes of the 2mm symmetry group. From ENDOR on the ligand ^{29}Si nuclei the wave function describing the electron with unpaired spin was found to be quite extended; this is consistent with a shallow character of the donor state. Both centers appear to exist in a large number of configurations, up to 17 have been reported, the versions with smaller binding energy and more isotropic g tensor developing upon increase of the heat-treatment time. These very similar, but yet distinct, configurations are not resolved in EPR at standard frequencies, only a continuous shift of the overall g tensor parameters is observed. For the spectrum Si-NL8 the model of a singly ionized shallow double oxygen-related donor is generally accepted; contrary to this, the situation with spectrum Si-NL10 remained more puzzling. The two main difficulties are, first, the existence of two different families of heat-treatment centers with very similar properties and, secondly, the observation of distinct ^{27}Al ENDOR interactions in the Si-NL10 spectrum together with the observation of Si-NL10 centers in silicon with definitely no aluminum present. Recently, a prominent role of hydrogen in the formation of Si-NL10 centers has been discovered. Hydrogen hyperfine interactions were detected by ENDOR and further studied by field-scanned ENDOR. In deuterium-doped material the quadrupole interaction of the local electric field gradient with the deuteron was measured. The direction of the hydrogen

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bond was found to be parallel to the <011> crystalline axis perpendicular to the oxygen-containing plane of the thermal donor. It also appeared that the true symmetry of this center is triclinic, i.e., lower than the orthorhombic symmetry as resolved in the EPR. On this basis an identification of the Si-NL10 center as a singly hydrogen-passivated thermal donor in its neutral charge state is proposed. It appears necessary to distinguish between aluminum-containing centers, Si-NL10(Al), and hydrogen-containing ones, Si-NL10(H). Infrared absorption spectra as reported in the literature, and related to so-called shallow thermal donors (STD's), are probably due to these Si-NL10 centers.

1. Introduction

Thermal donors (TD's) are heat-treatment centers of a shallow double donor character. These centers are generated in oxygen-rich silicon upon annealing in the 400-500°C temperature range and are most probably related to an oxygen aggregation process. For a recent review see [1]. Also for germanium formation of thermal donors has been observed [2]. While the effect of TD formation was reported already four decades ago the issue still lacks comprehensive understanding and constitutes perhaps the most fascinating subject in the physics of defect centers in silicon. The interest in TD's stems from the fundamental side and is closely related to such phenomena as aggregation and impurity reactions. However, it has at the same time also a considerable applied science component, since TD's can be generated in high concentration and therefore fully determine the electrical character of the material.

The most important features of TD's established so far include:

⋆ The electrical character of a TD is that of an effective mass theory (EMT) double donor, with the first ionization level at approx. 70 meV, and the second one at approx. 150 meV below the bottom of the conduction band.
⋆ The generation kinetics and the maximum concentration of TD's are related to the initial interstitial oxygen concentration available in the material.
⋆ TD's constitute a family of up to 17 species which develop subsequently upon heat treatment, with the more shallow species being generated later.
⋆ The overall symmetry of the TD is orthorhombic-I (C_{2v}).
⋆ Short heat-treatment at a higher temperature (T> 600°C) destroys the electrical activity of TD's. This effect is accompanied by a coincident increase of interstitial oxygen concentration.
⋆ Some other impurities - carbon, hydrogen and aluminum - were found to influence the TD generation process.

At the same time several questions remain open and clearly require further studies. The most prominent of these are:

⋆ The microscopic structure of the TD core and the origin of its double donor activity.
⋆ The growth mechanism and the related question of structural differences between different TD species.

⋆ The mechanism responsible for loss of electrical activity and (partial?) dissociation of the TD center.

By inspection of the above given list of unsolved problems related to TD's one concludes that whereas the general properties of these centers are well studied and, for the major part, understood, the microscopic picture is nearly completely missing. This is best illustrated by the fact that, in spite of intensive investigations, the theoretical model accounting for all the properties of TD's has yet to be developed.

In the studies of defects magnetic resonance has been frequently applied in view of its unique ability to provide information on a microscopic scale. As a result the majority of structural models of defect centers are based on data from magnetic resonance spectroscopy. In this paper we will review the results of EPR and ENDOR studies of TD's.

2. Electron paramagnetic resonance results

Among many other experimental techniques also EPR has been employed to investigate TD's. In an early study [3] several so-called *heat-treatment centers* have been reported in Czochralski-grown silicon annealed for various periods of time at a temperature of 450°C. In a later report [4] the actual number of these centers has been reduced to two - Si-NL8 and Si-NL10 and these were studied in a considerable detail. Both spectra are illustrated in Fig.1 for the three main crystallographic directions in the silicon lattice.

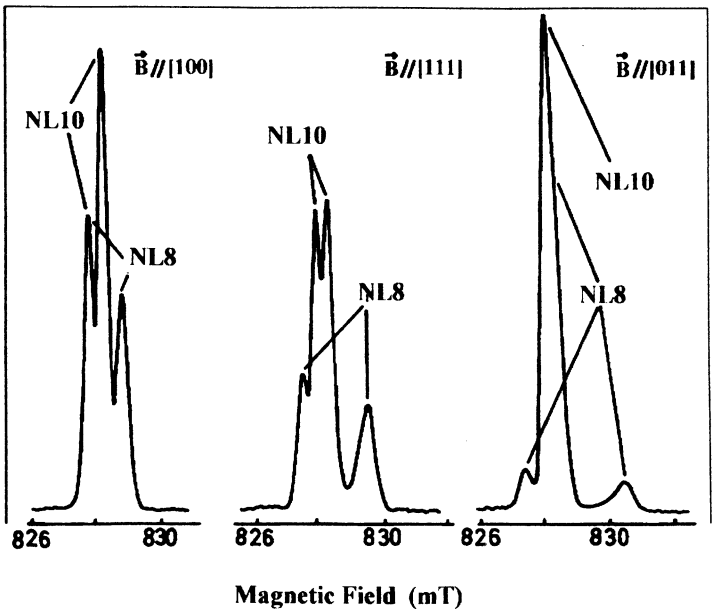

Figure 1. The TD-related EPR spectra Si-NL8 and Si-NL10 as measured in three main directions for the K microwave band of approx. 23 GHz.

Both spectra have spin S=$\frac{1}{2}$ and were found to be generated in oxygen-rich silicon. For p-type material the formation of Si-NL8 was practically independent of the particular acceptor (B, Al, Ga, In); formation of Si-NL10 was clearly enhanced by the presence of aluminum. Upon short annealing first the Si-NL8 center could be detected; its intensity increased with prolonged heat-treatment, reached a maximum and then decayed. The Si-NL10 spectrum appeared only for longer annealing; it could be observed also earlier but upon white-light illumination of the sample. It has been found that whenever the Si-NL8 spectrum has been detected then also the Si-NL10 would appear upon longer annealing. In n-type material [5] only Si-NL10 center could be observed.

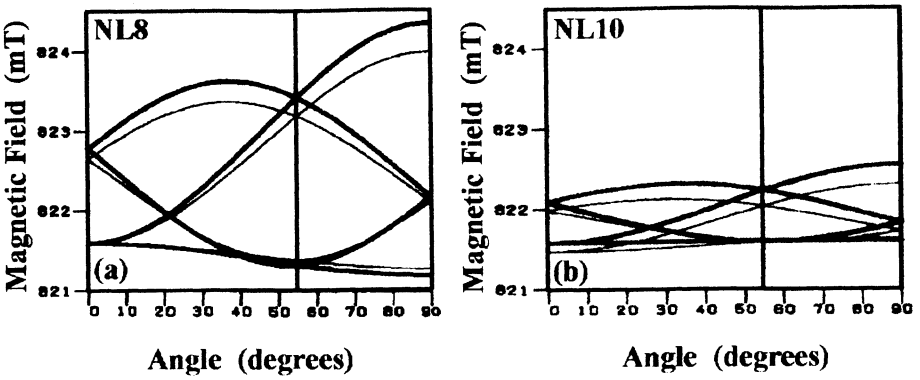

Figure 2. The angular dependence for the Si-NL8 (a) and Si-NL10 (b) EPR spectra. Thick and thin lines correspond to the annealing times of 10 and 100 hrs, respectively.

The angular dependence of both spectra as measured in the K microwave band is depicted in Fig.2. As can be concluded, both spectra are of the orthorhombic-I symmetry whose elements in the silicon lattice include 2 (perpendicular) mirror planes ((011)) and a twofold axis (<100>). The values of the g-tensors are in a close vicinity of 2 and their anisotropy is small. According to the general defects classification by Corbett and Sieverts [6], these characteristic features put both centers in the category of shallow donors. One notes further that the anisotropy of the Si-NL10 spectrum is clearly smaller than that of the Si-NL8. According to the earlier mentioned classification this indicates that the ionization energy of Si-NL10 center should be smaller than that of Si-NL8.

The observation of two TD-related EPR spectra, both with spin S=$\frac{1}{2}$, presented a problem for an interpretation. In general, a double donor DD can be paramagnetic in its singly ionized charge state DD^+, with S=$\frac{1}{2}$. Also the zero charge state DD^0 can be paramagnetic with S=1. However, in the latter case the paramagnetic state has usually higher energy than the S=0 state. Following the uniaxial stress measurements [7] the Si-NL8 spectrum has been identified with the singly ionized thermal donor TD^+. The particular identification of the other TD-related EPR spectrum - Si-NL10 - is still debated upon and several possibilities have been considered [8].

Fig.2 illustrates yet another characteristic feature of both TD-related EPR spectra. As can be seen the g-values of the spectra are not uniquely defined and change upon prolongation of the heat treatment; the longer the annealing the more isotropic the g-tensor becomes. This characteristic g-shifting effect is very unusual among defect centers in semiconductors. Its occurrence for TD-related spectra is illustrative of the multispecies character of TD's and is an EPR equivalent of the effect observed also in the IR absorption, where a somewhat different TD spectrum is found depending on the annealing stage. The g-shifting effect carries then the information about the TD transformation process and has been investigated further. It has been established that not all the components of the g-tensor were undergoing the transformation; the change was most pronounced for the off-diagonal g_{xy} element whose value is directly related to the splitting ΔT between the two spectral components as measured for the <111> orientation of the magnetic field. Fig.3 illustrates the evolution of the ΔT splitting with the annealing time for the Si-NL8 and Si-NL10 spectra.

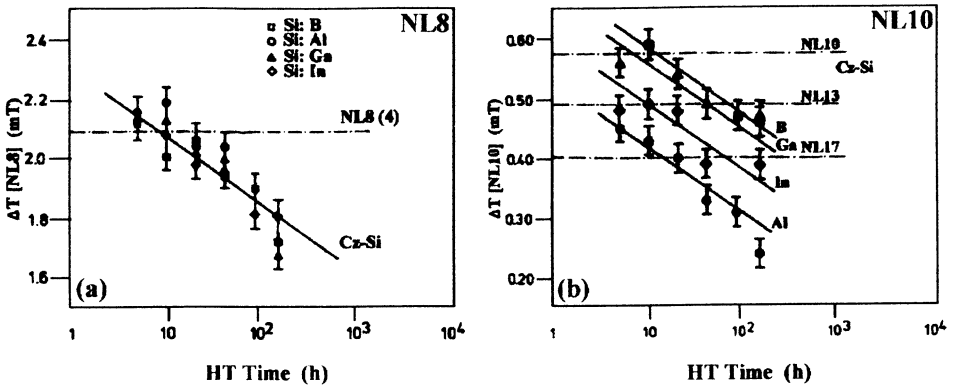

Figure 3. The annealing time dependence of the spectral splitting ΔT, as measured for the magnetic field **B** ||<111>, for (**a**) the Si-NL8, and (**b**) the Si-NL10 EPR spectra.

For the Si-NL8 center the g-shifting effect was found to be independent of the dopant. For the Si-NL10 such an influence can be concluded from the figure; the most isotropic spectra are observed for an aluminum-doped material. If we assume that the degree of anisotropy is related to the ionization energy of a given center then we conclude that in Al-doped silicon the most shallow NL10 species are generated. If we assume further that the g-value shift is indicative of the transformation process then we also have to acknowledge that the presence of aluminum has a catalytic effect on this process. The particular role of aluminum in the structure and generation of Si-NL10 centers still remains as one of the more puzzling questions in the EPR studies of TD's. We will come back to it in the next section. Here we only mention that the issue is being additionally complicated by the fact that while a substitutional aluminum in silicon is an acceptor, it becomes a double donor when displaced onto an interstitial site.

The fact that the g-shifting effect illustrates the varying composition of particular species present at a given annealing stage has been directly confirmed in a high-field EPR experiment conducted for a frequency of 350 GHz.

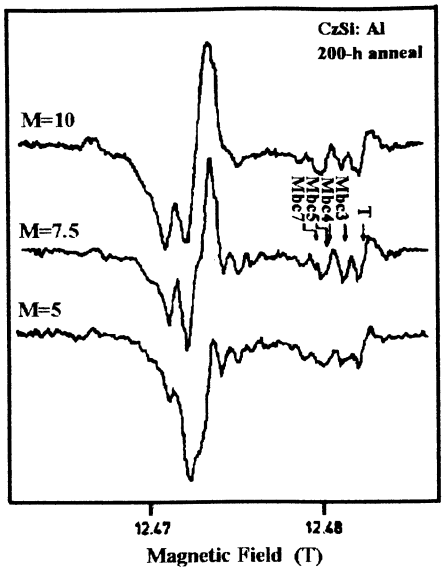

Figure 4. The Si-NL10 spectrum as measured for **B** ||<011> in the high-field EPR experiment - the resonance frequency ν=350 GHz

Fig.4 shows the Si-NL10 spectrum as measured for an Al-doped Cz-Si annealed for 200 hrs at 470°C, with magnetic field along the <011> crystallographic direction. As can be seen, the so-called U6 point of an orthorhombic-I spectrum is now clearly split into at least 5 distinct components indicating the presence of 5 different species of the Si-NL10 center; each one characterized by a somewhat different EPR spectrum. The fact that the species-related splitting is most pronounced for the U6 point relates to the property that the individual g-tensors differ mostly in their off-diagonal element g_{xy}. In view of a rather primitive EPR detection system used in this experiment the sensitivity was relatively low. Therefore the measurements were possible, so far, only for the most intense Si-NL10 spectrum in an aluminum-doped sample annealed for 200 hrs. Experiments for differently doped and annealed materials could directly reveal the influence of these parameters on the generation kinetics of individual Si-NL10 species. These experiments require, however, a more advanced high-field EPR experimental set-up; this became recently available in our laboratory and new results might be expected. Also similar investigations of the Si-NL8 center, disclosing details of the symmetry and generation kinetics of the TD^+, have yet to be performed.

3. Electron nuclear double resonance results

In an ENDOR experiment hyperfine interactions between the electron spin responsible for the paramagnetism of a given center and nuclear momenta at atomic sites accessible to the spin density are probed. In this way the so-called *spin mapping* can be realized, where the spin density on sites within the center and also in a more or less direct vicinity of the defect core can be determined. For a center with an extended spin localization hyperfine interactions with several shells of neighboring atoms can usually be detected. It is customary to distinguish between the self- and ligand ENDOR; the first case concerns the interactions with the nuclear spin of an atom (or atoms, for an extended defect) which forms the paramagnetic core of the center. The second case concerns the interactions with the crystal surrounding the defect core. From ENDOR an experiment details of the electronic and atomic structure of a defect are unraveled. The ENDOR ability to deliver microscopic information is usually superior to that provided by other experimental techniques commonly used in defect studies, such as IR absorption, photoluminescence and DLTS spectroscopy. Based on the analysis of ENDOR data reliable microscopic models of many defect centers were proposed.

The power of ENDOR spectroscopy has also been applied to the studies of TD's. Unfortunately in this case the high resolution of this technique results in a low intensity of signals, as the spectra related to different TD species do not overlap and are detected separately. Consequently high concentrations of TD's are required. This effectively low sensitivity seriously hampers ENDOR studies of TD's and lowers credibility of obtained results and conclusions which are based on them. In what follows results of ENDOR investigations concerning hyperfine interactions with different magnetic nuclei are presented.

3.1 SILICON ENDOR

An observation of ^{29}Si ENDOR is (nearly) always possible for defects in silicon. This follows from a relatively high natural abundance of this magnetic isotope of approx.5%. Based on the results of ^{29}Si ENDOR one can conclude about the extension of the spin localization within the crystal rather than about the core of the center. By summing up the spin localizations determined for individual neighboring atom shells the total electron localization may be found revealing information pertinent to the general character of the electronic structure of the defect: deep $\leftrightarrow$ shallow, isotropic $\leftrightarrow$ anisotropic.

The ^{29}Si ENDOR experiments have been conducted for both TD-related EPR centers [9,10]. The results can be summarized as follows:

$\star$ spin wave function character: In the LCAO (linear combination of atomic orbitals) analysis the spin wave function on an atomic site is approximated by locally available electron orbitals. For the standard sp^3 hybridization the ratio of $s-$ to $p-$orbital localizations α^2/β^2 is 1/3. For the investigated centers $\alpha^2/\beta^2 \approx 3$ was found indicating a preferred electron localization in spherically symmetric s-orbitals. In this aspect both centers resemble shallow EMT donors.

$\star$ spin localization: The total localization η^2 of the electron responsible for the S=$\frac{1}{2}$ para-

magnetism was found to be approx. 5.5% and 0.5% for Si-NL8 and Si-NL10, respectively. This is very small, even when compared to a classical example of a shallow donor such as a substitutional phosphorus atom, for which the total localization of $\eta^2 \approx 15\%$ is measured. Such a low η^2 value indicates a very delocalized character of both centers for which the commonly applied approach of LCAO analysis fails. Since η^2 for Si-NL10 is clearly smaller than for Si-NL8, we assume that this defect is also more shallow. In this way the ENDOR experiment confirms our earlier conclusion based on the comparison of g-value anisotropy for both centers.

We note that the fact that the spin wave function is so delocalized and yet the g-tensors of both centers show measurable anisotropy is very unusual and presents a considerable challenge to any theoretical model attempting to describe the electronic structure of the TD. It is also worth pointing out that the ^{29}Si ENDOR experiments failed to unravel a single Si atom with a prominent spin localization; this result strongly disfavors numerous TD core models where the donor activity originates from a silicon interstitial atom.

3.2 OXYGEN ENDOR

As has been mentioned before, the formation process of TD's has always been related to clustering of oxygen. In EPR the presence of a particular nucleus in the structure of a center manifest itself by a hyperfine interaction, which leads to a characteristic splitting of the spectrum. However, in silicon intentionally doped with the magnetic ^{17}O isotope of oxygen no such splitting could be observed neither for Si-NL8 nor for Si-NL10 spectrum. The presence of oxygen atoms in the structure of both centers has been finally concluded from ENDOR experiments; the magnitude of the hyperfine interaction with oxygen nuclei was found much too small to be observable in EPR [11,12].

Before we summarize the information on the structure of both centers as revealed by oxygen ENDOR we start by a short explanation on how such an information can be obtained from ENDOR data. In order to be able to discuss the structure of the centers and to present the symmetry arguments we shall introduce the labelling of various symmetry classes of ENDOR tensors. The symmetry of Si-NL8 and Si-NL10, as derived from EPR, is orthorhombic-I. Such a defect has 6 equivalent orientations in the silicon lattice, labelled *ab, ac, ad, bc, bd,* and *cd* [13]. Fig.5 presents a fragment of the silicon lattice, positions of the defect's two mirror planes and the principal axes of its g-tensor. The symmetry of an ENDOR pattern due to a particular shell of magnetic nuclei is the symmetry of the wave function of the center in conjunction with one of the nuclei in the shell. Clearly, the symmetry of ENDOR is lower or equal to the symmetry of the wave function. For an orthorhombic center one can discriminate between 4 types of positions (see Fig.5): if the nucleus is on the 2-fold symmetry axis of the center (T-position), the symmetry of its ENDOR pattern is orthorhombic; if it is situated in one of the defect's symmetry planes (Mad- and Mbc-positions) the symmetry is monoclinic-I, and, finally, if it is outside both mirror planes (G-position) the symmetry will be triclinic. We note further that the shell of triclinic symmetry (G-type) will contain 4 atoms, of monoclinic symmetry (Mad and Mbc) - 2 atoms in one of the mirror planes, and, finally, the orthorhombic shell will correspond to a single atom on the 2-fold axis of the defect.

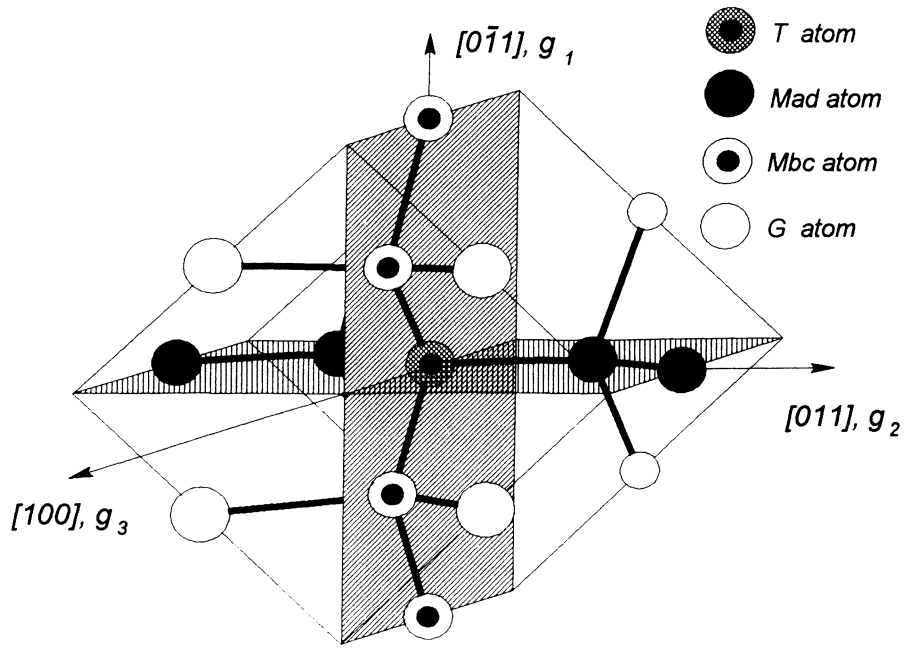

Figure 5. Principal directions of an orthorhombic-I center for *ad* orientation with respect to the silicon lattice. Two mirror planes of the defect are indicated together with atoms at four types of positions which can be distinguished in ENDOR.

Based on the above we can now use ENDOR data to understand the microscopic structure of a defect. Fig.6a shows a computer simulation of the angular dependence of the oxygen ENDOR spectrum as obtained for a single orientation of the Si-NL10 center [14]. As can be seen the pattern is rather symmetric with respect to the Zeeman frequency of ^{17}O uniquely identifying this nucleus as responsible for the hyperfine interaction. The symmetry type is Mbc and following our earlier reasoning we conclude that the relevant atomic shell contains two oxygen atoms in the mirror plane of the defect. In the experiment a series of at least 8 similar tensors have been observed - Fig.6b shows two of these. It is evident that superior resolution is necessary to discriminate between them. All the observed tensors were of the same symmetry type. Such a result indicated that oxygen atoms were always contained within a mirror plane of the same type. By the field stepped ENDOR (FSE) technique, which allows for a direct correlation between NMR and EPR transitions coupled in an ENDOR experiment, it has been shown that the oxygen tensors depicted in Fig.6b corresponded to different Si-NL10 species. In this way the oxygen ENDOR experiment directly confirmed the multispecies character of the Si-NL10 center and explained the occurrence of the g-shifting effect.

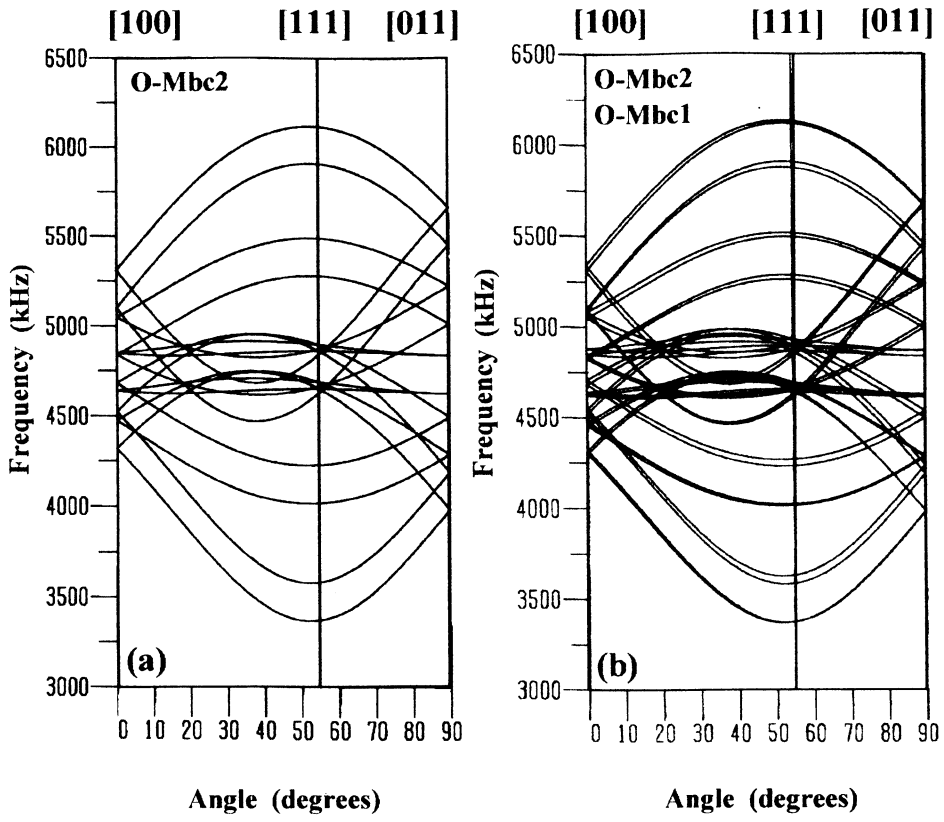

Figure 6. Computer simulation of the angular ENDOR pattern corresponding to a single EPR orientation (*bc*) for (**a**) one tensor (O-Mbc2) and (**b**) two similar tensors (O-Mbc1, O-Mbc2) corresponding to two different Si-NL10 species.

In order to fully analyze the oxygen ENDOR data not only the hyperfine but also the quadrupole interaction had to be taken into consideration. The hyperfine interaction tensor A was found to be nearly isotropic and of small magnitude; in terms of the LCAO analysis is corresponded to a minute spin localization of less than 0.01%. This results shows again an extremely delocalized character of the Si-NL10 center but bears very little information about the particular role of oxygen in the structure of this center. In this aspect the analysis of the quadrupole interaction was more fruitful. The experimentally measured quadrupole tensor could be interpreted as resulting from a superposition of two axial components, corresponding to two identical bonds within the mirror plane. The angle between these bonds was estimated as 155°. Taken together the ^{17}O ENDOR data resulted in a rather unexpected conclusion that the oxygen atom in the Si-NL10 center occupies a position very similar its usual bond site. No evidence for an "oxygen core" of the center, with a prominent spin localization, has been found.

The ^{17}O ENDOR experiment has also been performed for the Si-NL8 center [12]. Also in this case the a series of similar interaction patterns related to different species has been detected. The observed hyperfine interactions were again nearly isotropic but a total spin localization was considerably higher. The quadrupole interaction was found to be identical to that discussed earlier for the Si-NL10. In view of the preceding discussion we conclude that the local structure around oxygen must be identical for both centers. This observation is crucial for their mutual identification. Also for the Si-NL8 center no evidence of an electrically active oxygen core of TD has been found.

We finally note that, regretfully, both studies failed to produce any evidence that the individual species of the Si-NL8 and Si-NL10 centers differ by the actual number of oxygen atoms participating in the cluster. Such a role of oxygen is assumed in a vast majority of the so-far proposed TD models. Consequently, the particular role of oxygen in the formation and transformation of the heat-treatment centers remains unclear.

3.3 ALUMINUM ENDOR

In ENDOR experiments on the Si-NL8 center only hyperfine interactions with silicon and oxygen nuclei were observed. This is in line with the identification of this center as the TD^+ state and the general view that TD's are impurity independent, at least as far as their structure is concerned. In contrast to that, for the other TD-related EPR center Si-NL10, the hyperfine interactions with aluminum and hydrogen were also detected. Fig.7 shows aluminum ENDOR data as obtained for the Si-NL10 center generated in an oxygen-rich Al-doped sample. The observation of Al ENDOR was unexpected and consequently similar investigations were performed for differently doped samples. It has been established that the interactions with ^{27}Al could exclusively be observed in material where aluminum was introduced intentionally. In this way the possibility that the Si-NL10 center could be related to a residual presence of Al contamination has been excluded. Since, as discussed in the preceding section, the Si-NL10 center can be generated in any oxygen-doped silicon, such a conclusion meant that aluminum could be incorporated in the Si-NL10 structure without seriously changing its EPR spectrum. One should note here that the observation of well-defined ENDOR pattern ("characteristic" as opposed to "distant" ENDOR) means that the aluminum atom takes a characteristic position within the structure of the center, and the interaction cannot be viewed as that with Al nuclei randomly dispersed in the silicon crystal. In the latter case only one broad resonance at the nuclear Zeeman frequency of aluminum would have been seen. Following its first observation aluminum ENDOR of the Si-NL10 center has been studied in detail [14].

Similarly to the earlier described oxygen ENDOR also here a series of rather similar tensors has been observed; by the FSE technique each individual tensor was related to a different species of the Si-NL10 center. Fig.7a shows a computer simulation of the prominent ENDOR pattern as observed for a single EPR orientation. The pattern is clearly symmetric with respect to the nuclear Zeeman frequency of ^{27}Al and the symmetry type is orthorhombic-I. This means that this particular Si-NL10 species contains in its structure an aluminum nucleus located on the 2-fold <100> axis of the defect.

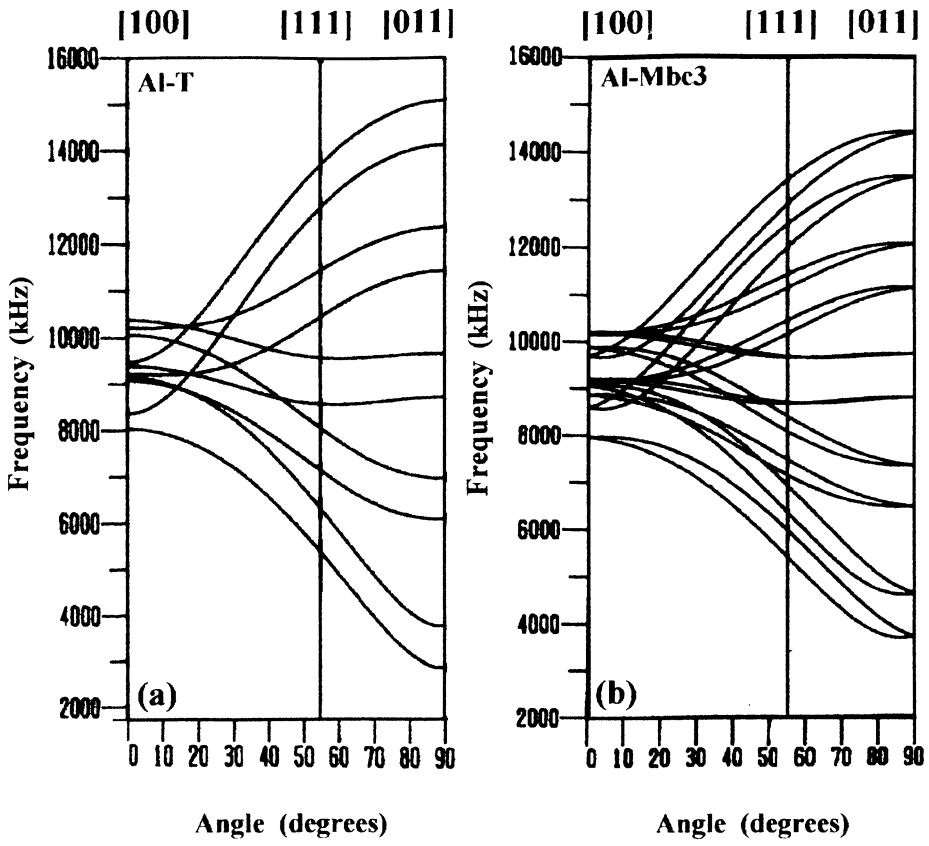

Figure 7. Computer simulation of the angular ENDOR pattern corresponding to a single EPR orientation (*bc*) for two similar tensors (**a**) orthorhombic Al-T and (**b**) monoclinic Al-Mbc3, related to two different Si-NL10 species.

In Fig.7b two Al ENDOR patters corresponding to different Si-NL10 species are shown; it is clear that the second one - Al-Mbc3 - is of the lower monoclinic-I symmetry type. Following the presented reasoning about different ENDOR shells, this means that the Si-NL10 species characterized by the Al-Mbc3 tensor contains two Al atoms located at one of the mirror planes. Such a conclusion stems from the assumed orthorhombic symmetry of the defect as a whole. Indeed the orthorhombic symmetry is concluded from the EPR spectrum. However, it might also be possible that the actual symmetry of the center is lower than that disclosed by EPR, but that the splitting due to the lowering of symmetry is small and therefore hidden within the experimental width of the resonance line. This possibility has been checked experimentally. The idea of the experiment and its outcome are depicted in Fig.8.

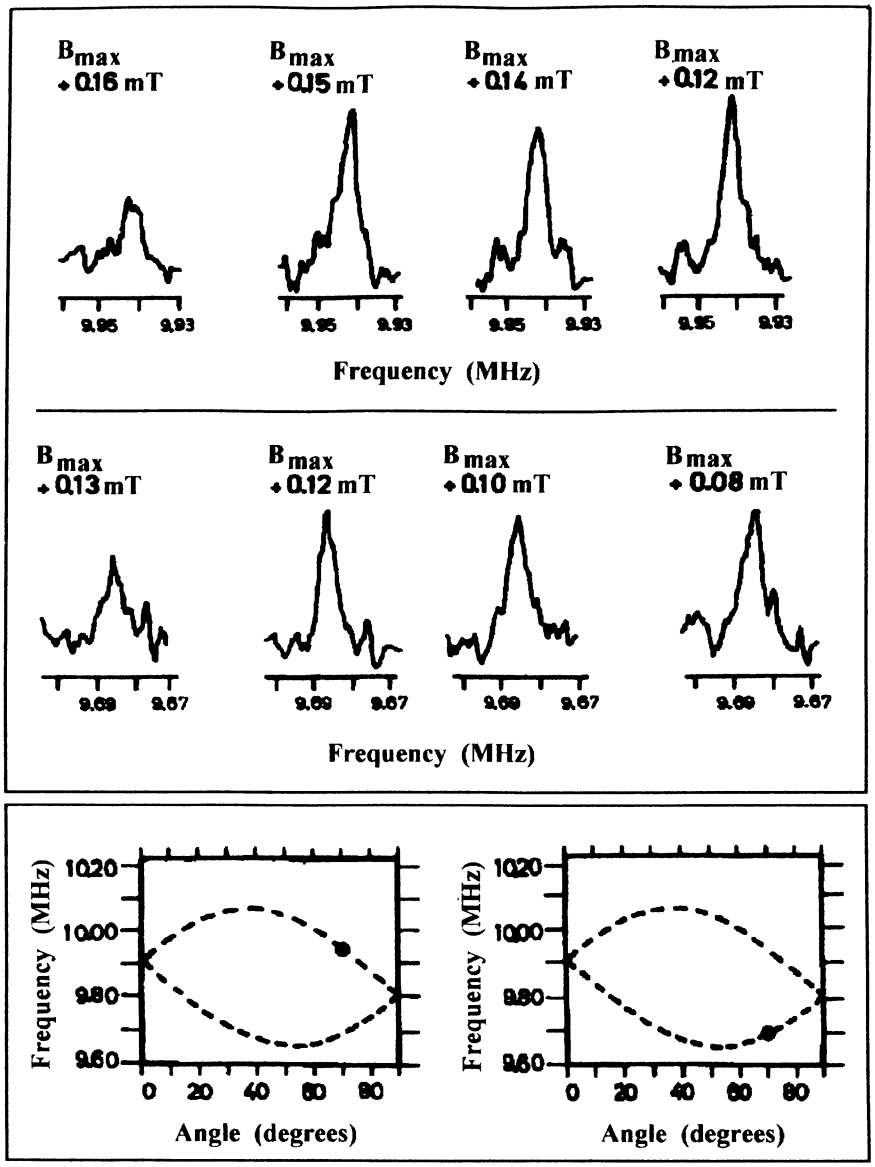

Figure 8. The application of the FSE technique to reveal the true symmetry of a Si-NL10 species related to a particular Al ENDOR tensor of monoclinic symmetry. The intensity of the ENDOR signal for the two resonances of one loop of the Al-Mbc3 tensor corresponding to the same EPR orientation, as indicated in the lower part of the figure, was recorded as a function of the magnetic field, with respect to the center of the EPR line B_{max}.

In the experiment, for one angle, two ENDOR signals belonging to the same loop of the Al-Mbc tensor were chosen, and their intensities were measured as a function of the field. For a truly orthorhombic center both branches of the loop are generated by the same EPR orientation and should attain maximum intensity for the same field value. If, however, the EPR orientation itself is split due to symmetry lowering then the intensity of ENDOR lines will follow the actual position of EPR components and will, in this way, reveal the splitting. In the figure the intensity of ENDOR lines is shown for several different magnetic field values measured with respect to the center of the EPR line B_{max}. As can be concluded from the figure, the ENDOR signals corresponding to different branches reach the maximum for different magnetic field values; this result proves that the real symmetry of the Si-NL10 species related to the Al-Mbc3 is monoclinic. Consequently, this ENDOR shell contains only a single Al atom located in a mirror plane of a monoclinic Si-NL10 defect.

Summarizing the results of the ^{27}Al ENDOR experiment, we conclude that the Si-NL10 center generated in an aluminum-doped material contains in its structure one Al atom. Out of several Si-NL10 species which were analyzed, only one has true orthorhombic symmetry and in this case the aluminum atom is found on the intersection of the two mirror planes; all the other species were monoclinic, with the Al atom in the remaining mirror plane. Spin localizations as found for the Al nuclei were also very small - $\eta^2 \approx 0.1\%$. One should note that this small localization value is nevertheless bigger than that determined earlier for oxygen atom sites.

3.4 HYDROGEN ENDOR

The evidence of the influence of hydrogen on the TD formation process has been accumulating for some time [15]. The effect was being linked to the hydrogen-enhanced oxygen diffusion and no direct participation of hydrogen in the structure of TD was expected. More recently it has been found that hydrogen can easily be introduced into silicon as contamination in a variety of ways including plasma exposure, high-temperature annealing in hydrogen gas or water vapor, and also some common technological operations such as etching and polishing. At the same time several reports appeared on generation of donor centers related to hydrogen. Shallow donor centers have been detected following hydrogen-plasma treatment of neutron irradiated silicon [16]. Also a series of hydrogen-related donors was found in Cz-Si after hydrogenation and heat treatment at 350°C [17].

Being aware of these findings we decided to investigate the possible involvement of hydrogen in the structure of the Si-NL10 center. In a sample with a strong Si-NL10 EPR signal we have indeed detected a new ENDOR spectrum. Due to the fact that the nuclear g-value of a proton differs from that of the other magnetic nuclei, the new ENDOR lines appear in a different frequency region and require very different experimental conditions than the ones used in our previous studies [14]. The observed ENDOR spectrum (see Fig.9a) is symmetrical with respect to the Zeeman frequency of a free proton. By recording ENDOR spectra for different resonance field values and monitoring the frequency shift - as depicted in Fig.9b - we unambiguously identify hydrogen as being responsible for the detected hyperfine interaction.

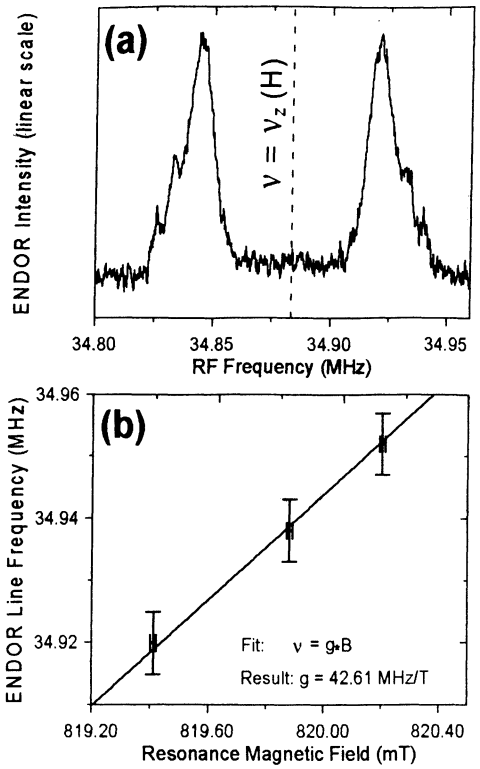

Figure 9. Hydrogen ENDOR spectrum observed in a Cz-Si:Al sample after 470°C/55 hrs heat treatment. (**a**) – spectrum, recorded with **B**||<110> direction, B=819.324 mT; (**b**) – displacement of the ENDOR line as a function of the magnetic field shift, fitted with a linear function. The value of the proportionality coefficient is equal within the experimental accuracy to the nuclear Zeeman frequency of a proton ν(MHz)=42.5758·B(T).

It should be emphasized that hydrogen has *not* been intentionally introduced into this material. In order to further investigate the influence of hydrogen on the formation of Si-NL10 centers, we have prepared a series of samples, intentionally doped with hydrogen. The samples were sealed in quartz ampoules, containing argon atmosphere and a few milligrams of water. Also an identical set of samples without any water in the ampoules has been prepared. All the samples, with or without water, were subjected to a standard procedure of heat treatment at 1250°C, followed by a quench to room temperature. This procedure served to disperse interstitial oxygen to ensure uniform starting conditions and/or to diffuse hydrogen. Subsequent to the quench the samples were annealed at 470°C for various periods of time. In all the samples diffused with hydrogen, an ENDOR spectrum, similar to that depicted in Fig.9a, has been observed. Its traces were also observed in almost all the samples that were not intentionally diffused with hydrogen, confirming the hydrogen contamination of commercially available high-grade silicon [18].

The angular dependence of the hydrogen ENDOR has been studied in hydrogen-doped Cz-Si:P and is shown in Fig.10. While the detailed analysis is difficult in view of a rather broad line width, the data are best fitted with two similar hyperfine tensors of

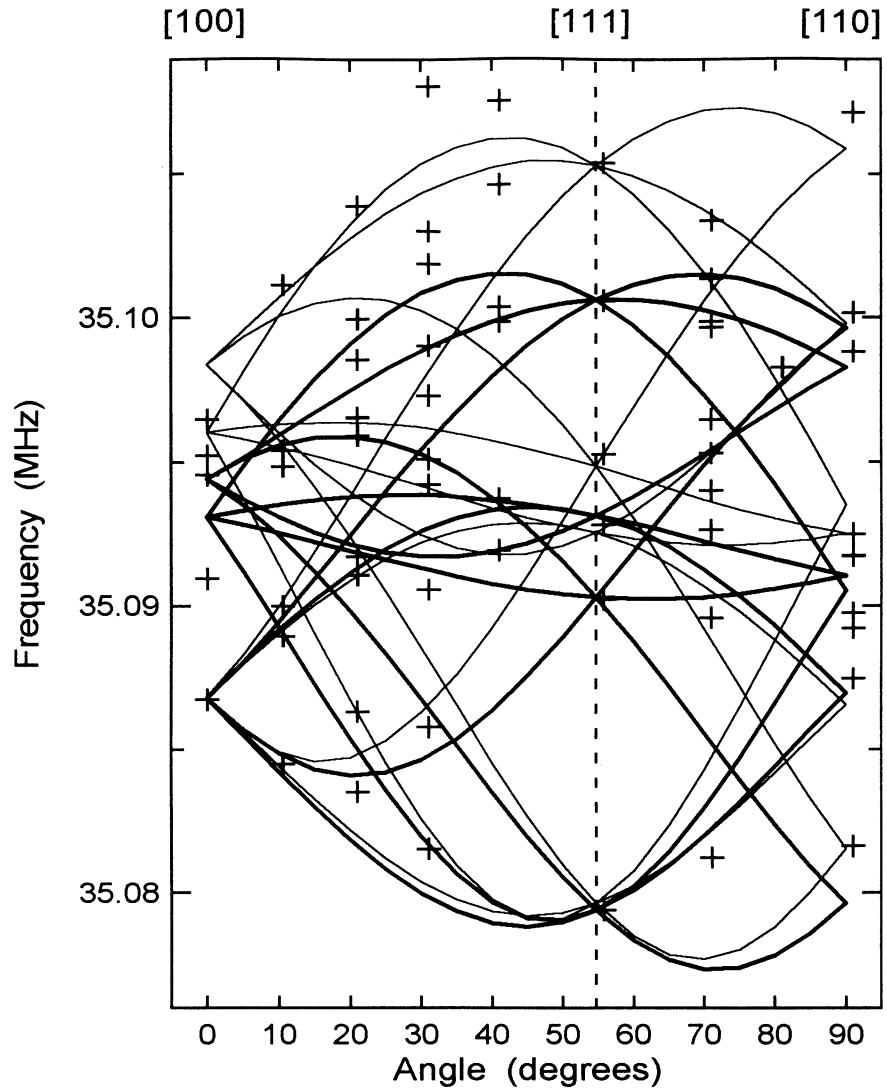

Figure 10. Angular dependence of hydrogen ENDOR as observed for Cz-Si:P sample. Experimental points and a computer fit of two tensors of triclinic symmetry are shown.

a triclinic symmetry. In view of the small value of the hyperfine interaction it is understandable that it cannot be observed in EPR. The isotropic part of the hyperfine tensor is proportional to the localization of the paramagnetic electron on hydrogen. Using the para-

meters of the hydrogen $1s$ wave function, we arrive at the localization $\eta^2 \approx 6 \times 10^{-3}\%$ for both species. Extremely small as it may appear, the value of localization is, nevertheless, comparable to that found for oxygen [14]. That means that hydrogen plays an important role in the Si-NL10 defect structure.

In order to propose a microscopic defect model for the H-containing Si-NL10 center it was essential to establish how many hydrogen atoms are actually involved in its structure. The results of an experiment relevant to this question are shown in Fig.11.

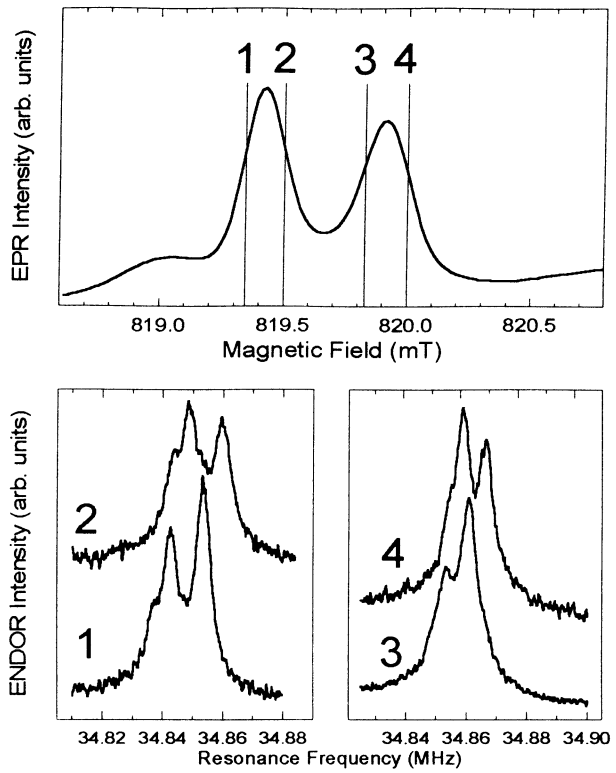

Figure 11. Determination of the true symmetry of the Si-NL10 defect. Top panel – EPR spectrum with **B**||<111> direction. Vertical lines, numbered 1 to 4 indicate the magnetic field values for which ENDOR spectra were recorded. Bottom left and bottom right panels present ENDOR spectra, recorded on low-field and high-field EPR lines, respectively.

From ENDOR data the triclinic symmetry of the hydrogen hyperfine interaction was found, whereas from EPR the g-tensor was concluded to be orthorhombic. Consequently, with the symmetry of the hyperfine interaction with the hydrogen nucleus, forming an essential constituent of the center, lower than the overall symmetry of the defect, this implies that there are more, in this case four, equivalent nuclei in the shell in question. However, in analogy to the earlier discussed case of ^{27}Al ENDOR, in EPR a small lower symmetry distortion of an otherwise almost orthorhombic tensor can be missed due to insufficient resolution of this technique. Following the detection of hydrogen ENDOR we have used

field-stepped ENDOR to determine the actual symmetry of the Si-NL10(H) center. Suppose, two ENDOR peaks correspond to two unresolved EPR lines with slightly different positions of maximum intensity. In this case if the resonance magnetic field is shifted towards the maximum of one of these lines, the relative intensity of the ENDOR peak associated with it will increase. If, on the other hand, both ENDOR peaks are due to the same EPR line, their relative intensities are independent from the position of the magnetic field and reach their maximum simultaneously, i.e., at the position of the EPR line maximum intensity. The FSE measurements were carried out for magnetic field $\mathbf{B}||<111>$. The orthorhombic EPR spectrum consists in this direction of two lines, each of them giving rise to two ENDOR peaks. Changes of the relative intensities of the peaks in the ENDOR spectra upon shifting of the magnetic field were observed for both EPR lines as illustrated by Fig.11. We conclude that the symmetry of the Si-NL10(H) center is, in fact, triclinic and each defect contains only one hydrogen atom.

The triclinic symmetry of the Si-NL10(H) center appears to be different from that determined for the Si-NL10(Al) defect in the preceding subsection. In order to investigate that we have performed FSE studies of Si-NL10 in a hydrogen-diffused Cz-Si:Al sample. The results of this experiment are shown in Fig.12. In this sample ENDOR lines due to hydrogen (Fig.12a) and aluminum (Fig.12b) were detected – see the upper-right corner inserts in both figures. By the FSE technique we could then find the EPR "images" of centers responsible for these lines of different origin. As can be concluded from Fig.12a the hydrogen-containing EPR species have a higher anisotropy of the g-tensor than that of the total EPR spectrum. This means that not all the Si-NL10 defects in aluminum-doped material are hydrogen-containing. In the same sample ^{27}Al FSE revealed the species with lower anisotropy (see Fig.12b).

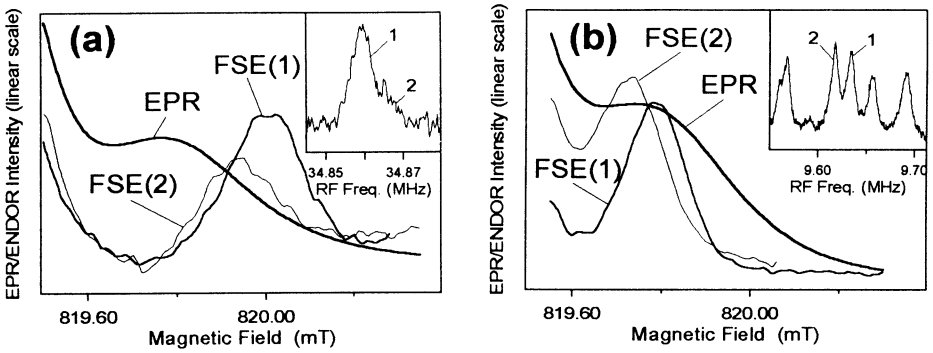

Figure 12. Hydrogen (**a**) and aluminum (**b**) FSE spectra in a Cz-Si:Al sample after hydrogen diffusion and 470°C/55 hrs heat treatment, compared to the EPR spectrum. On the inserts fragments of the respective ENDOR spectra are shown, lines indicated 1 and 2 were used to make FSE scans. T=7 K, ν=22.923 GHz, $\mathbf{B}||<110>$.

The detection of the hydrogen ENDOR brought again forward the puzzling question of the microscopic identification of the Si-NL10 center and its particular relation to TD's.

As mentioned in the introduction the identification of this center is an issue of a considerable dispute. The detection of the hydrogen ENDOR added here an important clue to the earlier revealed features of Si-NL10 which included: i) the center is closely related to TD's, ii) it is created subsequently to Si-NL8, iii) its oxygen structure is identical to that of Si-NL8, iv) the electron spin value is $S = 1/2$, and v) the wave function of the Si-NL10 paramagnetic electron has a more shallow character than that of Si-NL8.

Consistent with the above-listed features and in the light of the new finding the identification of the Si-NL10 center as a neutral thermal double donor with one of its two electrons passivated by hydrogen has been put forward. Following this model Si-NL8 and Si-NL10 would have an identical oxygen core, determining their symmetry and hyperfine interactions with the ^{17}O nucleus. However, the fact that one of the TD electrons is passivated, and not lost to the conduction band, would mean that the remaining electron is weaker bound than in the case of the $(TD)^+$ state that gives rise to the Si-NL8 spectrum.

To follow on our hypothetical identification we have studied the influence of hydrogen on the formation of both Si-NL8 and Si-NL10 spectra. In this case we used B-doped material, where the process of Si-NL10 formation is known to be rather slow [4]. The intensities of the Si-NL8 and Si-NL10 spectra in hydrogen-diffused and hydrogen-free Cz-Si:B samples were studied for various annealing times. In the samples diffused with hydrogen, the production of the Si-NL10 spectrum was significantly enhanced, while the formation of Si-NL8 was suppressed. We also could not detect any hydrogen ENDOR on the Si-NL8 spectrum. This brings us to the conclusion that hydrogen is not involved in the Si-NL8 defect formation, consistent with its assignment to $(TD)^+$ and in line with the infrared absorption measurements.

Being a dominant defect in Cz-Si after prolonged heat treatment, a singly passivated TD should manifest itself in a series of infrared-absorption lines due to transitions to the excited states of a shallow single donor. In line with this reasoning experimental evidence has recently been obtained relating the Si-NL10 EPR centers with the IR absorption series of *so-called* shallow thermal donors (STD's) [19].

Finally, we come back to the question of aluminum incorporation in the Si-NL10 center. So far aluminum was the only nucleus having a characteristic hyperfine interaction with the paramagnetic electron of the Si-NL10 defect, apart from silicon and oxygen. Following the current result the roles of aluminum and hydrogen in the defect structure seem, somehow, similar. An aluminum atom can be removed from its substitutional position by a self-interstitial, created during the process of oxygen clustering (Watkins kick-out mechanism [20]). Once made interstitial, aluminum, similar to hydrogen, is a fast diffusant. It would be able to diffuse towards the core of a TD, where it might compensate one of the two TD's electrons. According to the model the Si-NL10 defect must always contain either hydrogen or aluminum, as the presence of a passivating element in the structure is required. Future experiments should confirm this hypothesis. Although the roles played by hydrogen and aluminum in the Si-NL10, i.e., convertion from a double to a single donor, are similar, because of the different chemical nature of these atoms the microscopic structure of Si-NL10(H) and Si-NL10(Al) should also be different. This manifests itself by the small shift of the g-value, as evidenced by the FSE experiments illustrated in Fig.12. Regardless of this difference, the overall EPR symmetry for both centers is determined by their (oxygen) core structure and remains nearly orthorhombic.

While the hyperfine interaction carries information about the spin density within the center, the quadrupole interaction is determined by the electric field gradient. Since for Si-NL10 the spin localization is very low the observed quadrupole interaction is primarily indicative of local arrangements around the magnetic nucleus. To study these the samples were doped with deuterium which has a nuclear spin I=1 and, consequently, a quadrupole moment. If such a nucleus is placed in an inhomogeneous electric field additional energy shifting, detectable in an ENDOR experiment, can occur. In the sample treated in a heavy-water-vapor atmosphere an ENDOR spectrum, symmetrical with respect to the nuclear Zeeman frequency of a deuteron, was observed. This, together with the notion that the spectrum was only found in the samples treated in a D_2O atmosphere, allows us to identify deuterium as being responsible for the observed interaction. For the sake of comparison we prepared a sample containing both hydrogen and deuterium and measured D- and H-ENDOR in this sample. Fig.13 presents the angular dependence of deuterium ENDOR in this sample.

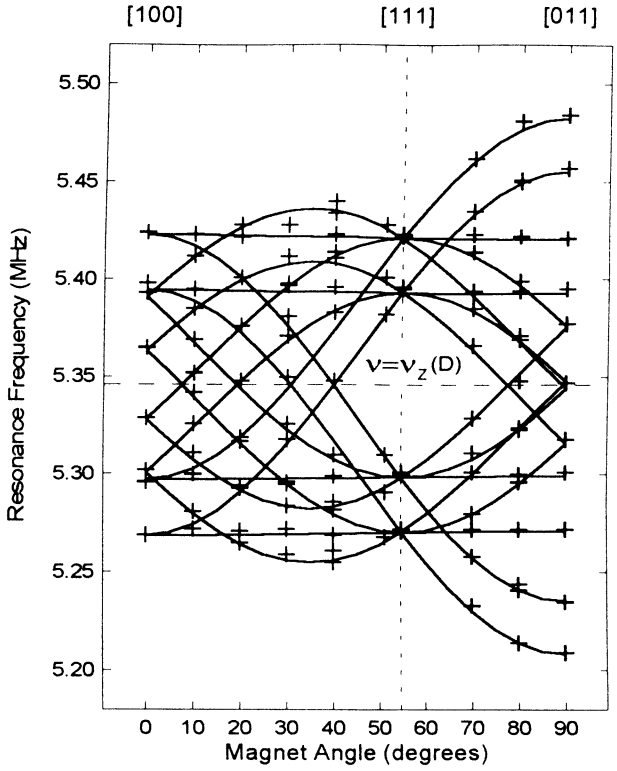

Figure 13. Angular dependence of ENDOR line positions of Si-NL10 in Cz-Si:In sample, treated 1/2 h at 1250°C in D_2O atmosphere and annealed 42 hrs at 470°C. Experimental points and computer fit to the data are shown.

It was fitted with an isotropic hyperfine and an orthorhombic quadrupole term. It should be noted here that since the symmetry of the TD-H center was established to be

triclinic, the symmetry of deuterium hyperfine and quadrupole tensors must not be higher than triclinic. However, the departures from the cubic and orthorhombic symmetry for these tensors, respectively, were below the resolution of our experiment. Similar to the hydrogen ENDOR experiment different deuterium-containing Si-NL10 species were found. These differed in the magnitude of the hyperfine interaction, but the quadrupole tensor was identical for all the observed TD-D species. This indicated a unique bonding arrangement of deuterium (hydrogen) in the structure of a passivated TD.

Since the magnitude of the observed quadrupole interaction by far exceeds that expected for the field of distant charges, it was interpreted in a usual manner [14] as arising from the unbalanced charge density on the deuteron which, in turn, is determined by the bond(s) that deuterium is forming with neighboring atom(s). The quadrupole interaction tensor appears to be almost axial, consistent with a single bond usually formed by hydrogen. However, the direction of the tensor axis (and therefore of the bond) is along the <011> crystalline direction, perpendicular to the oxygen-containing symmetry plane, and therefore at variance with the normally observed <111> direction for bond-centered or antibonding configuration of hydrogen. This particular observation is expected to play an important role for the future theoretical work on the modeling of the TD structure.

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