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# EPR line width and spin-relaxation rates of shallow and deep donors in isotopically controlled silicon

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**Abstract**

The results of a numerical calculation of the contribution of ligand superhyperfine interactions to the line width for the phosphorus donor electron in silicon are reported and show linear behavior at lower concentrations compared to deep centers. The linear dependence for the phosphorus center in silicon predicts an electron spin-relaxation time for isotopically purified $^{28}$Si:P longer than expected on the basis of the common square-root law. The confrontation of line width in deep-level centers with shallow states confirms that the behavior depends on the distribution of spin density around the paramagnetic center.


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## 1. Introduction

At present there is again a great interest in the relaxation processes in spin systems since it is connected with the development of spintronics and perspectives of building quantum computers on the basis of $^{28}$Si:P or GaAs quantum dots [1]. Silicon differs advantageously from GaAs by the fact that the enrichment of silicon by the $^{28}$Si isotopes makes it a spinless material. Therefore, in case of silicon quantum computer models the condition of spin coherency at quantum operations can be realized easier than for GaAs which is caused by a significant increasing of spin-relaxation time and spin-dephasing time at the isotopic enrichment.

In Ref. [2] we reported about linear dependencies of the superhyperfine interaction contribution of the electron localized on the intrinsic vacancy defect ($V^-$) and the iron impurity ($Fe^+$) in silicon to the EPR line width on the concentration of $^{29}$Si nuclei having nonzero spin. This behavior is caused by changing of the hyperfine fields shift distribution from Gaussian to Lorentzian. It is well known that interaction of electron spins with nuclear spins gives the most significant contribution to the spin-relaxation rate at low temperatures. Therefore, the enrichment of silicon by isotopes with zero nuclear spin and taking into account the linear contribution of superhyperfine interaction to the line width will give less contribution to the spin-relaxation rate compared to other relaxation processes. In contrast to centers with deep levels the wave function of the phosphorus donor electron in silicon interacts with many nuclei. Therefore, it is not possible to predict results in advance without computation of the contribution of the ligand superhyperfine interactions to the line width for the phosphorus donor electron in silicon. In this work we present results of such calculations.

## 2. Numerical calculation of the $^{29}$Si ligand superhyperfine interactions contribution to the line width

There is an existing opinion in the literature that the contribution of the ligand superhyperfine interactions to the line width for paramagnetic centers in solids has a

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square-root behavior (see, e.g. Refs. [3,4]). In Ref. [5] we suggest such a behavior for phosphorus shallow donors in silicon in contradiction to the deep centers reported in Ref. [2]. Using the methods described in Ref. [2] we calculated the contribution of the ligand superhyperfine interactions to the line width for the phosphorus donor electron in silicon. For calculations the superhyperfine constants for the phosphorus center in silicon obtained by electron–nuclear double resonance (ENDOR) in Ref. [6] were used. For improvement of the previous results we have taken into account the changing of the line shape with changing of nuclear concentration by applying deconvolution methods for finding the inhomogeneous contribution of the superhyperfine interaction to the calculated line shape. We used the idea of the works of Posener [7] and Stoneham [8] for numerical calculation of the convolution of the initial absorption line shape which was chosen Lorentzian and superhyperfine broadening which is Gaussian at high and medium concentrations of nuclei.

The convolution of the two line shapes could be expressed as [7]

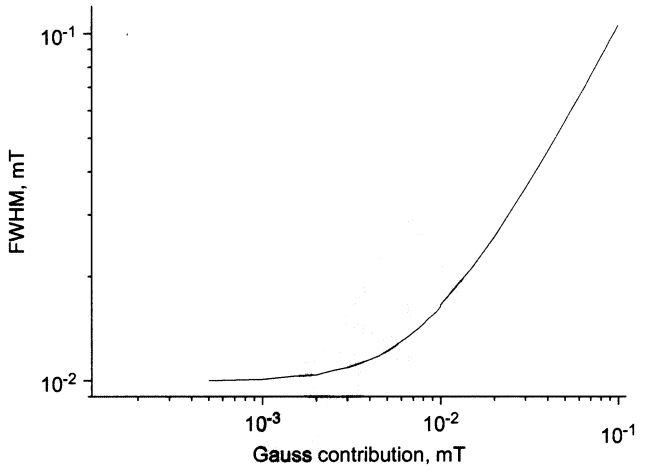


Fig. 1. Dependence of the convoluted line width on the width of the Gaussian distribution ${}^{G}\Delta H_{1/2}$ with a constant Lorentz contribution ${}^{L}\Delta H_{1/2} = 0.01\,\mathrm{mT}$.

$$Y(H - H_0) = \frac{(\ln 2)^{1/2}\,{}^{L}\Delta H_{1/2}}{\pi\,{}^{G}\Delta H_{1/2}} \int_{-\infty}^{\infty} \frac{e^{-x^2}\,dx}{\left(\frac{{}^{L}\Delta H_{1/2}}{{}^{G}\Delta H_{1/2}}\right)^2 \ln 2 + [2(\ln 2)^{1/2}((H - H_0)/{}^{G}\Delta H_{1/2}) - x]^2}, \quad (1)$$

where ${}^{L}\Delta H_{1/2}$ and ${}^{G}\Delta H_{1/2}$ are the full widths at half maximum (FWHM) for Lorentz and Gauss lines correspondingly. Since the Lorentzian contribution is known and was chosen constant (we used a value of the initial line width of 0.01 mT, much smaller than in the previous paper [2]) we could calculate the Gaussian contribution to the line shape. For this aim we made the integrations in Eq. (1) at different values of ${}^{G}\Delta H_{1/2}$ and obtained the dependence of the line width of the Lorentz and Gauss line shapes convolutions on the Gaussian contributions. The results are shown in Fig. 1. From this dependence we could derive the Gaussian contribution of the superhyperfine interaction to the line width using the algorithm of calculations as in Ref. [2]. As can be seen from the calculated dependencies of the width (FWHM) of resonance lines for phosphorus and iron ($Fe^+$) centers in silicon represented in Fig. 2 the line width decreases linearly under decrease of concentration of $^{29}Si$ magnetic nuclei below some small but different concentrations for deep and shallow centers. In the range of high concentrations (>3% for P- and >10% for $Fe^+$-center) the dependencies obtain a square-root character. It is seen that the deconvolution is mostly effective at some range of nuclear concentrations below 5%. It is negligible at very low concentrations, where there is a Lorentz contribution to the Lorentz line shape and at high concentrations where large Gauss and small Lorentz parts contribute to the convolution of the line shapes. This can be confirmed by using experimental data on superhyperfine tensors for phosphorus and iron in silicon. One can calculate the sums of $a_k^2$, $a_k^4$ and $a_k^2 a_j^2$ (in formulas (9) and (10) of Ref. [2]) and obtain the ratios of fourth and second moments. The changes of ratios $M_4/3M_2^2$ for phosphorus and iron centers in silicon are shown in Fig. 3. Again one can see the line shape transformation from Lorentzian to Gaussian type for the phosphorus center as well as for iron when the concentration of $^{29}Si$ nuclei increases.

For the iron center there is a dip around 4% of concentration which was not mentioned in the earlier paper [2] and which appeared because we used for calculations a smaller width ${}^{L}\Delta H_{1/2} = 0.01\,\mathrm{mT}$ of the initial line and which arises from the fact that only a small number of isotropic hyperfine constants were measured in the ENDOR experiment for the $Fe^+$ center [9] which leads to unsmoothness of the line shape (Fig. 4). This dip was only slightly decreased after the deconvolution procedure. To examine this dip in more detail we used for calculations also anisotropic hyperfine constants in addition to isotropic ones. In this case resonance fields were calculated using the first-order perturbation formula which included the hyperfine interaction constants for the $i$th nucleus with the paramagnetic center: isotropic $a_i$ and anisotropic $b_{ik}$, where $k$ enumerates interactions with all atoms in the shell:

$$B_{\mathrm{sh},z} = B_{0,z} + \Sigma_{ik} m_{I,i}(a_i + b_{ik,z})/g\mu_B, \quad (2)$$

where $B_0$ is the center of resonance line, without hyperfine shift, $B_{\mathrm{sh}}$ is the field with hyperfine shift, $m_{I,i}$ is the projection of spin of the $i$th nucleus on the direction of magnetic field, $g$ value is the spectroscopic splitting factor. One can see in Fig. 4 that adding of the anisotropic hyperfine constants for iron in silicon essentially affects the

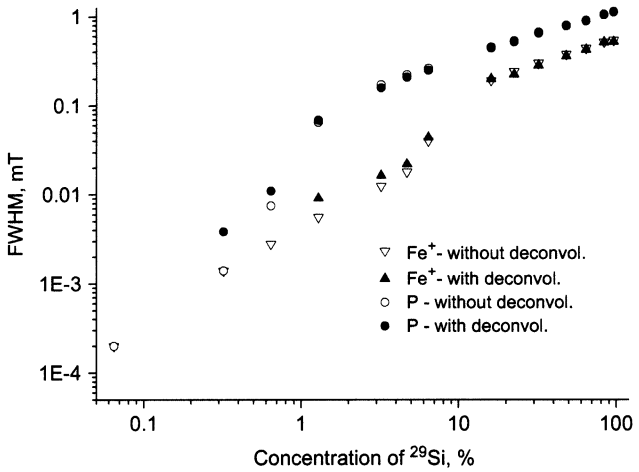


Fig. 2. Dependence of the full width at half maximum (FWHM) of EPR lines of P and $Fe^+$ centers in silicon on magnetic nuclear $^{29}Si$ concentration. Dependencies calculated without deconvolution means that the FWHM is calculated as the difference between calculated line width and initial line width (FWHM of the initial line of Lorentz shape was chosen as 0.01 mT). With deconvolution—FWHM calculated as Gauss contribution to the line shape convolution of Lorentz and Gauss.

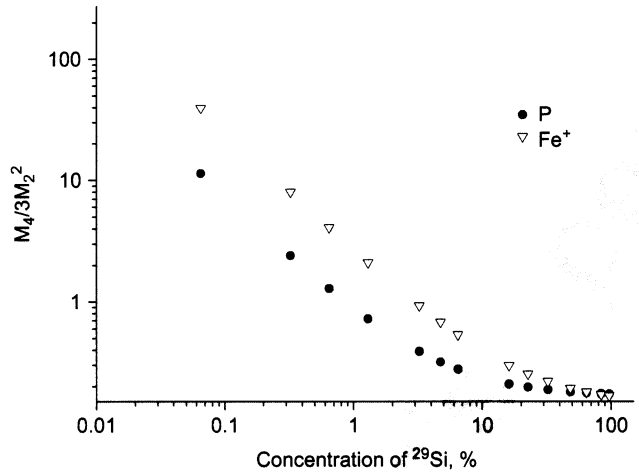


Fig. 3. Line shape parameter $M_4/3M_2^2$ as a function of the concentration of the $^{29}Si$ isotope for the phosphorus and the $Fe^+$ impurity in silicon.

results. Nevertheless, we could not obtain a gradual transition from square root to linear behavior since the line shape is not a simple convolution of Lorentz and Gauss at the decreasing of the concentrations of nuclei but has a more complicated discrete structure.

Though deconvolution and anisotropic hyperfine constants have influences on the dependencies of the contribution of ligand superhyperfine interactions to the line width, they could not make an impact on the linear character of these dependencies on concentration of magnetic nuclei as well as decrease the difference in behavior for deep and shallow donor centers. The linear character of the superhyperfine contribution to the line width at low concentration of magnetic nuclei causes more substantial increasing of the relaxation time in the electron spin-relaxation

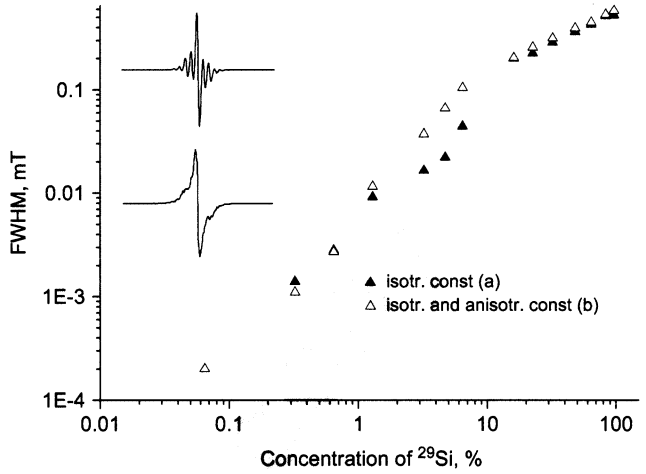


Fig. 4. Dependence of the FWHM of EPR lines of $Fe^+$ centers in silicon on magnetic nuclear $^{29}Si$ concentration calculated with adding of anisotropic hyperfine constants for the [1 1 1] direction. In the insets the first derivative of EPR absorption lines for $Fe^+$ center, calculated with using only isotropic hyperfine constants (a) and with isotropic and anisotropic hyperfine constants (b) are shown. Concentration of $^{29}Si$ nuclei is 4.7%.

processes due to more rapid decreasing of the electron–nuclear spin interaction at the enrichment of silicon by the $^{28}Si$ isotope. In this case interaction of the electron spin with nuclear spins can give much smaller contribution to the spin-relaxation processes compared to some other processes. The line widths so far measured for phosphorus in monoisotopic $^{28}Si$ samples have a great dispersion of values (0.022 mT [10], 0.008 mT [11], 0.045 mT [5]). It means that measured values depend on the history of samples and therefore on the action of additional relaxation mechanisms. Among them could be combined spin–spin and spin–lattice relaxation with participation of other defects.

The additional broadening mechanisms can lead also to unresolved superhyperfine interaction. In case of the $Fe^+$ center in silicon with natural abundance of isotopes the ligand superhyperfine broadening must lead to 0.07 mT line width but the experimental value is 0.3 mT which is caused by the additional mechanisms. For the $Cr^+$ center one can compare the calculated contribution of ligand superhyperfine interactions to the line width for enriched $^{28}Si$ (99.873% $^{28}Si$; 0.095% $^{29}Si$) with the line width measured at low temperature. The calculated line width in this case is 0.0003 mT and measured is 0.086 mT. (The full set of results for $Cr^+$ center in Si will be presented in a future paper.)

Decreasing of the spin-relaxation rate caused by isotopic purification of $^{28}Si$ can also lead to a more substantial increasing of the coherence time or completely suppress the flip-flop decoherence rate in the echo experiments. Following the results of Ref. [12] the condition for suppressing of the flip-flop rates is that the energy which is released at a nuclear spin flip ($(A_n - A_m)/2$) must be absorbed by the nuclear dipolar system, the energy of which is proportional

to $1/R_{nm}$. When the concentration of nonzero nuclear spins decreases sufficiently the first energy can only increase since the possibility to find pairs of close nuclear spins decreases, but at the same time the dipolar energy can only decrease. Hence at low concentrations of the $^{29}Si$ nuclei this mechanism of dephasing processes must be negligible. This could be confirmed comparing the expressions obtained for the moments of distributions of hyperfine interaction constants (see Ref. [2]) and for the flip-flop processes in Ref. [12]. The first one contains only the hyperfine constants and therefore depends only on the distribution of the electronic spin density around the paramagnetic center and the second one strongly depends on the distances between nuclei since it contains the dipolar energy.

## 3. Conclusion

In conclusion, we have analyzed the contribution of ligand superhyperfine interactions to the line width of paramagnetic shallow phosphorus and deep iron centers in silicon by numerical modeling of the shape of the EPR line and computation of resonance line moments. Results have shown linear behavior of the line width for phosphorus and iron centers in silicon at low concentrations of magnetic nuclei and square-root character for high concentrations. The dependence of the contribution of ligand hyperfine interactions to the EPR line width on magnetic nuclear concentration is sensitive to the degree of localization of the electron wave function of the paramagnetic center. Shallow phosphorus centers have quite a different, more extended, wave function. For them we obtained a different behavior than for deep iron centers. Nevertheless, for the low concentration approximation all centers exhibit linear superhyperfine contribution which leads to essentially less contribution to the spin-relaxation processes.

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