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The contribution of ^{29}Si ligand superhyperfine interactions to the line width of paramagnetic centers in silicon

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Abstract

The results of a numerical approach for the modeling of the contribution of ligand superhyperfine interactions to the line width of the paramagnetic negative vacancy and of positively charged iron centers in silicon are reported. The dependence which is obtained for the contribution to the line width on the concentration of magnetic nuclei has a linear character for low concentrations of nuclei with non-zero spin, and transforms to a square-root dependence at high concentrations. It is shown that the behavior depends on the distribution of spin density around the paramagnetic center. The results of the numerical approach are confirmed by a theoretical analysis using computations of resonance line moments.

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Keywords: Electron paramagnetic resonance; Line width; Hyperfine interaction; Silicon; Paramagnetic centers

1. Introduction

Latest realistic models of solid-state NMR quantum computers create an actual problem of growing spin-less semiconductors, in particular monoisotopic silicon-28, and developing methods for the control of its parameters. It is well known that the line width in electron paramagnetic resonance (EPR) spectra of defects in semiconductors depends very strongly on the content of nuclei with non-zero spin among ligand atoms which surround the paramagnetic center. In an early work of Feher et al. [1] on EPR of phosphorus in silicon it was shown that the line width narrows from 0.27 mT in silicon with natural isotopic composition to 0.022 mT in silicon with 99.88% of ^{28}Si abundance. This fact obtained particular importance after the latest progress in the growing of high-purity monoisotopic silicon-28 [2,3]. It is hard to overestimate the importance of silicon [4] in the study of defects in solids by EPR spectroscopy. It is known that many of semiconductor materials such as GaAs, InSb, and InAs, in a natural abundance, have 100% of isotopes with non-zero nuclear spins, which makes the EPR method much less usable for study of defects in these materials. Owing to the small content of 4.7% of the magnetic nucleus ^{29}Si in the natural isotopic composition, silicon has narrow EPR lines. The isotopic abundance and high structural perfection of silicon crystals can lead to EPR lines whose widths are close to the fundamental resonance limits. Technological difficulties of growing monoisotopic silicon cause the necessity of studies on the influence of the magnetic nucleus on silicon crystals properties in a wide range of concentrations. In this work, we will describe methods of analysis of the line width dependencies on the concentration of the magnetic nucleus of the ^{29}Si isotope.

Enrichment of silicon by one of its isotopes causes a series of isotopic effects in EPR [5,6]. Changing of concentration of ^{29}Si isotope leads to an alteration of hyperfine interaction and spin–spin relaxation rates in the nuclear system. Modifying the dynamical disordering as a result of changing of isotopes distribution changes the

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interaction between electrons and phonons and influences the spin–lattice relaxation processes. The mentioned isotopic effects must be visible in changing of the EPR line widths ΔB which can be expressed as [5,6]

$$(\Delta B)^n = (\Delta B_{sh})^n + (\Delta B_{rel})^n + (\Delta B_{rest})^n, \quad (1)$$

where ΔB_{sh} represents the line width contribution from ligand hyperfine interaction (inhomogeneous broadening), ΔB_{rel} the line width contribution from relaxation mechanisms and passage conditions (homogeneous broadening) and ΔB_{rest} defines rest interactions, such as electron spin–spin and interactions with elastic fields. Exponent n will assume values between 1 and 2 depending on whether the line shape is Lorentzian or Gaussian.

In this work, we will consider only the contribution from ligand hyperfine interaction. This isotopic effect is caused by the distribution of electron spin density in the crystal on ligand silicon atoms, some of which have the magnetic nucleus of the ^{29}Si isotope. Fermi contact interaction between electron and nuclear spins changes the resonance frequency for a given paramagnetic center. A magnetic nucleus which occupies one of the few nearest co-ordinated spheres can yield a substantial frequency shift, so split EPR lines can be observed. A broadened EPR line will be formed from unsplit lines with unresolved hyperfine interaction. We could find an expression for the dependence of the hyperfine ligand fields contribution to EPR line width on magnetic nucleus concentration in [7]:

$$(\Delta B_{sh})^2_{FWHM} = (2\ln 2/g^2\mu_B^2)\sum_{l,i} \alpha a_{l,i}^2. \quad (2)$$

In this expression, $a_{l,i}$ is the isotropic part of the hyperfine interaction constant, α the relative content of ^{29}Si and l, i are indices which enumerate the co-ordinated shells and number of atoms inside each shell, respectively. However, this formula is valid only when the frequencies of transitions have a Gaussian distribution, which is correct for high concentrations of magnetic nuclei that is typical for A_3B_5 compounds with natural abundance of isotopes, or for silicon enriched by ^{29}Si. For silicon, this approach perhaps will not be valid for the natural abundance of isotopes.

2. Numerical approach for modeling of EPR line allowing for hyperfine ligand interaction

Calculations were made for vacancy V^- and iron Fe^+ centers in silicon for which hyperfine interaction constants were obtained by ENDOR experiments [8,9]. We consider a system of 10^5 non-interacting paramagnetic centers with electron spin $S = 1/2$. It was assumed that each paramagnetic center can interact only with a magnetic nucleus distributed within the nearest 50 co-ordinated spheres. This could be true for localized paramagnetic centers in crystals. For each paramagnetic center a random distribution of nuclei with spin $I = 1/2$ and random sign of spin projection was generated, and resonance fields were calculated using the following formula:

$$B_{sh} = B_0 + \sum_i m_{I,i} a_i / g\mu_B, \quad (3)$$

where B_0—center of resonance line without hyperfine shift, B_{sh}—field with hyperfine shift, a_i is the hyperfine interaction constant for i-th nucleus with paramagnetic center, $m_{I,i}$ is the projection of spin of the i-th nucleus on the direction of magnetic field, g value is the spectroscopic splitting factor. For the vacancy in silicon, an orthorhombic center, the average g value is $g_V = 2.007$, and cubic iron has an isotropic g value $g_{Fe} = 3.524$. An EPR absorption line of Lorentz form and unit amplitude, and initial line width of, alternatively, 0.01, 0.025, 0.05 or 0.1 mT was assigned to each center. The calculated spectrum was composed as the sum of resonance lines arising from all paramagnetic centers. The concentration of magnetic nuclei was varied from 0.06% to 97%. As was shown, the 10^5 paramagnetic centers sufficiently describe the behavior of such a spin system. Calculations for a system of 10^6 spins give only an inessential correction—less than 1%—at ten times longer time for calculations.

Results of calculations of the full-width at half-maximum (FWHM) of resonance line shapes are shown in Fig. 1. As can be seen, the line width increases linearly under increase of concentration of ^{29}Si magnetic nuclei between 0.06% and 2%, and in the range of high concentration (>40%) the dependence obtains a square-root character.

The dependence of the contribution of ligand hyperfine interactions to the EPR line width on magnetic nuclear concentration has to be sensitive to the degree of localization of electron wave function of the paramagnetic center. In the more localized Fe center distant magnetic nuclei have much less influence on the line width than in the vacancy which has a spin density distributed up to 50 co-ordinated spheres, compared to iron for which 28% of spins is distributed on eight co-ordinated spheres. As a

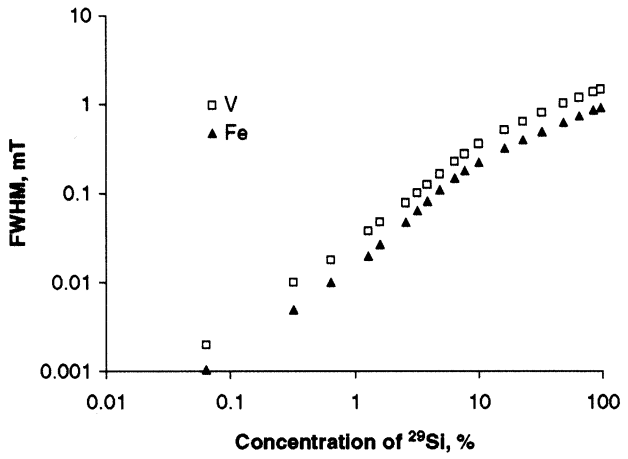

Fig. 1. Dependence of the full-width at half-maximum (FWHM) of EPR lines of V^- and Fe^+ centers in silicon on magnetic nuclear ^{29}Si concentration.

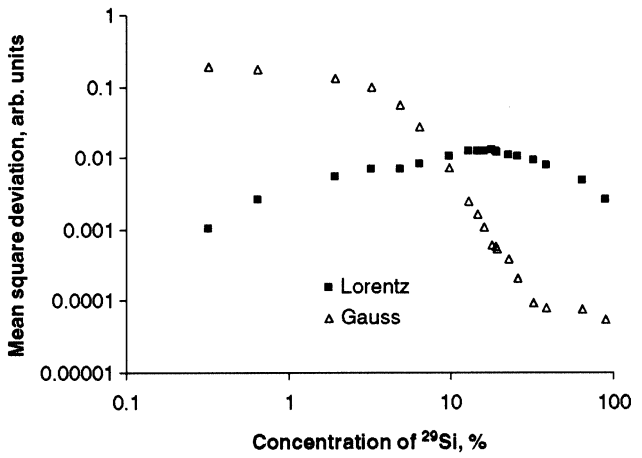

Fig. 2. Mean square deviations of calculated lines from the forms of Lorentzian and Gaussian as a function of concentration of magnetic nuclei for the negative vacancy in silicon.

result, we could observe a different behavior of the two deep-level centers vacancy and iron. Shallow centers, like phosphorus and thermal donors, have quite a different, more extended wave function. For them, we may expect a different behavior than for vacancy and iron. Such a study considering both shallow and deep centers will be the subject of a future paper.

In Fig. 2, the mean square deviations of calculated lines from the forms of Lorentzian and Gaussian as a function of concentration of magnetic nuclei for the vacancy in silicon are shown. As can be seen from this figure, the line shape transforms from Lorentzian to Gaussian forms when the concentration of magnetic nucleus is increasing. Fig. 3 shows a calculated line, both for the lowest concentration 0.3% and for the highest concentration 97%. As can be seen, the line shapes demonstrate the transition from Lorentzian to Gaussian form.

3. Computation of second and fourth moments for EPR line shape analysis

For EPR line shape analysis for the case of ligand superhyperfine broadening, we applied also the method of computation of resonance line moments. Such an analysis for a system which consists of two types of spins with dipole–dipole and exchange interactions was made by Van Vleck in Ref. [10]. However, in our case the system is different since we consider non-interacting electronic spins surrounded by magnetic nuclei. For this case, we can make the analysis for one paramagnetic center which interacts only with nuclei and with the neglect of interaction between different nuclei.

The Hamiltonian which describes the Zeeman energy of the spin system in an external magnetic field B parallel to the direction z is

$$H_z = g_e \mu_B B S_z + g_n \mu_N B \sum_k I_{z,k}. \quad (4)$$

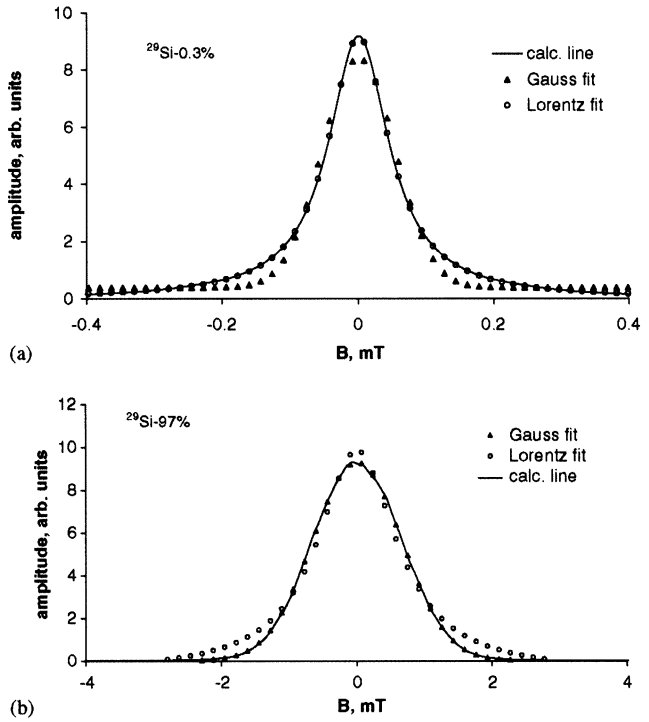

Fig. 3. Comparison of calculated lines with Lorentzian and Gaussian forms of lines for (a) lowest concentration 0.3% and (b) a high concentration 97% of ^{29}Si isotope for the vacancy in silicon.

The Hamiltonian for isotropic ligand hyperfine interaction can be written as

$$H_{HF} = S_x \sum_k a_k I_{x,k} + S_y \sum_k a_k I_{y,k} + S_z \sum_k a_k I_{z,k}. \quad (5)$$

This Hamiltonian commutes with Eq. (4) which is important for the computation of moments. However, the first and second terms on the right-hand side which describe dynamical broadening are inessential, since resonance frequencies for electrons and nuclei are different. Therefore, we can neglect them, and the Hamiltonian can be written as

$$H_{HF} = S_z \sum_k a_k I_{z,k}, \quad (6)$$

where S_z is the projection of electronic spin on direction of magnetic field, $I_{z,k}$ the projection of the k-th nuclear spin on the direction of magnetic field and a_k the superhyperfine interaction constant. For the correct calculation of line shape it is informative to obtain the second and fourth moments using the formulas [11]:

$$M_2 = -\mathrm{Sp}[H, S_x]^2/\hbar^2 \mathrm{Sp} S_x^2, \quad (7)$$

$$M_4 = \mathrm{Sp}([H, [H, S_x]]^2)/\hbar^4 \mathrm{Sp} S_x^2. \quad (8)$$

Making the analogous transformations as in Ref. [12], we can obtain the dependencies of superhyperfine contributions

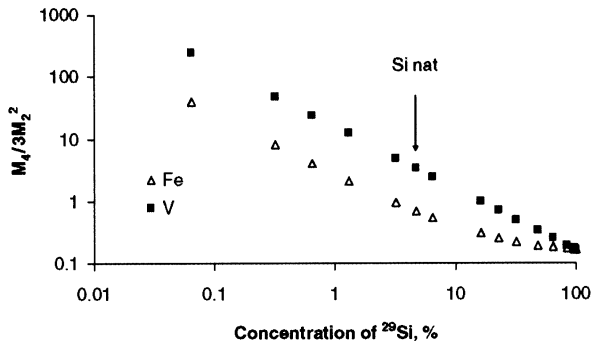

Fig. 4. Line shape parameter $M_4/3M_2^2$ as a function of the concentration of the ^{29}Si isotope for the vacancy V^- and the Fe^+ impurity in silicon.

to the second and fourth moments on magnetic nuclear concentration:

$$M_2 = (1/3)I(I+1)c\sum_k a_k^2, \tag{9}$$

$$M_4 = (1/15)I(I+1)(3I(I+1)-1)c\sum_k a_k^4 + (1/9)I^2(I+1)^2c^2\sum_{k\neq j} a_k^2 a_j^2, \tag{10}$$

where c is the concentration of magnetic nuclei. From the evaluation of ratio $M_4/3M_2^2$ we obtain that for small concentration of magnetic nuclei, when we can neglect the member which is proportional to c^2, the line shape can be described by Lorentz form, and the line width is proportional to the concentration:

$$\Delta = (\pi/\sqrt{3})(M_2^{3/2}/M_4^{1/2}) \propto c. \tag{11}$$

At a high concentration of magnetic nuclei the shape of the absorption line is Gaussian and its width Δ is proportional to the square root of concentration

$$\Delta = M_2^{1/2} \propto \sqrt{c}. \tag{12}$$

By using experimental data on superhyperfine tensors for vacancy and iron in silicon, one can calculate sums of a_k^2, a_k^4 and $a_k^2 a_j^2$ in formulas (9) and (10), and obtain the ratios of fourth and second moments. The changes of ratios $M_4/3M_2^2$ for vacancy and iron centers in silicon are shown in Fig. 4. Again, one can see the line shape transformation from Lorentzian to Gaussian type when the concentration of ^{29}Si nuclei increases.

The result of linear behavior of line width versus concentration of magnetic nuclei is not unexpected, since such a behavior of shape and width of lines takes place in systems of identical spins at negligibly small exchange and hyperfine interactions [12] which, in some aspects, are similar to our system.

4. Conclusion

In conclusion, we have analyzed the contribution of ligand superhyperfine interactions to the line width of paramagnetic vacancy and iron centers in silicon by numerical modeling of the shape of EPR line and theoretical computation of resonance line moments. Both methods have shown linear behavior of the line width for vacancy and iron centers in silicon at low concentration of magnetic nuclei, and square-root character for high concentrations.

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