Donor clusters in silicon. II. ESR simulations

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Previously reported ESR studies of P-doped silicon have been analyzed in terms of donor clusters. Simulated spectra based on a Poisson distribution of clusters and a binomial distribution of hyperfine intensity inadequately described the peak heights of the experimental data. In the present report, an alternative approach is taken which simulates the effects due to topological hyperfine and cluster-cluster interactions. A computer-generated system of donors is partitioned into clusters, retaining all interdonor exchange energies greater than some critical J_c. The matrix eigenvalue problem for each cluster is solved numerically and the results used to calculate transition energies and probabilities. Simulated spectra produced in this manner show good quantitative agreement with the data.

I. INTRODUCTION

ESR transitions associated with strongly coupled donors have been understood since the explanation of donor-pair lines by Slichter.[1] Since that time there have been many ESR studies of donor clusters, both experimental[2–8] and theoretical.[9–11] The early measurements of Feher *et al.*[6] showed signals from clusters of two, three, and four donors in the low-concentration regime. Also observed, as the concentration is increased to the intermediate regime, is the "broad background line" studied by Cullis and Marko.[3] Theoretically, Marko[9] and Shimizu[10] have extended the pair calculation to include weakly coupled pairs. Shimizu's work also predicted transitions arising from strongly coupled donor triads, including some transitions lying outside the main hyperfine lines. These results were used to explain features of the broad background line.

In a previous report,[12] hereafter referred to as I, experimental results of ESR experiments on Si:P were described. The ratio of the integrated intensity under the outer hyperfine lines to the total integrated intensity was found to vary with donor concentration in a manner consistent with a Poisson distribution of donors. Simulations based on Poisson statistics and a simple binomial distribution of hyperfine (hf) intensity, however, inadequately described the detailed features of the ESR spectra. The differences between the ESR simulations and the data were described qualitatively in terms of topological hyperfine broadening and cluster-cluster interactions. Topological hyperfine broadening first appears in clusters of three as seen in the results of Shimizu.[10] The cluster-cluster effects arise from interdonor interactions that are inevitably ignored when a system of donors is partitioned into clusters.

In the present work, computer-generated systems of donors are partitioned into clusters in an approach different from the Poisson method used in the previous work. In addition, the matrix eigenvalue problem is solved numerically for each cluster, with transition energies and probabilities calculated. The resulting calculated spectra simulate the effects of the above mechanisms, and allow quantitative comparison with the data.

Background information is presented in Sec. II. Section III discusses the approach used in defining clusters and presents the resulting donor-cluster statistics. The ESR simulation methods and results are presented in Sec. IV, with conclusions given in Sec. V.

II. BACKGROUND INFORMATION

The ESR spectra of Si:P for donor concentrations less than 10^{16} cm^{-3} show only the two lines arising from isolated donors and centered at the resonant magnetic field $h\nu/g\mu_B$. The splitting of 42.6 G arises from the hyperfine interaction between the donor electron and its nucleus,[13] with two lines corresponding to the two magnetic sublevels of the phosphorus nucleus. The linewidth of the hyperfine lines in this concentration range arises primarily from unresolved hyperfine interactions with nearby ^{29}Si nuclei. As the concentration is increased above 5×10^{16} cm^{-3}, a line, first observed by Fletcher *et al.*,[14] appears midway between the hyperfine lines. As explained by Slichter,[1] this line arises because of strongly coupled pairs. The spin Hamiltonian for two donors was taken to be

$$\mathcal{H}=\sum_{i=1}^{2} g\mu_B H_0 S_{z_i}-\sum_{i\neq j} J_{ij}(\mathbf{R})\mathbf{S}_i\cdot\mathbf{S}_j+\mathcal{H}_{\rm hf}\,, \tag{1}$$

where $\mathcal{H}_{\rm hf}$ is generally expressed as

$$\mathcal{H}_{\rm hf}=\sum_{i=1}^{n} A\mathbf{I}_i\cdot\mathbf{S}_i=A(\mathbf{I}_1\cdot\mathbf{S}_1+\mathbf{I}_2\cdot\mathbf{S}_2)\,, \tag{2}$$

with $\mathbf{S}_1$ and $\mathbf{S}_2$ being the electron spins, $\mathbf{I}_1$ and $\mathbf{I}_2$ being the nuclear spins, and J representing the exchange energy. In the limit that $J\gg A$, the total spin remains a good quantum number and, keeping the diagonal terms, the energies become

$$E=\frac{A}{2}(m_1+m_2)M+\frac{J}{2}[S(S+1)-\tfrac{3}{2}]+g\mu_B H_0 M\,. \tag{3}$$

The allowed transitions, $\Delta S=0$ and $\Delta M=\pm 1$, are located at $H_0 \pm A(m_1+m_2)/2$. For Si:P, this corresponds to three equally spaced lines at $-A/2$, 0, and $A/2$ (relative to H_0) with intensities of 1:2:1, respectively. Calculations carried out in the same spirit for higher-order clusters lead to similar results. For clusters of size k, neglecting off-diagonal terms, there will be $k+1$ equally spaced lines between $-A/2$ and $A/2$, and $A/2$, with relative intensities given by the binomial coefficients. Lines have been observed at the positions described above for clusters of size 2, 3, and 4.

The relative magnitude of the various cluster lines were used in I to gain insight into the question of donor-cluster statistics. One approach is the partitioning of the silicon host into cells of volume V_c, where V_c is a measure of the range at which interdonor interactions have a significant effect on the spin properties of interest. The distribution of donors in these cells, assuming the donors enter into the host in a uniformly random manner, is determined by Poisson statistics. Given a value of V_c, the relative number of clusters of size k is known to be

$$\frac{N_k}{N}=\frac{\langle n\rangle^{k-1}e^{-\langle n\rangle}}{k!}, \tag{4}$$

where $\langle n\rangle = N_D V_c$. Assuming Poisson statistics and a binomial distribution of hf intensity, simulations of ESR spectra can be generated for different values of $\langle n\rangle$. Simulations are presented in paper I based on the above assumptions, using the same trial line shape for each line i of the spectrum. It was found that in each case studied, there was no single value of $\langle n\rangle$ that produced cluster-line peak heights in agreement with the data for all cluster lines simultaneously.

The ratio of the integrated intensity under the outer lines to the total integrated intensity, as determined from Poisson statistics, is $I_{\text{outer}}/I_{\text{total}}=e^{-\langle n\rangle/2}$. It is shown in I how this ratio, as determined from experiment, varies with N_D. The dependence is in agreement with Poisson statistics, with the slope yielding a value of $V_c=8.2\times 10^{-18}$ cm^3. Assuming a spherical volume, this value of V_c corresponds to a critical radius of 125 Å.

Marko[9] and Shimizu[10] have carried out calculations for $J\sim A$. In this intermediate case, deviations from the simple binomial distribution of hf intensity appear. Shimizu[10] has also determined the spectra of clusters of three donors in the limit that the three interdonor exchange energies are much larger than A. The results can be expressed in terms of a single parameter, Θ, where

$$\tan(2\Theta)=\sqrt{3}(J_{23}-J_{31})/(J_{23}+J_{31}-2J_{12}) .$$

Cullis and Marko[5] noted the inadequacies of the Shimizu[10] calculation, pointing out the importance of higher-order terms in the hyperfine energy. These effects are of major importance in explaining the differences between the data and simulations in paper I.

Computer-generated distributions of donors have been used to analyze a variety of spin properties in doped silicon.[15–21] Kummer *et al.*[18] and Walstedt *et al.*,[19] in their work on amorphous antiferromagnetism in n-type silicon, developed a model for the spin susceptibility. There, random systems of donors were computer generated within some volume, and then partitioned into clusters by breaking bonds when the interaction potential became less than some critical value. Cluster eigenstates were calculated exactly for each cluster and used to calculate the spin properties of interest. Interactions between clusters were treated in a mean-field approximation. Franzen and Berggren[17] extended the calculation to find the magnetic field dependence of the specific heat in n-type silicon, also using a mean-field approach to cluster-cluster interactions. They used the donor-donor spacing as the criterion for defining clusters, breaking bonds between donors separated by more than 200 Å. Bhatt and Rice[21] calculated spin susceptibilities in a pair approximation assuming Poisson statistics. The cell volume was assumed to depend on temperature, and was modified to account for the presence of clusters greater than size 2. Andres *et al.*[15] extended the pair approximation and also used computer-generated clusters in a manner similar to Walstedt *et al.*[19] and Kummer *et al.*[18] A more sophisticated approach has been used by Bhatt and Lee[21] to study spatially random, antiferromagnetically coupled spin systems. In their approach, high-lying energy levels are discarded iteratively, with the system scaled to preserve the low-lying states.

III. COMPUTER-GENERATED CLUSTER STATISTICS

In this work, the donors are situated on randomly chosen silicon lattice sites. The pairwise exchange interactions in the Heitler-London formalism are as given by Miller and Abrahams.[22] In addition, there is a phase factor, which arises from the discrete nature of the silicon lattice.[3] The spatial average of this phase factor is $\frac{1}{6}$. Hence, a distinction can be made between the complete form of the exchange energy, including the phase factor, and the spatially-averaged exchange energy, which depends only on the magnitude of the interdonor spacing, the phase factor having been replaced by its average.

The system of donors is partitioned into clusters using a critical exchange energy, J_c, in much the same way as done in Kummer *et al.*[18] and Walstedt *et al.*[19] A donor is taken to be a member of a given cluster if it is exchange coupled to at least one other donor in the cluster with energy greater than J_c. This has been done for a system of 1000 donors at 2.5×10^{17} cm^{-3} using nine values of the critical exchange energy. Each value of J_c corresponds to a value of $R=R_c$ via the spatially averaged exchange-energy expression. In Fig. 1, the fractional number of clusters of size 1, 2, 3, and 4 is plotted versus $(R_c/R_{\text{av}})^3$, where $R_{\text{av}}=N_D^{-1/3}$ is the average donor spacing. The probability that the nearest neighbor of a given donor lies at a distance between R and $R+dR$ is

$$4\pi N_D R^2 \exp(-4\pi N_D R^3/3)dR .$$

The probability that a donor has no other donors within a distance R_c is then known to be

$$\exp(-4\pi N_D R_c^3/3)=\exp(-4\pi R_c^3/3R_{\text{av}}^3) .$$

In the absence of the phase factor discussed earlier, this is simply equal to the ratio N_i/N. Figure 1 shows that N_i/N does indeed decrease exponentially, although not as

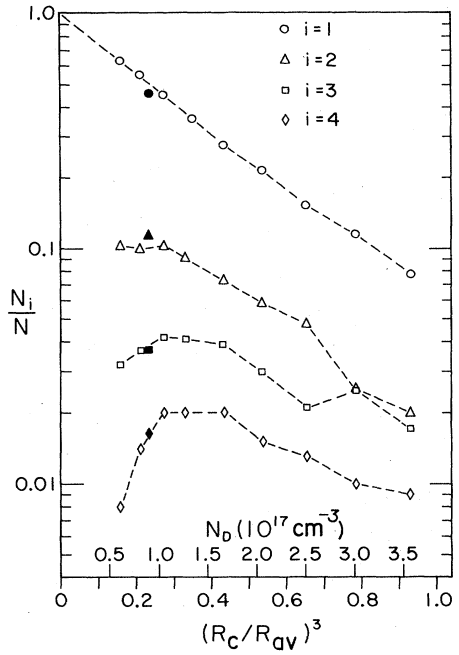

FIG. 1. Modified cluster statistics based on computer-generated donor distributions. Open points are the results of partitioning a 2.5×10^{17} cm^{-3} system using a variety of critical exchange energies. Solid points correspond to the partitioning of a 9×10^{16} cm^{-3} system with a J_c of 4.4 mK. Results are plotted versus (R_c/R_{av}), where R_c and R_{av} are defined in the text.

fast as occurs in the absence of the phase factor. As noted by Bhatt and Rice,[21] the distribution of phase factors reduces exchange couplings by more than the average value of $\frac{1}{6}$, leading to an enhancement of the number of isolated donors in Fig. 1. To compare the statistics embodied in Fig. 1 with Poisson statistics, it is useful to establish a connection between their respective predictions for isolated donors. The partition using $J_c=J(R=8a^*)=4.4$ mK (where a^* represents the effective Bohr radius of phosphorus donors in silicon) yields the same number of isolated donors as predicted by Poisson statistics using the value of V_c given by intensity analysis. This value of J_c can be compared to the hyperfine energy $A=5.6$ mK. This comparison is of interest since the results studied here and in paper I are analyzed in the high-temperature limit. In this limit, population effects are not involved (cf. Bhatt and Rice,[21] Franzen[16]), and the hyperfine energy is the parameter of interest. The solid points in Fig. 1 show the results for a generation of 2500 donors at 9×10^{16} cm^{-3} for $J=4.4$ mK. The donor concentration scale in Fig. 1 is obtained by fixing $R_c=8a^*=138$ Å. The increase of R_c from the value of 125 Å reported in I arises from the effects of the phase factor noted above.

Having fixed R_c to give results for isolated donors similar to those predicted by Poisson statistics, some comparisons can be drawn. A significant result is the decrease in the number of pairs and the increase in the number of higher-order clusters relative to Poisson statistics. The fractional number of pairs N_p/N for the 9×10^{16} cm^{-3} system is 0.18 according to Poisson statistics, while the computer calculation gives a value closer to 0.1. By the time one reaches 2.5×10^{17} cm^{-3}, one expects $N_p/N=0.13$ from Poisson statistics, while the computer calculation gives a value between 0.02 and 0.03. As a typical example of where Poisson statistics, as a technique for defining clusters, breaks down is a pair where one member interacts with $J>J_c$ only with the second member, while the second member interacts strongly with both the first donor and others as well. The Poisson approach yields results that depends on the placement of the origin of the network of cells of volume V_c. This approach inevitably discards some exchange energies larger than J_c. The approach used above unambiguously describes the size of a cluster and keeps all exchange energies greater than J_c.

IV. SIMULATED SPECTRA

The results of Marko[9] and Shimizu[10] are obtained by calculating the matrix elements of the Hamiltonian given in Eq. (1) using single-particle spin functions. The matrix eigenvalues and eigenvectors are used to evaluate transition energies and probabilities. The results of Shimizu can be obtained in the same way, ignoring off-diagonal terms in the hyperfine energy. Shimizu[10] used the results for pairs to simulate the ESR spectrum of a low-concentration sample, assuming Poisson statistics. In the present work, 20 generations of 50 donors each at 9×10^{16} cm^{-3} were partitioned using a $J_c=15.4$ mK. All clusters of size greater than 4 were then broken up into smaller clusters. The matrix elements of the hyperfine and exchange interactions, for clusters of size k, were calculated using the 2^k combinations of single-particle spin functions. The resulting $2^k\times2^k$ matrix was then solved using the scientific subroutine package available on the Digital Equipment Corporation VAX-11/780 minicomputer at the University of Rochester. The resulting eigenvectors and eigenvalues were used to calculate transition energies and probabilities. The process was repeated for the various combinations of nuclear spin states. The same line shape used in the simulation of Fig. 2 of I was attributed to each transition generated here. This approach automatically includes topological effects apparent in Table II of Shimizu[10] for donor triads. These effects were considered qualitatively in I (see the discussion of Fig. 8 of I). A mean-field approach to intercluster interactions was not used here and, in fact, these interactions were ignored in each simulation. Trends arising from the inclusion of progressively smaller values of J_c simulate effects of these interactions. Hence, the process described above has been repeated for several values of J_c.

The results for the 9×10^{16} cm^{-3} system are shown in Fig. 2. Curve (a) of Fig. 2 is generated using the binomial distribution of hf intensity as was done in Figs. 2 and 5 of I but with statistics determined in the manner described above rather than using Poisson statistics. Spectra (b), (c), and (d) of Fig. 2 are the results of explicit evaluation of matrix elements as described above for $J_c=15.4$, 4.4, and 0.78 mK, respectively. Also shown, superimposed on curve (d) of Fig. 2 as a dashed curve, is the experimental data shown in Fig. 2 of paper I. The entire process was repeated for nine samples of 50 donors at 2.5×10^{17} cm^{-3}. The results are shown in Fig. 3.

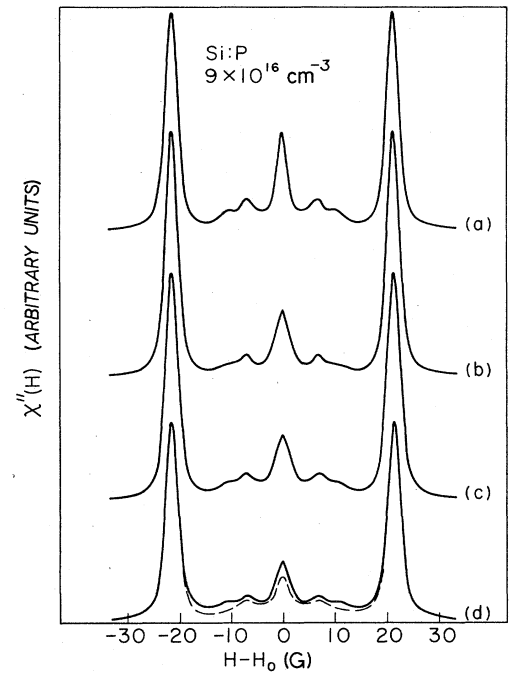

FIG. 2. Simulated ESR spectra for the 9×10^{16} cm^{-3} Si:P system. Simulation (a) assumes a binomial distribution of hyperfine intensity with statistics corresponding to $J_c=4.4$ mK. Simulations (b), (c), and (d) are generated from explicit solution of the matrix eigenvalue problem for partitions corresponding to $J_c=15.4$, 4.4, and 0.78 mK, respectively. Experimental data from Ref. 12 is superimposed (dashed line) on (d).

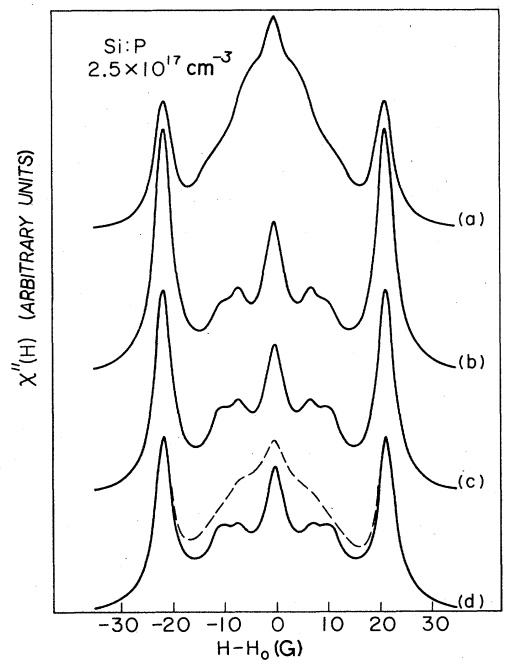

FIG. 3. Simulated ESR spectra for the 2.5×10^{17} cm^{-3} Si:P system. Simulations (a) through (d) are the same as those described for Fig. 2.

Experimentally, parameters of interest are the ratio of the central line peak height to the outer line peak height (y_c/y_{outer}) and the ratio of the triad peak height to the outer line peak height (y_t/y_{outer}). Table I gives (y_p/y_{outer}) for both systems and (y_t/y_{outer}) for the 9×10^{16} cm^{-3} system. The results show that the modifications in statistics inadequately explain the disagreement of the central-to-outer line peak height ratio between theory and experiment. The number of pairs in the 9×10^{16} cm^{-3} system is reduced by nearly a factor of 2, with most of these pairs going into a cluster of three and four donors. Those pairs going into odd-size clusters no longer contribute to the central-pair line. In general, the enhancement of higher-order clusters also reduces the cluster contribution to the outer lines (e.g., $\frac{1}{4}$ of the intensity of two pairs reside in each of the two outer lines, while $\frac{1}{16}$ of the intensity of a cluster size of 4 lies there). For the 9×10^{16} cm^{-3} system, where most of the intensity of the outer lines arise from isolated donors, the peak height ratio of the central-to-outer lines decreases. In the 2.9×10^{17} cm^{-3} system, where the outer lines arise primarily from clusters, the outer line is reduced more than the central line and the ratio actually increases.

Comparison of curves (a) and (c) of Figs. 2 and 3, both of which are generated for $J_c=4.4$ mK, provide a measure of the effects of topological hyperfine interactions as well as including some of the effects of clusters with $J\gg A$. For both systems, agreement improves dramatically. The simulations in curves (b), (c), and (d) of Figs. 2 and 3 include progressively smaller exchange energies. In the sense that simulations in curves (c) and (d) of Figs. 2 and 3 each include the largest pairwise exchange energies between the clusters of the previous simulation, this approach models the effects of cluster-cluster interactions. This approach shows little effect in the 9×10^{16} cm^{-3} system, while the agreement with experiment in the 2.9×10^{17} cm^{-3} system improves as smaller interactions are included. It should be noted that the limitation to clusters of size 4, while not very restrictive in the 9×10^{16} cm^{-3} system, should have more serious consequences in the 2.9×10^{17} cm^{-3} system. Visual inspection of the simulations show that the effect of including weaker interactions is a broadening that reduces the magnitude of both outer and central lines.

TABLE I. ESR simulation results.

	9.0×10^{16} cm^{-3}		2.5×10^{17} cm^{-3}
	y_c/y_{outer}	y_t/y_{outer}	y_c/y_{outer}
Poisson statistics	0.56	0.19	1.37
Modified statistics	0.45	0.16	1.65
$R_c=7.27$	0.28	0.09	0.64
$R_c=8$	0.29	0.12	0.74
$R_c=9$	0.30	0.14	0.84
Data	0.23	0.11	0.99

V. CONCLUSIONS

The approach used in this work to define clusters assumes a randomly distributed system of donors, as does the Poisson approach. The present approach has the advantage of unambiguously characterizing the clusters, and retaining all interdonor exchange energies above a given value, J_c. The resulting statistics show fewer donor pairs in the concentration range of interest, relative to Poisson statistics, with a greater number of clusters of size 4 and larger. The modification of statistics by itself inadequately explains the differences between the earlier simulations and the experimental data.

The discrepancies arise partially because of the choice of $J_c = 4.4$ mK used in the partition of the system of donors. The ESR spectrum of a cluster with exchange energies slightly greater than 4.4 mK are not well described by the binomial distribution of hf energy, since this energy is comparable to the hf energy of 5.4 mK. In addition, it is incorrect to ignore exchange interactions less than, but comparable to, 4.4 mK in magnitude, since these interactions also have impact on the allowed ESR transition energies. Finally, topological effects, such as those described by Shimizu,[10] cause deviations from the simple binomial hf intensity distribution, even for strongly coupled clusters.

Comparison of spectra (*a*) and (*c*) in Figs. 2 and 3 shows the effects of those donor clusters with exchange couplings comparable but greater than 4.4 mK, as well as the topological effects in those clusters. Comparison of spectra (*b*), (*c*), and (*d*) shows the effect of including ever smaller exchange energies in the calculation. The first comparison is of primary importance in the 9×10^{16} cm^{-3} system; while the 2.5×10^{17} cm^{-3} system is more sensitive to the inclusion of smaller exchange energies. In both systems, the simulations attain satisfactory quantitative agreement with the data.

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