Magnetic resonance spectroscopy in silver-doped silicon

N. T. Son,[a)] T. Gregorkiewicz, and C. A. J. Ammerlaan
Van der Waals-Zeeman Laboratorium der Universiteit van Amsterdam, Valckenierstraat 65,
NL-1018 XE Amsterdam, The Netherlands

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In silver-doped silicon, several new electron paramagnetic resonance spectra were observed. Three of these, labeled Si-NL45, Si-NL46, and Si-NL47, were detected in *n*-type samples. The spectra have trigonal symmetry; the effective electron spin value S equals 1/2. The spectra Si-NL45 and Si-NL46, with the perpendicular g values close to 6 and 8, can alternatively be described by electron spins $S=5/2$ and $S=7/2$, respectively, and g values close to 2. The Si-NL47 center has both principal g values significantly deviating from 2. They can be accounted for by taking crystal-field splitting and spin-orbit coupling into consideration. On the basis of the correlation of the production of these centers with the Si-NL44 center and the analysis with high values of electron spin, all these centers are tentatively identified as silver-related complexes.

I. INTRODUCTION

The elements of group Ib of the periodic table, i.e., copper, silver, and gold, attract considerable attention as dopants in silicon. This is due to their interesting physical properties as well as the possible applications of these impurities in silicon devices. The free-atom electronic configuration of these elements comprises 1 *ns* electron outside a completely filled $(n-1)d$ shell, with $n=4$, 5, and 6, for Cu, Ag, and Au, respectively.

All three elements diffuse relatively easily in silicon. Copper, which is one of the major contaminants in silicon device manufacturing processes, has the highest diffusion constant, with the relevant mechanism being fully interstitial. Due to its high mobility, copper has never been observed as an isolated impurity; at the same time, several copper-related complexes have been identified.

In contrast to copper, the diffusion of gold is 90% substitutional and proceeds via a kick-out mechanism. As a result, the observation of an isolated substitutional gold impurity has been reported by infrared and photoluminescence studies. It was found to have amphoteric character with deep donor and acceptor levels at $E_V+0.35$ eV and $E_V+0.63$ eV, respectively. Consequently gold, which is commonly used in the electronics industry for contacts, can also serve as an effective minority-carrier lifetime-controlling center. A puzzling question concerning the isolated gold impurity in silicon is its paramagnetism; in spite of numerous efforts, no electron paramagnetic resonance (EPR) spectrum could be assigned to this center, whereas that of its isoelectronic equivalent, substitutional Pt^-, has been identified.[1] On the other hand, several gold-related impurity complexes have been observed.

Considerably less is known about the silver dopant, which has attracted more interest only recently.[2] This follows from the fact that, as a common contaminant of gold, silver is unavoidably present in the evaporation equipment. At the same time, silver has rather high diffusivity in silicon and SiO_2, even at low temperatures. As a result, in MOS (metal-oxide-semiconductor) structures, it can penetrate the protective oxide layer leading to the degradation of a relevant device under its operating conditions. In close resemblance to gold, infrared spectroscopy has identified the isolated silver center and revealed its amphoteric character with deep donor and acceptor levels at, respectively, $E_V+0.34$ eV and $E_C-0.54$ eV. However, in striking contrast to the published data on gold, the isolated silver impurity was shown to be paramagnetic.[3] In the same study two more spectra, due to silver-impurity pairs, were found. The present work reports on the observation of three other silver-related centers that are characterized by high values of the electron spin S.

II. EXPERIMENT

For the preparation of samples, float-zone, dislocation-free, *n*-type, phosphorus-doped silicon with room-temperature resistivity of ≈ 1 and $\approx 8\ \Omega$ cm was used. Typical dimensions of the samples were $1.5\times1.5\times15$ mm^3, with the length along the $[0\bar{1}1]$ crystallographic direction. For the diffusion, high-purity natural silver was used. It contained two isotopes with nearly equal abundance. Alternatively, samples were diffused with monoisotopically enriched ^{107}Ag or ^{109}Ag. The diffusion process was conducted at a temperature of 1250 °C in a closed quartz ampoule filled with 200 mbar of argon. Depending on the isotope, the duration of the process was in the range of 24–40 h. After diffusion, the samples were quenched in water to room temperature and stored in liquid nitrogen.

Magnetic resonance measurements were performed on X-band (microwave frequency $\nu\approx 9$ GHz) and K-band ($\nu\approx 23$ GHz) superheterodyne spectrometers tuned to observe the dispersion part of the magnetic susceptibility. The sample was mounted with the $[0\bar{1}1]$ direction perpendicular to the plane of rotation of the magnetic field. All EPR spectra were measured at liquid-helium sample temperature.

[a)] Permanent address: Department of Physics, University of Hanoi, Vietnam.

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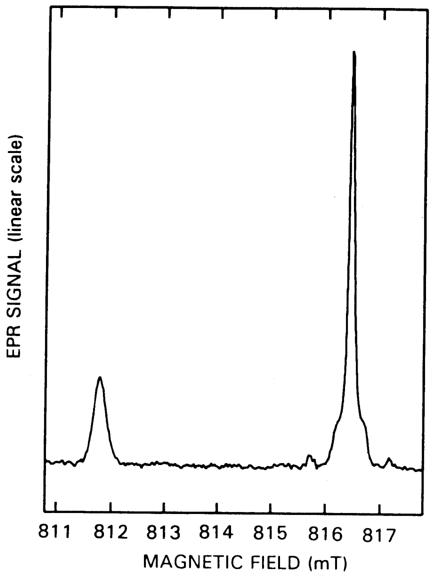

FIG. 1. Part of the EPR spectra Si-NL45 (near $B=816.4$ mT) and Si-NL46 (near $B=811.8$ mT), recorded at an angle 1° away from the [111] direction, in the region $g\approx 2.020$. The hyperfine structure due to silicon is observed only for the Si-NL45 spectrum. The microwave frequency is $\nu=23.211$ GHz.

III. RESULTS AND ANALYSIS

A. Si-NL45 and Si-NL46 centers

Following the quenching, two new strongly anisotropic spectra, labeled Si-NL45 and Si-NL46, respectively, were observed. They appeared simultaneously with the well-known signals of Fe_i^0 and P_s^0. As illustrated in Fig. 1, the line intensity and the line shape of the two spectra differ significantly. In all samples, the intensity of the Si-NL45 spectrum is much larger than that of Si-NL46. For both spectra, the line intensities vary considerably between EPR orientations and are angular dependent. The maximum intensity is obtained in the [111] direction and for the higher magnetic field values. No hyperfine interactions, expected to arise from the silver impurity, could be detected. The well-resolved hyperfine interaction with silicon neighbors, as shown in Fig. 1, was observed only for the Si-NL45 spectrum. Unfortunately, due to the low intensity of the resonance lines of some EPR orientations, the silicon hyperfine interaction could not be followed over the full range of angles. For the Si-NL46 spectrum, no silicon hyperfine structure could be observed. The linewidth of the Si-NL46 spectrum was rather broad, but it was more narrow in the single-isotope-doped sample. This could be understood as an experimental indication of the involvement of silver in that center. By the angular dependences, as given in Figs. 2 and 3, the trigonal symmetry was confirmed for both centers. Due to the large anisotropy and a small misorientation of the sample, all four $\langle 111\rangle$ orientations of the trigonal centers are separately visible. After the sample was stored at room temperature for a few hours, the intensity of both spectra had decreased considerably. The decrease was accompanied by a simultaneous appearance of the Si-NL44 spectrum, which was earlier identified as silver related.[3] By illuminating the samples, regardless of their initial phosphorus concentration, the intensities of the spectra could only be lowered.

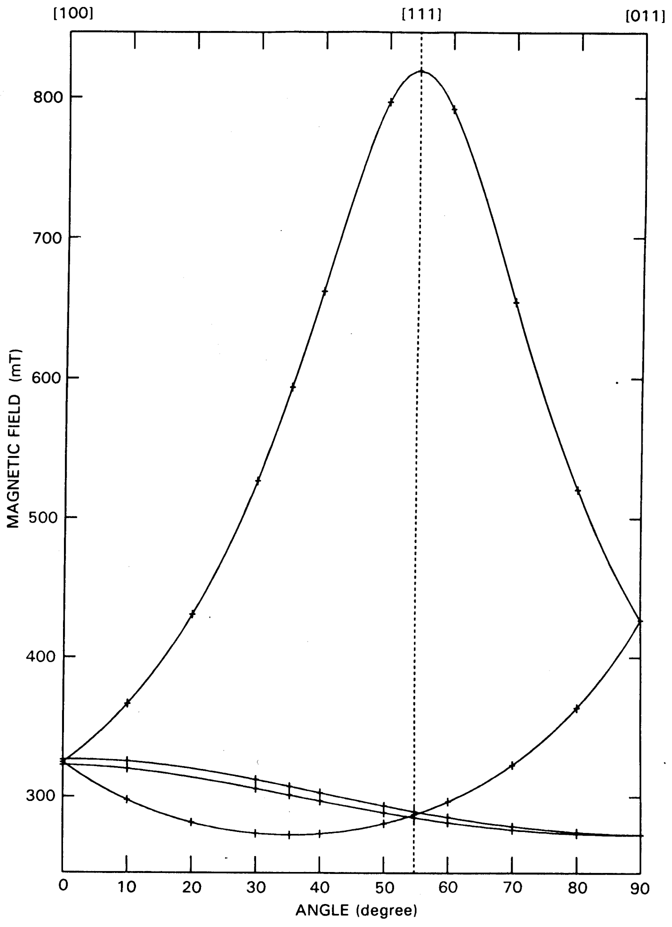

FIG. 2. Angular dependence of the EPR spectrum Si-NL45. The magnetic field is rotated in the $(0\bar{1}1)$ plane. The solid curves represent a fit to the experimental data according to Eq. (2). The microwave frequency is $\nu=23.211$ GHz.

The experimental data of both spectra can be fitted using the simple spin Hamiltonian

$$H=\mu_B \mathbf{B}\cdot\mathbf{g}\cdot\mathbf{S}, \tag{1}$$

with electron spin $S=1/2$. Results for both centers are given in Table I. The fit is not very good with the deviation between experimental and calculated points exceeding a few mT, especially for the high-field points in the [111] direction. Both centers have unusually high perpendicular g values, $g_\perp=6.090$ and $g_\perp=7.999$ for Si-NL45 and Si-NL46, respectively. The deviation of g values from the value of the free electron can be caused by the orbital momentum via the spin-orbit interaction or, for systems with spin values $S>1/2$, by the spin-spin interaction. For high-spin centers with trigonal symmetry, and for the case when there is no orbital momentum contribution, the effective g value for the axial direction, $g_\parallel$, will be close to 2. In the perpendicular directions, however, the effective g value is approximately given by $g_\perp(S+1/2)$, with $g_\perp\approx 2$.[4–6] The g values of the Si-NL45 and Si-NL46 spectra indicate that there is no significant contribution of the or-

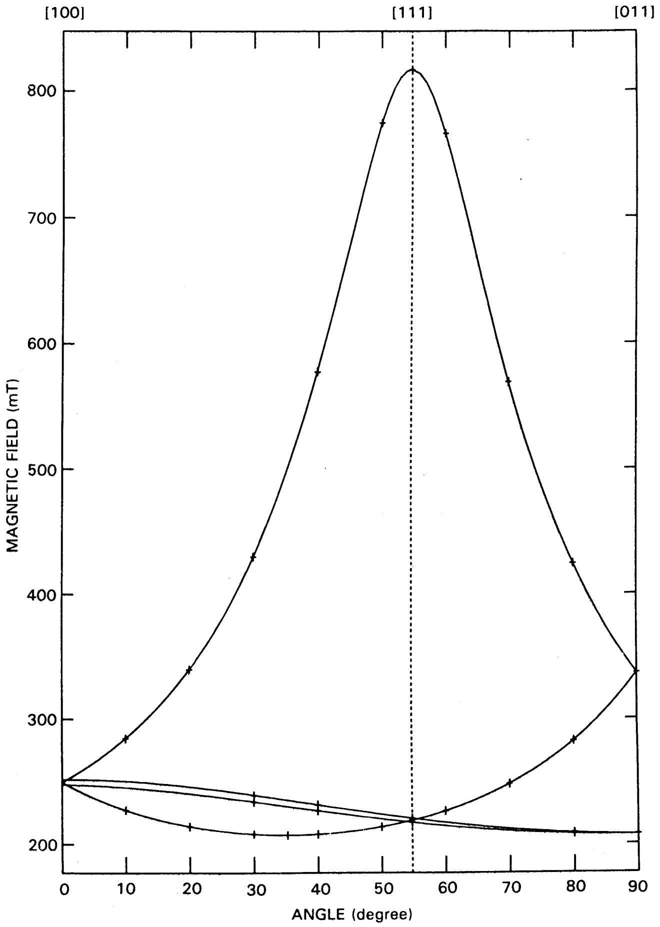

FIG. 3. Angular dependence of the EPR spectrum Si-NL46. The magnetic field is rotated in the $(0\bar{1}1)$ plane. The solid curves represent a fit to the experimental data according to Eq. (2). The microwave frequency is $\nu=23.211$ GHz.

bital momentum and that an analysis with higher effective spin would be more appropriate. For such an analysis, the spin Hamiltonian is written as

$$H=\mu_B\mathbf{B}\cdot\mathbf{g}\cdot\mathbf{S}+D[S_z^2-(1/3)S(S+1)], \qquad (2)$$

where D is the zero-field-splitting value that represents the separation between the doublets induced by an axial crystal field. To fit the data for the Si-NL45 and Si-NL46 spectra with the Hamiltonian Eq. (2), the effective spins $S=5/2$ and $S=7/2$ were used. In both cases, principal g values close to $g=2$ were obtained and the agreement with the experimental data was significantly improved (especially for the Si-NL46 center). Resulting parameters are also given in Table I.

TABLE I. Principal g values of the Si-NL45, Si-NL46, and Si-NL47 centers and their other spin-Hamiltonian parameters for analyses with different values of the electron spin S.

Center	Symmetry	S	$g_\parallel$	$g_\perp$	D (GHz)
Si-NL45	trigonal	1/2	2.020	6.090	
		5/2	2.020	2.036	95
Si-NL46	trigonal	1/2	2.019	7.999	
		7/2	2.018	2.036	44
Si-NL47	trigonal	1/2	5.776	1.096	

Since no silver-related hyperfine structure could be observed for either Si-NL45 or Si-NL46 and since the intensity of these spectra was too low to permit an electron-nuclear double resonance (ENDOR) measurement, no direct identification of the relevant impurities was possible. However, it was noted that, after keeping the sample at room temperature for a few hours, the intensity of both spectra had decreased considerably, with the simultaneous appearance of the Si-NL44 spectrum, for which the involvement of silver was directly confirmed.[3] It seems, therefore, not unreasonable to assume that also the Si-NL45 and Si-NL46 centers are silver related. In view of the small silver-hyperfine constant of the Si-NL44 center (a few MHz only), it is possible that for the Si-NL45 and Si-NL46 centers, with much higher g values, the silver-hyperfine structure is not resolved. From the analysis with the spin Hamiltonian Eq. (2), it can be concluded that the true spins of the Si-NL45 and Si-NL46 centers are 5/2 and 7/2, respectively. Based on the high spin values and trigonal symmetry on the one hand and on the electronic configuration of silver on the other, it is difficult to imagine relevant microscopic models that would consist of a single atom only. For both centers, the structure of an impurity pair appears far more likely. With the $4d^{10}5s$ electronic configuration as a free atom, a substitutional silver atom in the silicon crystal will have a $4d^7$ configuration, with 4 electrons being contributed to the bonds. This configuration is expected to give a spin $S=3/2$, and the parallel coupling between spins of two substitutional silver atoms will give rise to a spin $S=3$. A possible microscopic model of the Si-NL45 center would then be $\mathrm{Ag}_s^0\mathrm{Ag}_s^-$, with one atom in the $4d^7$ configuration, with $S=3/2$, and the other atom in an ionised $4d^8$ state, with $S=1$. In the positively ionized state, such as $\mathrm{Ag}_s^+\mathrm{Ag}_s^0$, one silver atom is transformed into the $4d^6$ configuration with spin $S=2$. In this case, the ferromagnetic coupling between the two spins gives total spin $S=7/2$, as observed for the Si-NL46 center. In this interpretation, the Si-NL45 and Si-NL46 spectra correspond to different charge states of the nearest-neighbor substitutional silver pair. Such amphoteric behavior of the AgAg pair seems certainly possible in view of the earlier mentioned amphoteric character of the isolated (substitutional) silver atom.

B. Si-NL47 center

The spectrum Si-NL47 was observed in a n-type, silver-doped sample. It appeared simultaneously with the spectra of interstitial iron, Fe_i^0, substitutional phosphorus, P_s^0, and the silver-related Si-NL44 center. It is illustrated in Fig. 4. Similar to the case of Si-NL46, this spectrum shows rather broad lines without any hyperfine structure. As shown by the angular dependence, which is given in Fig. 5, the spectrum has trigonal symmetry and is rather anisotropic. The intensity of the resonance lines varies strongly between EPR orientations and is angular dependent. In the region between 10 and 50°, it was not possible to observe

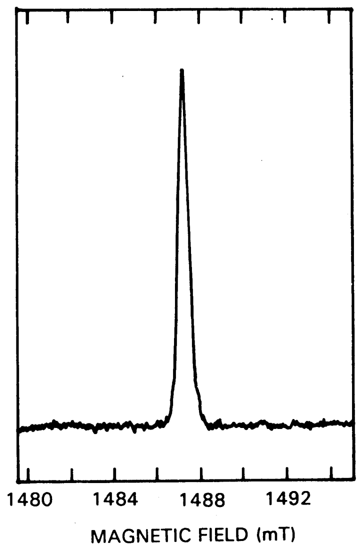

FIG. 4. Part of the EPR spectrum Si-NL47 for magnetic field B parallel to the [011] direction. The microwave frequency is $\nu=23.280$ GHz.

the lower-field orientation; in the [011] direction, however, the resonances are relatively strong with all orientations clearly visible. Also, the temperature dependence of the intensities of resonance lines varied with the angle. As in the case of the previously described centers, the intensity of the Si-NL47 spectrum was rather low and it was not possible to identify the origin of the spectrum in an ENDOR experiment. The g values of the center, as obtained from the analysis of the experimental data with $S=1/2$ and Eq. (1), are given in Table I. In view of the trigonal symmetry and the high g values, the center can be expected to correspond to an impurity pair. The high g values are characteristic for centers related to transition metals. More precisely, because of the fact that the spectrum was only observed in the samples doped with silver, it is natural to postulate silver involvement in the center. The unusually broad lines, in this case, may result from unresolved hyperfine interaction due to both silver isotopes.

In contrast to the Si-NL45 and Si-NL46 spectra described in the previous section, the parallel g value, $g_{\parallel}$, of Si-NL47 is much larger than its perpendicular g value, $g_{\perp}$, with both significantly deviating from 2. This is indicative of the situation in which the deviation of g values from 2 is not caused by spin-spin interaction only, but also by spin-orbit coupling. The presence of orbital momentum in transition metals in silicon is well described by the Ludwig–Woodbury model.[6] Comparing the spectrum Si-NL47 with data obtained for iron-acceptor pairs, one recognizes its close similarity to spectrum Si-NL27 of the trigonal FeAl pair.[7] The electronic structure of this center can be understood by a model in which the paramagnetism of the pair arises from the three unpaired electrons of the iron impurity in a $3d^7$ configuration. This configuration gives a spin $S=3/2$ and an effective orbital momentum $L=1$. The anisotropic g values can then be interpreted in terms of crystal fields and spin-orbit coupling. Considering the silver-impurity pair as a possible model for the Si-NL47 center, one can assume that the silver atom occupies a substitutional site and is in the $4d^7$ configuration. Following this analysis, the effects of the crystal field and spin-orbit interaction on the ground state are considered. For the trigonal symmetry, the effect of crystal field represents the action of a $\langle 111 \rangle$ axial field (taken along the z direction). Hamiltonian operators representing the effects of an axial crystal field (cf), spin-orbit coupling (so), and magnetic field (mf) are given by

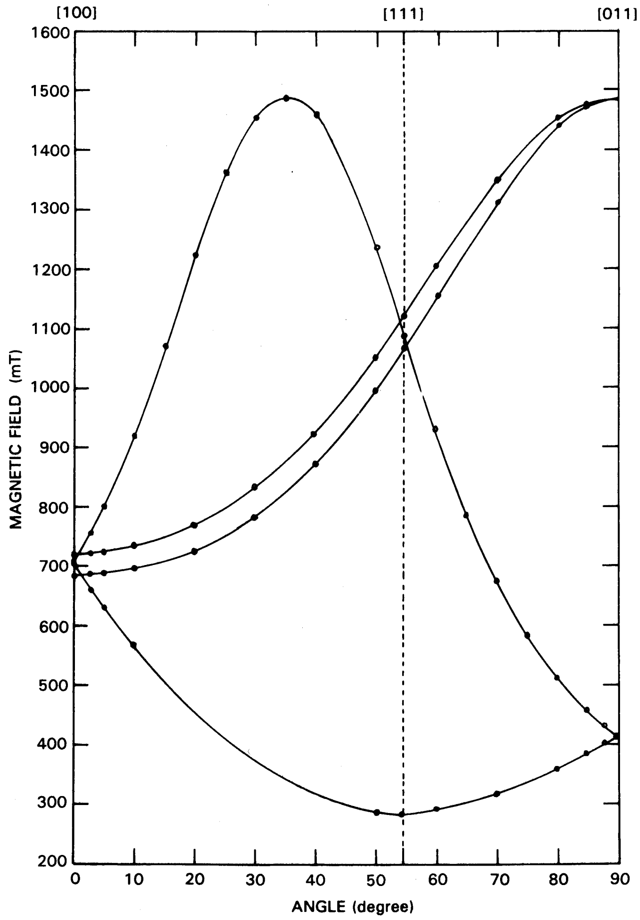

FIG. 5. Angular dependence of the EPR spectrum Si-NL47. The magnetic field is rotated in the $(0\bar{1}1)$ plane. The microwave frequency is $\nu=22.820$ GHz.

$$H_{\mathrm{cf}}=+\Delta_{\mathrm{ax}}(1-L_z^2), \tag{3}$$

$$H_{\mathrm{so}}=-\alpha\lambda\mathbf{L}\cdot\mathbf{S}, \tag{4}$$

$$H_{\mathrm{mf}}=-\alpha\mu_B\mathbf{B}\cdot\mathbf{L}+2\mu_B\mathbf{B}\cdot\mathbf{S}, \tag{5}$$

where Δ_{ax} is the strength of the axial crystal field, λ is the spin-orbit coupling constant, and α is the orbital Landé factor. The Hamiltonian operators H_{cf} and H_{so} will split the $L=1$ orbital triplet and $S=3/2$ spin quartet into 12 mixed states. Due to Kramers degeneracy, the twelve-dimensional matrix of this Hamiltonian with respect to these basis states can be reduced to two identical six-dimensional submatrices. Application of an external magnetic field $\mathbf{B}$, lifting the remaining degeneracy, is accounted for by the H_{mf} operator. The splitting of the lowest doublet, in which the resonance is observed, can be described with effective spin $J=1/2$. The effect of the magnetic field is then given by the Hamiltonian $H=\mu_B \mathbf{B}\cdot \mathbf{g}\cdot \mathbf{J}$, with an effective g tensor. The results of diagonalizing the matrix of $H_{cf}+H_{so}$ were first reported by Abragam and Pryce.[8] The solutions of the g values and the energies E of the doublets given in their work are summarized by

$$E=\alpha\lambda(x+3)/2, \tag{6}$$

$$g_{\parallel}=2-\frac{4(\alpha+2)(x^2-12x-12)}{(x^4+4x^3+18x^2+24x+24)}, \tag{7}$$

$$g_{\perp}=\frac{4\{x^4+4x^3+16x^2+24x+2\alpha x^2(x+2)\}}{(x^4+4x^3+18x^2+24x+24)}, \tag{8}$$

with

$$\Delta_{ax}=\alpha\lambda(x-2)(x+1)(x+6)/2x(x+2). \tag{9}$$

The parameter x is obtained by solving the cubic Eq. (9). As the spin-orbit-coupling constant λ for silver in the $4d^7$ configuration is negative, $\lambda=-239.32$ meV,[9] the lowest energy E corresponds to the positive root of Eq. (9). The g values are calculated from Eqs. (7) and (8). Elimination of x between these two equations establishes a relation between $g_{\parallel}$ and $g_{\perp}$, still as a function of α. With the theoretical value $\alpha=3/2$, the calculation gives g values quite different from those observed in the experiment. One can, however, use this relation and the experimentally determined g tensor to calculate an "empirical" Landé factor. Such a procedure yields $\alpha=0.013$, indicating nearly totally quenched orbital momentum. The relation between $g_{\parallel}$ and $g_{\perp}$ for this value of α is plotted in Fig. 6. Such a calculation then allows to interpret the observed g values of the Si-NL47 center. Unfortunately, at this moment, a detailed structural model of the center cannot be presented.

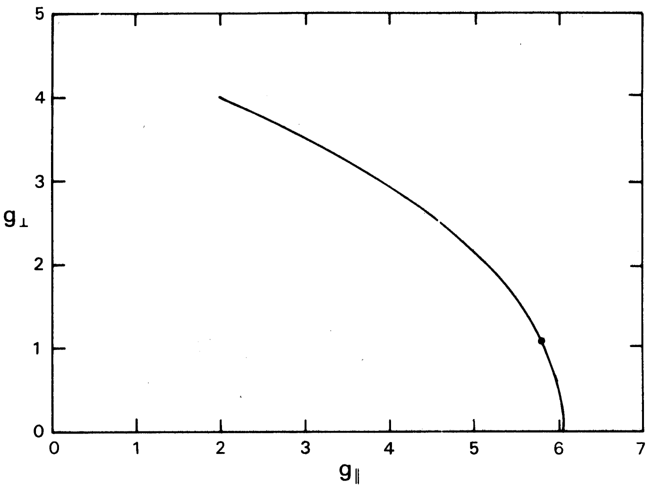

FIG. 6. Theoretical Zeeman splitting factors $g_{\parallel}$ and $g_{\perp}$ for a $4d^7$ ion in an axial crystal field with the value of the Landé factor $\alpha=0.013$. The g values of the Si-NL47 spectrum are represented by the dot.

IV. CONCLUSION

In our EPR studies of silver-doped silicon, three new spectra were observed in addition to the ones identified earlier. These trigonal spectra have rather uncommon g values for an effective electron spin $S=1/2$. On the basis of an analysis with high spins, the true spin values were concluded to be $S=5/2$ and $S=7/2$ for the Si-NL45 and Si-NL46 centers, respectively. From the correlation with the silver-related Si-NL44 center, these two spectra are tentatively identified as silver related. Based on the experimental findings, an atomic model involving a pair of nearest-neighbor substitutional silver atoms is proposed for both centers. The models are the negatively and positively charged silver pairs, corresponding to the spectra Si-NL45 and Si-NL46, respectively. The third reported spectrum, Si-NL47, is assumed be silver related on the basis of the production conditions. Its g tensor was analyzed with a spin $S=3/2$ and an angular momentum $L=1$ from electrons in the d shell of a silver atom. An interpretation of the g values was given by taking into account the effects of an axial crystal field and spin-orbit interaction.

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