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K. Morigaki, Michel Rosso

Institutions: École Polytechnique

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ELECTRON SPIN RESONANCE STUDY OF INTERACTING DONOR CLUSTERS IN PHOSPHORUS-DOPED SILICON AT 100 GHz AND LOW TEMPERATURES

K. MORIGAKI (*) and M. ROSSO

Laboratoire de Physique de la Matière Condensée (**) de l'Ecole Polytechnique,
Plateau de Palaiseau, 91120 Palaiseau, France

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Résumé. — Nous avons étudié, par résonance de spin électronique à 100 GHz, à 1,4 K et 4,2 K, le silicium dopé au phosphore de la région de concentration en donneurs comprise entre $1{,}9 \times 10^{17}\ \text{cm}^{-3}$ et $2{,}8 \times 10^{18}\ \text{cm}^{-3}$. Le déplacement de la raie centrale par rapport aux deux raies hyperfines a été étudié en fonction de la concentration en donneurs, de la température et de la puissance hyperfréquence. A faible puissance hyperfréquence, le déplacement de la raie centrale est dû à une asymétrie du spectre, interprétée dans un modèle proposé par un des auteurs, qui tient compte du regroupement des donneurs en amas en fonction des interactions d'échange entre leurs spins électroniques et de l'interaction hyperfine entre électrons et noyau ^{31}P. L'augmentation du déplacement avec la puissance hyperfréquence est attribuée à une augmentation de la polarisation nucléaire par effet Overhauser.

Abstract. — ESR experiments have been performed on phosphorus-doped silicon with concentrations ranging from $1.9 \times 10^{17}\ \text{cm}^{-3}$ to $2.8 \times 10^{18}\ \text{cm}^{-3}$ at 1.4-4.2 K and 100 GHz. The peak shift of the central ESR line with respect to the center of the two hyperfine lines has been investigated as a function of donor concentration, temperature, and microwave power. In general, it consists of a microwave power-dependent part and of a microwave power-independent one.

The former part is interpreted in terms of the Overhauser effect; the latter one is due to an asymmetry of the spectrum, understood on the basis of a new model proposed by one of the authors, which takes into account the clustering of nearby donors according to the exchange interaction between their electronic spins, and the hyperfine interaction with ^{31}P nuclei.

1. **Introduction.** — Recently, magnetic properties of heavily doped semiconductors have received much attention in connection with the metal-non metal transition which occurs in these materials at low temperature [1]. In this paper we are concerned with the peak shift of the central Electron Spin Resonance (ESR) line of phosphorus doped silicon, with concentrations just smaller than $3.5 \times 10^{18}\ \text{cm}^{-3}$, at which the metal-non metal transition occurs. According to previous studies [2, 3] the peak position of the central ESR line attributed to clusters of donor impurities depends on the donor concentration, the magnetic field, and the temperature. Such a behaviour of the central ESR line has been interpreted in a molecular field approximation, with the assumption of a weak ferromagnetic exchange coupling between donor cluster spins [2, 3]. However, several authors [4, 5] have shown that the interaction between individual electronic spins is antiferromagnetic and the origin for such a ferromagnetic exchange between donor clusters was not clear. The purpose of this work is to clarify the origin of the peak shift of the central ESR line by extending the previous measurements at 46 GHz [2] to the higher frequency of 100 GHz, at which we may expect a better resolution of the spectrum and a larger polarization of the electronic spins.

As a result of the present measurements and also of further ones at 46 GHz [6] it has been found that the peak shift can be divided into two parts, one of which depends on the microwave power and the other is independent of it. The power-dependent peak shift arises from the appearance of the nuclear field as a result of the nuclear polarization due to the Over-

(*) On leave from Institute for Solid State Physics, University of Tokyo, Roppongi, Tokyo 106, Japan; now returned.

(**) Equipe de Recherche du Centre National de la Recherche Scientifique.

hauser effect. The power-independent peak shift is due to an asymmetry of the spectrum which may be interpreted in terms of a new model recently proposed by one of the authors [7], in which the clustering of donor impurities and the hyperfine interaction with ^{31}P nuclei are taken into account.

The magnetic resonance experiment described in this paper provides a better understanding of the magnetic interactions in a disordered spin system, which are extensively studied with reference to the problem of amorphous magnetic systems [8], and the metal-non metal transition.

2. **Experimental.** — Electron spin resonance measurements are performed in the temperature range from 1.4 K to 4.2 K at 100 GHz. The microwave power is generated by a klystron delivering a power of 30 mW in the frequency range from 95 to 105 GHz (OKI-100 V 10 A), and its frequency is stabilized on an external cavity. A conventional reflection type spectrometer is employed, with or without the use of a Fabry-Pérot type cavity. For the sake of convenience, most of the results are taken without the cavity. In this case, the sample is put on the end face of an overdimensioned circular waveguide coming from one branch of the magic tee or the directional coupler.

Reflections on discontinuities of the inside waveguide surface cause a pseudo-cavity to be formed at the end of the waveguide; the Q of this pseudo-cavity is almost as large as the Q of the Fabry-Pérot cavity, which is of the order of 1 000. In both cases the maximum rotating field H_1 available at the sample is of the order of 100 mOe. The magnetic field of 35 kOe is produced by a superconducting magnet (Oxford Instruments) of stability and homogeneity of the order of 10^{-5}, and is modulated with a frequency of 1.5 kHz or 300 Hz.

The shift of the peak position of the central ESR line is measured from the center of the two hyperfine (HFS) lines when these lines can also be observed. Otherwise, it is measured by comparing the signal to be measured with the reference from metallic lithium colloid in neutron-irradiated LiF ($g = 2.002\,3$) [9].

The samples of P-doped silicon were of a rectangular shape ($2 \times 1 \times 0.3\ \mathrm{mm}^3$), the widest face being the (110) plane of the crystal. Their donor concentrations were estimated from the room temperature Hall coefficient R_H using the relation $N_D = (R_H\, ec)^{-1}$. Sample characteristics are listed in table I, where the magnitudes of the resistivities at 300 K and 4.2 K and also the ESR line-widths measured at 1.4 K and 4.2 K are shown.

TABLE I

Characteristics of the samples

Sample	N_D (cm^{-3})	Resistivity (ohm-cm) 300 K	4.2 K	$\Delta H_{m,sl}$ (Oe) (*) 4.2 K	1.4 K
—	—	—	—	—	—
M3	1.9×10^{17}	0.05			
M4	3.1×10^{17}	0.04		11	8
M5	4.4×10^{17}	0.03		7	6
M6	1.0×10^{18}	0.02	10^9	4	3.5
M7	5.9×10^{17}	0.025		6	5
M8	1.5×10^{18}	0.015	5×10^6		
M14	2.8×10^{18}	0.011 4			
M18	1.8×10^{18}	0.014 2	2×10^4		
MA1	1.5×10^{18}		5×10^6		
T18	1.6×10^{18}	0.014 5	0.5×10^6		

(*) $(\Delta H)_{m,sl}$ designates the peak to peak separation of the absorption derivatives measured at 100 GHz, in the low power limit.

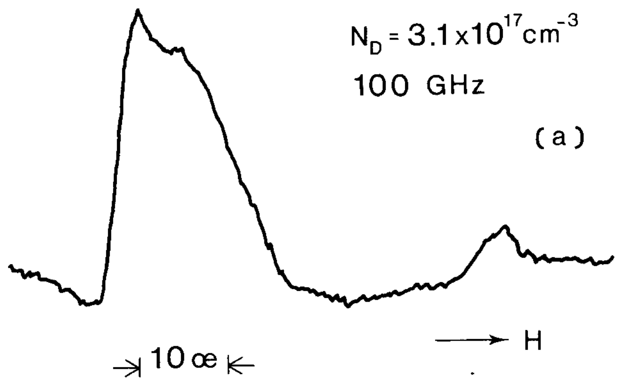

FIG. 1*a*. — Typical trace of ESR spectrum at 1.4 K, 100 GHz and the microwave power level of − 3 dB for sample M4 ($N_D = 3.1 \times 10^{17}\ \mathrm{cm}^{-3}$).

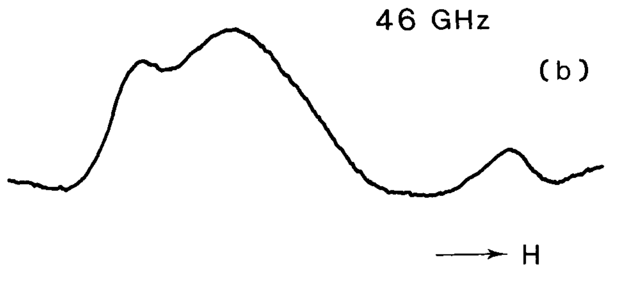

FIG. 1*b*. — ESR spectrum at 1.5 K, 46 GHz, and the microwave power level of − 6 dB for sample M4 ($N_D = 3.1 \times 10^{17}\ \mathrm{cm}^{-3}$).

3. **Experimental results.** — The behaviour of ESR spectra observed at 100 GHz and 1.4 K as a function of donor concentration is similar to that observed at 46 GHz and 1.5 K [2], showing no distribution of the g values of the centers participating in the resonance. However, there is a difference between the two cases in the magnitude of the shift of the peak position of the central ESR line, especially in samples with low donor concentration.

For example, figure 1*a* shows a typical example of the spectrum observed in a sample with

$$N_D = 3.1 \times 10^{17}\ \mathrm{cm}^{-3}\ (\mathrm{M4}),$$

which is to be compared with the figure 1*b* taken at 46 GHz [6].

Previous experiments had not studied the influence of microwave power on the shape of the resonance spectrum : the present experiments and new experiments at 46 GHz [6] have shown that the peak shift depends on microwave power. In figure 1*a* the microwave power is about 0.15 mW and the shift from the center of the HFS lines ($\Delta H \simeq -15$ Oe) is enhanced by a factor 1.5 in comparison with the shift observed in the low power limit. The dependence of the peak shift on the microwave power at 46 GHz can be seen in figure 2 [6]. At this frequency, results taken with a cavity at high power level showed a great relative enhancement (by a factor 5) of the hyperfine line on the low field side, for the samples with low donor concentrations ($N_D \simeq 3 \times 10^{17}$ cm^{-3}). Because of the low power delivered by our klystron and the poor Q of our cavity, we could not obtain such a large enhancement at 100 GHz. However, for samples with concentrations ranging from 4.5×10^{17} to 10^{18} cm^{-3} (samples M5, M6, M7) we have observed line shapes depending on the direction of passage, very similar to those observed, for example, by Guéron and Ryter in LiH [10]. As will be discussed in the next section, these power-dependent effects are attributed to dynamic polarization of ^{31}P nuclei in presence of saturation of the electronic resonance line.

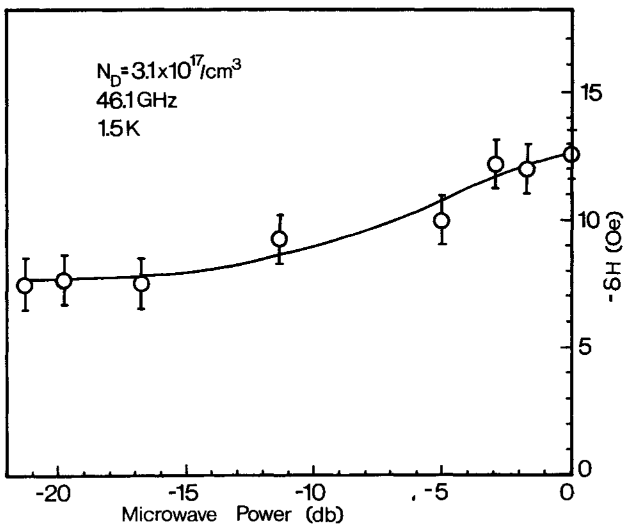

FIG. 2. — Peak shift, δH, as a function of microwave power at 1.5 K and 46 GHz for sample M4 ($N = 3.1 \times 10^{17}$ cm^{-3}) (after ref. [6]).

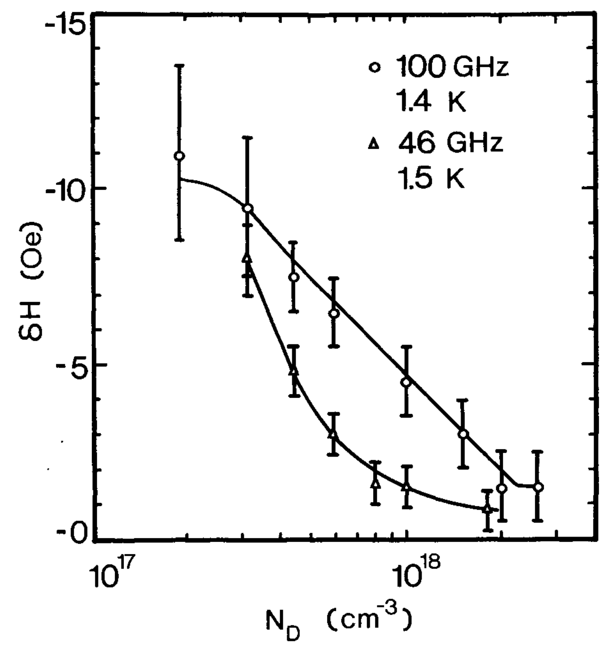

FIG. 3. — Peak shift, δH, as a function of donor concentration, N_D, at 1.4 K and 100 GHz and also at 1.5 K and 46 GHz, in the low power limit.

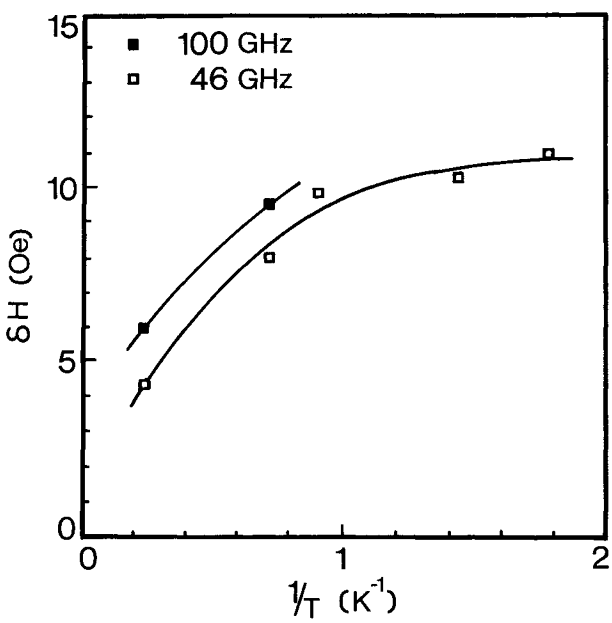

FIG. 4. — Peak shift, δH, as a function of temperature at 100 GHz and also at 46 GHz for sample M4 ($N_D = 3.1 \times 10^{17}$ cm^{-3}), in the low power limit.

Thus we have measured the magnitude of the shift of the peak position at microwave levels as weak as possible. The *low power limit* shift is plotted as a function of donor concentration in figure 3 as well as that measured at 46 GHz [6]. As seen from this figure, it is confirmed that the peak shift depends on the microwave frequency, that is to say on the resonant magnetic field, and also on the donor concentration as previously pointed out. It also depends on temperature as shown in figure 4, where results taken at 46 GHz [11] are also shown.

However, a careful study of ESR line shapes has shown that, even in the low power limit, the central line remains asymmetric. Thus the definition of the shift is ambiguous as the peak position, which we have been concerned with up to now, does not coincide with the center of gravity of the line. In all cases, the peak shift remains of the same order of magnitude as the linewidth (see table I), and we may conclude that both are due to the same cause. This will be discussed in more detail in the next section.

Remark. In samples with concentration from 10^{18} to 2×10^{18} cm^{-3}, several lines were observed at 100 GHz instead of the two lines observed at

46 GHz [2] : The origin of these lines is not clear at present, but it seems more complicated than was expected from the two systems model that was proposed previously. Further work is required for the detailed study of this concentration range, and this will appear in a forthcoming paper.

4. **Discussion.** — As has been pointed out in section 3, the peak shift of the central ESR line may be divided into two parts : the microwave power-dependent one and the low power limit part.

First, we consider the microwave power-dependent peak shift. When the resonance line is saturated by microwave irradiation, the nuclear spins interacting with the electron spins may be polarized as a result of the Overhauser effect. This effect gives rise to a nuclear field acting on the electronic spins [12]. Such a nuclear field, H_n, is expressed as :

$$H_n = \frac{8\pi}{3} \mid \psi(r_n) \mid^2 \gamma_n \hbar \langle I_z \rangle \qquad (1)$$

where $\mid \psi(r_n) \mid^2$ is the electron density at the position r_n of the nuclear spin, γ_n the gyromagnetic ratio of the nuclear spin under consideration, and $\langle I_z \rangle$ the average value of the nuclear spin. When the nuclear spins of ^{29}Si and ^{31}P are completely polarized, the values of the nuclear field given by eq. (1) are as follows : $H_n = -10.1$ Oe for ^{29}Si, using the electron density determined by Lampel and Solomon [13] and $H_n = +21$ Oe for ^{31}P, using the electron density of the donor electron localized at the donor impurity [14].

The nuclear polarization, P, enhanced through the Overhauser effect is given by [15]

$$P = \tanh \left[- \frac{\hbar \omega_n}{2 k_B T} \left(1 - s' \frac{\gamma_e}{\gamma_n} \right) \right] \qquad (2)$$

where ω_n, k_B, T and γ_e designate respectively the resonance frequency of the nuclear spin, the Boltzmann constant, the temperature and the gyromagnetic ratio of the electron spin; when $k_B T$ is greater than the electronic Zeeman energy, s' is equal to the saturation factor, s, which is given as follows for the homogeneous broadening case :

$$s = \frac{\gamma_e^2 H_1^2 T_1 T_2}{1 + \gamma_e^2 H_1^2 T_1 T_2} \qquad (3)$$

where T_1, T_2 and H_1 designate the spin-lattice relaxation time of the electron, its transverse relaxation time, and the magnitude of the microwave magnetic field respectively.

In order to make a comparison with experiment, we consider the result of the microwave power-dependent peak shift observed in the sample with $N_D = 3.1 \times 10^{17}$ cm^{-3}. In this case, the microwave power-dependent peak shift is -5.5 Oe for a microwave level of -3 dB; this shift is obtained by subtracting the microwave power-independent shift of 9.5 Oe from the observed peak shift ($\simeq -15$ Oe). The shift of the power-dependent peak to the low field side is compatible with that deduced from the above mentioned nuclear fields due to ^{31}P and ^{29}Si nuclei. For a quantitative comparison, the observed peak shift can be understood by using eq. (1) and (2) with $s' = 0.5$; this magnitude of the saturation factor seems reasonable in our experimental conditions if we take the following values for the parameters involved in eq. (3); $H_1 = 60$ mOe for the microwave power level of -3 dB, $T_1 \simeq 10^{-4}$ s and $T_2 \simeq 10^{-8}$ s. These magnitudes of T_1 and T_2 are extrapolated from their observed values (1) at 9 GHz by assuming that T_1 and T_2 are almost independent of the magnetic field for concentrations above 10^{17} cm^{-3}. As such, the microwave power-dependent peak shift may be reasonably interpreted in terms of nuclear fields due to ^{31}P and ^{29}Si nuclei. This has also been confirmed by a recent double resonance experiment at 46 GHz [6].

Next, we consider the low power limit peak shift illustrated in figure 3; A preliminary attempt [2] to explain this shift has been made in the framework of a molecular field approximation; in this attempt, the peak shift is deduced by assuming that there exists an exchange interaction between donor clusters. Although the hyperfine interactions with ^{31}P and ^{29}Si nuclei are neglected in this calculation, so that no shift is expected in this framework, the peak shift may be obtained on the basis of the moment method, by considering that each donor cluster spin has a slightly different effective g-value arising from the different natures of donor clusters; these differences may be due to the differences between the sizes of the donor clusters and the strength of the exchange coupling within the clusters. In addition, Ginodman *et al.* [3] have derived the peak-shift by using the moment method and taking into account weak exchange interactions between donor clusters, and the hyperfine interaction with ^{31}P nuclei.

However, in both interpretations, we must assume that the exchange interaction between donor clusters is of the ferromagnetic type in order to understand the direction of the peak shift to the low magnetic field side. This sign of the exchange interaction seems difficult to understand. It is an essential difficulty for this phenomenological interpretation of the peak shift.

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(1) The magnitude of T_1 for Si : P has been measured at 9 GHz by Feher and Gere (at 1.25 K) and also by Maekawa and Kinoshita (at 1.25 K) [5, 16]. Their magnitude of T_1 is 10^{-4} s for
$$N_D = 3 \times 10^{17} \text{ cm}^{-3}.$$
We have no direct measurements for T_2 at 9 GHz for
$$N_D = 3 \times 10^{17} \text{ cm}^{-3}.$$
However Chiba and Hirai [17] have calculated $T_2 \simeq 2 \times 10^{-8}$ s, from their steady state spectra, by using the experimental data of T_1 at 1.6 K.

Recently, an alternative model has been proposed by one of the authors [7] which attributes the peak shift to an asymmetry of the spectrum rather than to a displacement of the ESR line. This model is based upon the clustering of donors with exchange interaction larger than the hyperfine interaction A with ^{31}P nuclei. We shall now give the main features of this model.

Neglecting the hyperfine interaction with ^{29}Si nuclei, we may write the electronic spin Hamiltonian as :

$$\mathcal{H} = \sum_i g_i \mu_B \mathbf{H}.\mathbf{S}_i + A \sum_i \mathbf{I}_i \mathbf{S}_i + \sum_{i<j} J_{ij} \mathbf{S}_i \mathbf{S}_j \qquad (4)$$

where $\sum_i g_i \mu_B \mathbf{H}\mathbf{S}_i$ is the Zeeman energy, $A \sum_i \mathbf{I}_i \mathbf{S}_i$ is the hyperfine coupling between the electronic spin $\mathbf{S}_i$ and the donor nuclear spin $\mathbf{I}_i$, $\sum_{i<j} J_{ij} \mathbf{S}_i \mathbf{S}_j$ is the exchange interaction between $\mathbf{S}_i$ and $\mathbf{S}_j$. The hyperfine term and the exchange term do not commute with each other ; Shimizu [18] has shown that in the case of the exchange interaction J_{ij} being of the same order of magnitude as the hyperfine coupling A, the ESR spectrum for a donor pair is asymmetric. Now the exchange interactions between individual spins vary over a very wide range from far below, to far above A. However, due to the non-commutation cited above, the exchange interactions $J \lesssim A$ are *picked out* in the following manner : donors with $J \gg A$ constitute clusters with spins $S > \frac{1}{2}$. These clusters interact with each other or with isolated donors, the average interactions between these different centers being of the order or smaller than A. Then, the asymmetry and width of the central line result from the distribution of these interactions.

The spectrum due to isolated donors and pairs has been explicitly calculated, without adjustable parameters for a sample with $N_D = 2 \times 10^{17}$ cm^{-3}. In this calculation, clustering of donors is calculated by the use of a Monte Carlo method. One also takes into account the fact that strongly coupled pairs with $J > g\mu_B H$ do not contribute to the resonance. A detailed account of this model is described elsewhere [7]. The observed spectrum at 1.4 K is compared with the result of the calculation in figure 5. The shape of the calculated ESR spectrum is in good agreement with the observed one. The dependence of the peak shift on temperature, magnetic field, and donor concentration can be *qualitatively* understood in terms of this model. Because of the increasing importance of large clusters and of the appearance of infinite clusters, the actual calculation of the spectrum is limited to the case of low donor concentrations such as $N_D \lesssim 2 \times 10^{17}$ cm^{-3}. Moreover, the number of donors interacting with their nearest neighbors with J greater than $g\mu_B H$ increases by increasing the donor concentration and these donors constitute clusters having either a spin $\frac{1}{2}$ or a spin 0 in their lowest state. However, their contribution to the resonance is expected to be rather weak, at least for the lower concentration range that we have considered ($N_D \lesssim 5 \times 10^{17}$ cm^{-3}).

FIG. 5*a*. — Recorded trace of the ESR absorption line, observed at 1.4 K and 100 GHz for sample M3 ($N_D = 1.9 \times 10^{17}$ cm^{-3}), in slow passage conditions.

FIG. 5*b*. — Integrated curve from the experimental trace shown in figure 5*a*.

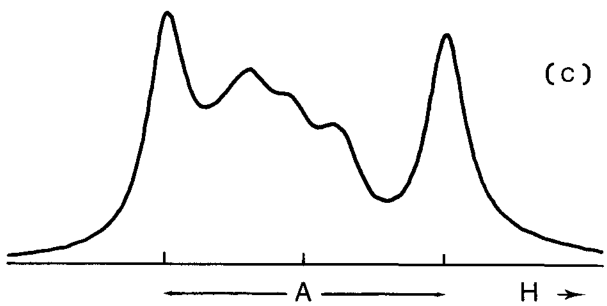

FIG. 5*c*. — ESR absorption line calculated at 0 K and 100 GHz for $N_D = 2 \times 10^{17}$ cm^{-3} (after ref. [7]).

5. **Conclusion.** — We have made ESR experiments at 100 GHz and 1.4 K in phosphorus-doped silicon with donor concentrations ranging from 1.9×10^{17} cm^{-3} to 2.8×10^{18} cm^{-3} : it has been found that the peak shift of the central ESR line from the center of the two hyperfine lines depends on the donor concentration, the temperature, and the microwave power. Such a peak shift may be regarded as due to an asymmetry over which is superposed a microwave power-dependent shift. The latter is interpreted in terms of the Overhauser effect which gives rise to an important nuclear field due to ^{31}P and ^{29}Si nuclei under partial or complete saturation of the central ESR line. The asymmetry is explained in terms of a new model [7] which takes into account the clustering effect of donors, as a function of the exchange interaction J, and the hyperfine interaction with ^{31}P nuclei. The comparison between the observed spectrum and the one calculated for

$N_D = 2 \times 10^{17}$ cm^{-3} shows satisfactory agreement. The dependence of the peak shift on the donor concentration, the magnetic field, and the temperature can be qualitatively understood in terms of this model. However, further study is required to understand quantitatively the variation of the spectrum for samples with higher donor concentrations, in which motional narrowing effects should be considered in order to understand the resonance spectrum and mutual interactions among the cluster spins. This study provides a better understanding about disordered spin systems and the donor states involved near the metal-non metal transition.

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