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An ESR hole burning study of dynamic nuclear polarisation of ^{29}Si in Si:B

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Abstract. Pulsed electron spin resonance (ESR) experiments are presented to study hole burning in the ESR spectrum of p-type Si:B. The results are used to determine the electron spin–lattice relaxation process and to prove that spectral diffusion is absent. It follows that dynamic nuclear polarisation of ^{29}Si nuclei in this substance arises from the 'solid effect'. Additional holes due to the transitions, where electron and nuclear spins flip simultaneously, are also observed. A study of these additional holes yields the probability of this latter type of transition.

1. Introduction

This paper considers hole burning experiments on the electron spin resonance (ESR) spectrum of boron acceptors in silicon. Our study is undertaken to clarify the mechanism of dynamic nuclear polarisation (DNP) where the high polarisation of the electron spins associated with the acceptors is transferred to the ^{29}Si spins by means of a microwave field (Dirksen 1989)

Two types of mechanism may be responsible for DNP in insulating solids. The distinction between the two is determined by the strength of the mutual interactions of the electron spins. When these interactions are strong, spectral diffusion will establish a quasi-thermodynamic equilibrium, characterised by two spin temperatures (Provotorov 1961), and the ESR line responds to a saturating microwave field as a homogeneously broadened line. In this situation holes cannot be burned in the ESR lineshape and DNP is caused by so-called 'thermal mixing' (Wenckebach *et al* 1974). If, in the other extreme case, the mutual interactions between the electron spins are negligible, the spins can be viewed as isolated from each other. Then one can perform so-called 'hole burning' experiments in the inhomogeneously broadened ESR line, i.e. one can saturate the electron spins with a resonance frequency in a narrow frequency interval (a 'spin packet') leaving the other spins undisturbed. Then, DNP is caused by the so-called 'solid effect'.

The observation of holes burned in the inhomogeneous ESR line of As-doped silicon has been reported by Feher and Gere (1959) and they gave two possible explanations for the occurrence of so-called subsidiary holes. In this paper we will show that similar holes can be burned in the ESR line of boron acceptors in silicon and that this phenomenon can be used to prove that the solid effect is responsible for the observed DNP. With this mechanism the large electron polarisation is transferred to the nuclear spins by so-called forbidden transitions, i.e. simultaneous flips of electron and nuclear spins. From the hole burning experiment we will also obtain an estimate of the forbidden transition probability.

2. The system Si:B

Silicon contains 4.7% ^{29}Si with nuclear spin $I = 1/2$ and a gyromagnetic ratio $\gamma = (2\pi)8.46 \times 10^6$ s^{-1} T^{-1}. The other nuclei have no nuclear spin. The electron spins needed for DNP were created by doping a dislocation-free single crystal of Si with 8×10^{22} m^{-3} boron acceptors.

All measurements are made at liquid helium temperatures, where the holes are bound to the boron acceptors. Furthermore, because of the low concentration, impurity bands do not occur. ESR signals can be observed of the $J = 3/2$ ground multiplet of the bound hole. Random stresses, however, broaden this ESR spectrum, rendering its observation difficult (Feher *et al* 1960) and making it useless for DNP (Abragam 1961). The ESR linewidth is reduced by applying uniaxial stress of 4 kbar along the [111] axis which we denote as the x axis. The energy levels characterised by the quantum numbers M_J of the operator J_x, then consist of two Kramers doublets $M_J = \pm 1/2$ and $M_J = \pm 3/2$, split by about 10 meV, of which the $M_J = \pm 1/2$ doublet has the lower energy.

The Zeeman interaction may be treated as a first-order perturbation and since at liquid helium temperatures the stress splitting between the two doublets is much larger then kT, ESR is observed of the $M_J = \pm 1/2$ doublet only. It is this doublet that we use for DNP. We will denote it as the electron spin $S = 1/2$ of the acceptor. In our experiments we orient the static magnetic field parallel to the z axis and hence perpendicular to the uniaxial stress. Then the g-value is equal to $g_\perp = 2.48$ and to first order stress independent, while the residual ESR linewidth, still arising from mainly random stresses, is about $(2\pi)50$ MHz.

3. Hole burning

Our hole burning studies are performed at 9.4 GHz, using a specially designed loop-gap resonator allowing for uniaxial stress, optical access and NMR detection (Dirksen 1989). A typical experiment is shown in figure 1. It is performed at 1.2 K while an uniaxial stress of 4 kbar is applied. It starts at $t = 0$ with a burning pulse of a length $\delta = 5$ μs at frequency ω_b as shown in figure 1(*a*). The major effect of this burning pulse is to saturate the spin packets with a Larmor frequency centred around ω_b, i.e. it burns a hole in the ESR line as shown in figure 1(*b*). We investigate the time evolution of this hole by measuring the ESR line intensity at a second frequency ω_p at a later time τ. For this purpose we monitor the amplitude of an electron spin echo, created with a $(\pi/2, \pi)$ probe pulse sequence, as shown in figure 1(*b*). The microwave power being 0.5 mW, the length of a $\pi/2$ pulse is typically equal to 3 μs, corresponding to a spectral resolution of approximately 80 kHz.

The absence of spectral diffusion to neighbouring spin packets is demonstrated very strikingly in figure 2(*a*) where it is seen that the hole maintains its shape and width during its time evolution after a short burning pulse with a length $\delta = 5$ μs. The results are obtained by scanning ω_p around ω_b at various values of τ. The maximum hole

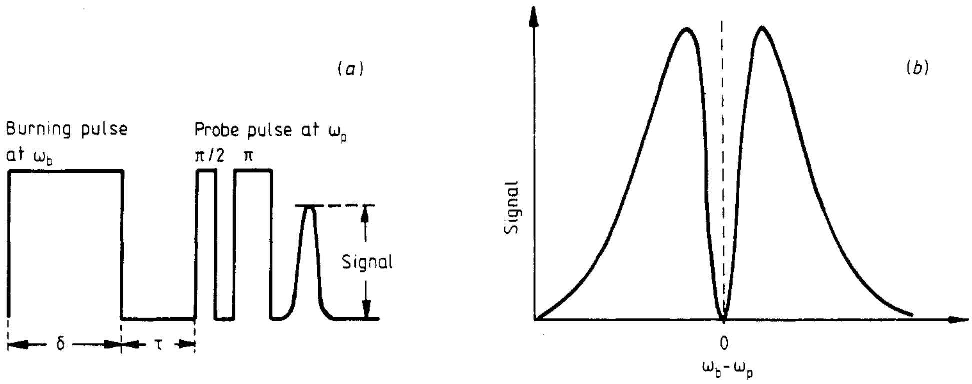

Figure 1. The hole burning experiment.

depth is observed after a short delay $\tau = 0.1$ ms. Then, the electron spin polarisation of the spin packets with a Larmor frequency ω_b is equal to zero. The hole depth is seen to diminish with increasing values of τ, until the polarisation has recovered to its equilibrium value.

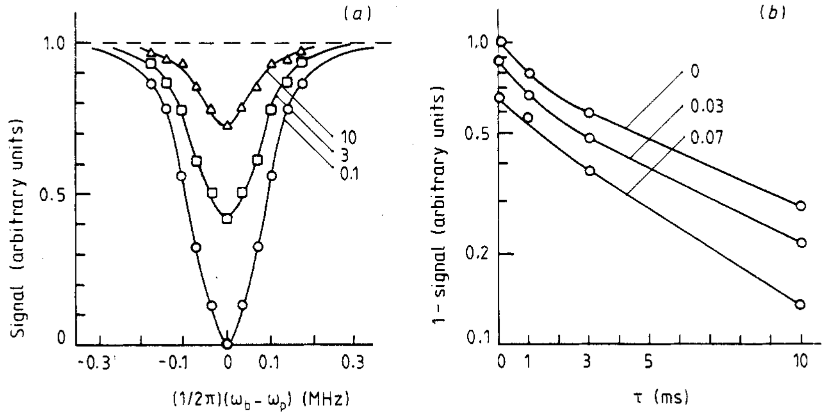

Figure 2. (*a*) The results of measurements of the hole burned in the inhomogeneously broadened ESR line with the ESE probe pulse at various delays τ (ms). (*b*) The decay of the intensity of the hole as a function of τ at three values of $(\omega_b - \omega_p)$ (MHz).

The conservation of the hole shape is even more clearly demonstrated in figure 2(*b*) where a semi-logarithmic plot is shown of the filling of the hole for various values of ω_p. Within our measuring accuracy, we find parallel curves for the various values of ω_p. The recovery curves are not exponential. However, the tails of the recovery curves can be described by a time constant $\tau_1 = 9 \pm 1$ ms, for each of the frequencies ω_p. Apparently the filling of the hole is not due to spectral diffusion to neighbouring spin packets and should be explained by either spectral diffusion to spin packets at a frequency strongly different from ω_b (Feher and Gere 1959) or by spin–lattice relaxation.

We could prove that spin–lattice relaxation is responsible for the filling of the hole and that consequently τ_1 has to be identified as the electron spin–lattice relaxation time T_{1S}. This conclusion was reached by measuring τ_1 as a function of temperature in the interval $1.2 < T < 4.2$ K, and as a function of the uniaxial stress from 0 to 7.5 kbar. The results for the temperature dependence are shown in figure 3 for a constant uniaxial stress of 7.5 kbar.

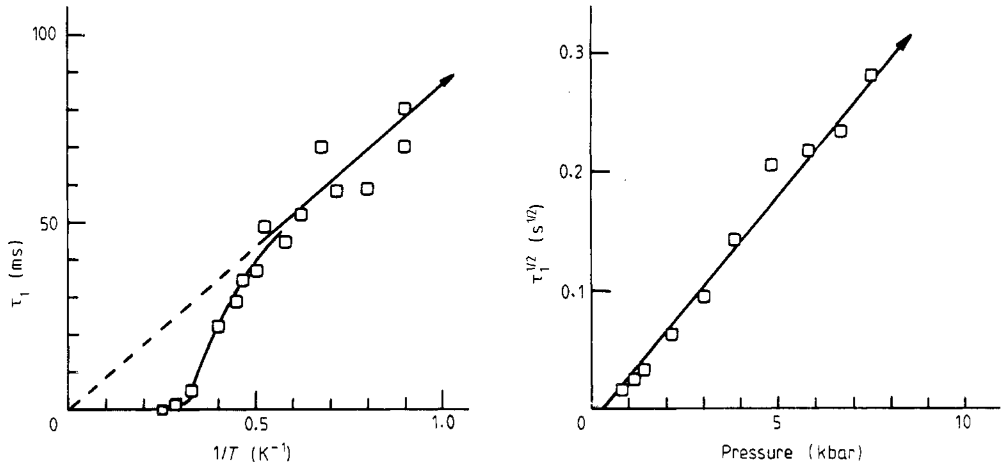

Figure 3. The relaxation time τ_1 under various experimental conditions.

Between 1.2 K and 2 K, τ_1 is found to be proportional to T^{-1} indicating a direct spin–lattice relaxation process. This interpretation is also supported by the observed dependence of τ_1 on the uniaxial stress shown in figure 3 at $T = 1.2$ K. As predicted by the theory for the direct process in Si:B (Orbach 1961) the spin–lattice relaxation time increases proportionally with the square of the splitting between the $M_J = \pm 1/2$ and $\pm 3/2$ doublets, and hence with the square of the pressure. The sudden decrease of τ_1 above 2 K (figure 3) is caused by the onset of the Orbach or Raman process (Orbach 1961) to the higher lying $M_J = \pm 3/2$ doublet as demonstrated already by Shimizu and Nakayama (1964).

4. The forbidden transitions

Two extra holes appear to be burned in the ESR spectrum when the length δ of the burning pulse is increased to about 100 μs or more. This is shown in figure 4(a), where the burning pulse length is varied from 10 μs to 10 ms. The experiment is performed at 1.2 K, while the uniaxial stress is 4 kbar and the delay time between the saturating pulse and the probe pulse sequence $\tau = 2$ ms. In contrast to the previous experiment the width of the total spectrum covers now a much larger range of about 3 MHz. The two additional holes appear at frequencies separated exactly by the Larmor frequency ω_I of the ^{29}Si spins from ω_b.

They can be explained to arise from so-called forbidden transitions $\Delta(S_z + I_z) = 0$ or 2, i.e. simultaneous flips of nuclear spins and electron spins in spin packets with a Larmor frequency $\omega_S = \omega_b \pm \omega_I$ (Abragam and Goldman 1982). They are induced by the microwave field and can be observed because dipolar interactions between electron spins and nuclear spins slightly mix their states. They lead to dynamic polarisation of

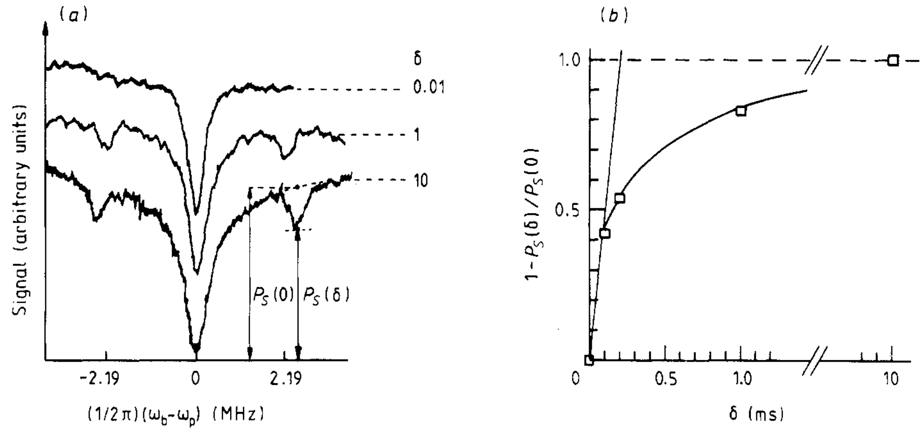

Figure 4. (*a*) The effect on the ESR lineshape of the burning pulse for various pulse lengths δ (ms). (*b*) The relative intensity of the 'forbidden holes' as a function of δ.

the nuclear spins (DNP) via the solid effect. The polarisation $P_S = \langle S_z \rangle / S$ of the electron spins in the spin packets at $\omega_S = \omega_b - \omega_I$ is transferred directly to the nuclear spins, thus leading to positive enhancement of the nuclear polarisation $P_I = \langle I_z \rangle / I$. On the other hand, the polarisation of the electron spins in the spin packets at $\omega_S = \omega_b + \omega_I$ is inverted in sign before being transferred to the nuclear spins. So this transition leads to negative enhancement of the nuclear polarisation. In both cases, the electron spin polarisation diminishes, however. So, if enough microwave power is available the forbidden transitions are 'saturated' and two extra holes at frequencies $\omega_S = \omega_b \pm \omega_I$ are observed.

The spectrum as shown in figure 4(*a*) is obtained by repeating the pulse sequence shown in figure 1 at intervals of 80 ms. If the neighbouring nuclear spins relax so rapidly in these intervals that their polarisation P_I is equal to zero at the beginning of each pulse sequence, the electron spin would share its polarisation P_S with all N_I neighbouring nuclear spins with which it mixes. Then P_S would be almost reduced to zero, and the forbidden holes would be as deep as the central hole around ω_b. However, we see that the holes burned in the ESR line remain relative shallow, despite the fact that the transitions are saturated. So, during the experiment the neighbouring nuclear spins apparently become highly polarised and subsequent transfer of their polarisation to other nuclear spins via spin diffusion and spin–lattice relaxation takes longer than 80 ms. Dirksen (1989) presents a quantitative model to calculate the effect of these processes on DNP and compare it with DNP experiments.

In figure 4(*b*) we show the relative intensity of the forbidden holes as a function of the burning time. The initial slope yields a value for the transition probability W for simultaneous electron and nuclear spin flips. From figure 4(*b*) we find 5×10^3 s^{-1} at a power level of 5 mW. The transition probability being proportional to the microwave power P, $W \simeq 10^6 P$ s^{-1} W.

It is well known that modulating the static magnetic field yields a pronounced increase of the DNP rate in crystals where the solid effect applies (Abragam *et al* 1971). This 'modulation effect' is usually described as arising from an increase of the number of electron spin packets participating in the DNP process. Without field modulation only those electron spin packets participate with resonance frequencies within a width

$\Delta\omega_0$ of the forbidden holes burned in the ESR line. With field modulation, this width is increased by the modulation amplitude $\Delta\omega_m$. Thus the DNP rate is enhanced by a factor that is at most $(1 + \Delta\omega_m/\Delta\omega_0)$.

Figure 5 shows a demonstration of this modulation effect by means of a hole burning experiment. The spectrum is obtained with a burning pulse of $\delta = 10$ ms, so that forbidden transitions are induced. In addition, we apply field modulation with an amplitude $\Delta\omega_m$ and a frequency of 1 kHz during the burning pulse. At large modulation amplitudes one clearly observes that the width of the forbidden holes increases to $\Delta\omega_m$.

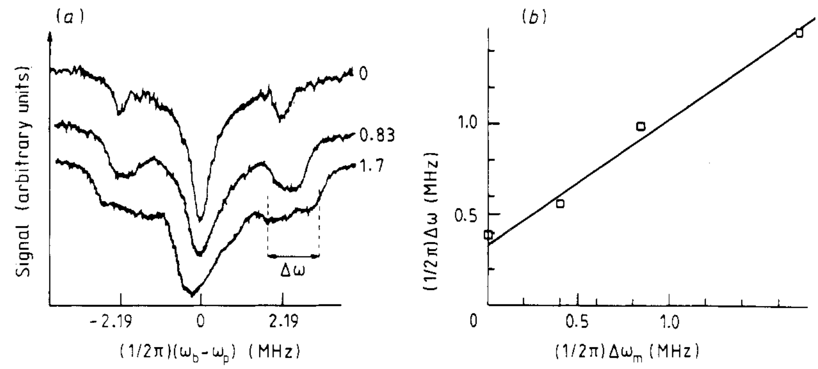

Figure 5. (*a*) The effect of field modulation on the holes burned in the ESR lineshape by a burning pulse with $\delta = 10$ ms. The frequency of the field modulation is 1 kHz and its amplitude is varied up to $(2\pi)1.7$ MHz. (*b*) The width of the forbidden holes as a function of the modulation amplitude.

5. Conclusions

To summarise, we have shown that at 1.2 K and with an uniaxial stress of 4 kbar holes can be burned in the ESR spectrum of Si:B and that spectral diffusion is not observed. These holes only fill due to electron spin–lattice relaxation. From this result we conclude that DNP in Si:B must be described by the solid effect. Beside a hole associated with the allowed transition, we observe two additional holes which we attribute to forbidden transitions $\Delta(S_z + I_z) = 0$ or 2. From the time evolution of these holes we estimate the forbidden transition probability to be $W = 10^6 P$ s^{-1} W. The broadening of these additional holes with field modulation during the burning pulse, supports the interpretation that the 'modulation effect' in a DNP experiment arises from an increase of the number of electron spin packets participating in the DNP process.

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