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Published on: 01 Feb 1978 - Journal De Physique Lettres (Les Editions de Physique)

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D. Kaplan, I. Solomon, N.F. Mott. Explanation of the large spin-dependent recombination effect in semiconductors. *Journal de Physique Lettres*, Edp sciences, 1978, 39 (4), pp.51-54. 10.1051/jphyslet:0197800390405100 . jpa-00231440

HAL Id: jpa-00231440

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Submitted on 1 Jan 1978

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Classification
Physics Abstracts
 72.20J

EXPLANATION OF THE LARGE SPIN-DEPENDENT RECOMBINATION EFFECT IN SEMICONDUCTORS

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(Reçu le 5 décembre 1977, accepté le 4 janvier 1978)

Résumé. — Les théories précédentes concernant la variation de photoconductivité à la résonance de spin (expériences de Lépine dans le silicium) prédisent un effet de 10 à 100 fois trop faible.

Nous proposons un modèle où, par suite du temps de vie plus court d'une paire électron-trou en configuration singulet, la distribution des spins des paires contient un surplus d'états triplets. Ce surplus est supprimé par saturation de la résonance, ce qui raccourcit ainsi le temps de recombinaison.

La variation peut atteindre 10 % et l'effet ne dépend pas du champ appliqué, en accord avec l'expérience.

Abstract. — Previous theories to explain the variation of photoconductivity upon saturation of electron spin resonance, as observed by Lépine in silicon, predict an effect 10 to 100 times smaller than experiment.

In the present model we show that, due to the shorter lifetime of electron-hole pairs in singlet configuration, the steady state spin distribution shows a surplus of triplet pairs. Saturation of resonance restores the random distribution, resulting in a shortening of the recombination time.

The relative variation can be as large as 10 %, and is field independent as confirmed by experiment.

This letter describes a model which explains *spin-dependent recombination* effects in semiconductors [1]. By this we mean the type of experiments whereby one saturates an electron spin resonance (ESR) and observes a modification of the carrier recombination rate. Typically one measures photoconductivity in a sample placed in an ESR microwave cavity with an applied dc magnetic field H_0 . When the magnetic field is swept through resonance a decrease of photoconductivity is observed which can be related to an increase in recombination rate. Various experiments of this kind have been reported in the case of silicon since the pioneering work of Lépine *et al.* [2], notably for surface recombination [3, 4], recombination in plastically deformed crystals [5, 6] and more recently

for amorphous films grown by silane decomposition [7]. A similar effect has been observed on the current of a p-n junction which depends on the recombination rate in the space charge region of the diode [8].

An understanding of this phenomenon can start from the implications of spin angular momentum conservation : if the spin-orbit interaction is not large, as is the case for silicon, recombination transitions will conserve total spin. If after the transition the system is without a spin (as for instance for free electron-free hole recombination) then the initial configuration must be $S = 0$ (singlet configuration) for the transition to take place. This consideration can be generalized to processes involving recombina-

nation centers, in which one or both of the carriers are trapped, provided the final state is an $S = 0$ state. A microwave field, strong enough to saturate the ESR of either the electron or hole, will produce an isotropic spin distribution in which the probabilities of singlet and triplet configurations will be $\frac{1}{4}$ and $\frac{3}{4}$ respectively. This will produce a change in recombination rate if the initial distribution was not isotropic. The center of the problem is the origin of this departure from isotropy.

The applied magnetic field H_0 polarizes the spins and so is responsible for some anisotropy. To calculate this one can write the projection operators π_T and π_S on the singlet and triplet manifolds as :

$$\begin{aligned}\pi_T &= \frac{3}{4} + \mathbf{S}_e \cdot \mathbf{S}_h \\ \pi_S &= \frac{1}{4} - \mathbf{S}_e \cdot \mathbf{S}_h\end{aligned}\quad (1)$$

where \mathbf{S}_e and \mathbf{S}_h are the electron and hole spin operators. Averaging over equilibrium spin populations one obtains a probability for the singlet configuration :

$$P_S = \frac{1}{4}(1 - p_e p_h) \quad (2)$$

where p_e and p_h are the equilibrium spin polarizations in the applied magnetic field. This was the model first proposed by Lépine [3]. From these formulae it is apparent that the maximum change ΔR of the recombination rate R is $\Delta R/R = p_e p_h$.

This is of order 10^{-6} at room temperature in a field $H_0 = 3000$ G. However some experiments performed under these conditions [3, 6-8] have yielded changes ΔI_p in the photoconductivity current as large as :

$$\frac{\Delta I_p}{I_p} \simeq 10^{-4}$$

Several attempts have been made to resolve this discrepancy : a) by considering situations where $\Delta I_p/I_p = \alpha \Delta R/R$ with α larger than unity [3]; b) by assuming a spin larger than $\frac{1}{2}$ due to ferromagnetic exchange interactions [6]; c) by a model of resonant heating of the spins system which can also produce a change of the recombination rate proportional to the product $p_e p_h$ [9]. We conclude however that the magnetic field polarization falls short of explaining the magnitude of the effect in the general case.

We present here a model in which the departure from isotropy does *not* have its origin in the applied magnetic field. The new ingredient in this model is the concept of a pair : we assume that before recombination takes place the electron and hole go through an intermediate state in which they are in a situation of proximity. From this pair state the electron-hole system can either recombine or dissociate, but not recombine with other electrons and holes.

Examples of such recombination involving pairs are exciton recombination and donor-acceptor recombination [10]. More generally if both the electron and

the hole are trapped before recombining, as for instance in highly disordered systems such as amorphous semiconductors, the concept of a pair will in many cases be approximately applicable : the recombination of a trapped electron with the nearest neighbour trapped hole will have a higher probability than with holes further away.

To understand how the existence of pairs introduces a spin correlation effect, we take the extreme case where pairs are created with random spin orientations and no spin relaxation occurs in the pair state. If this is the case, pairs created in singlet configurations have a shorter lifetime than pairs created in triplet configurations, consequently their steady state population will be smaller than in the random situation and we are left with a net surplus of triplet configurations. If one saturates the electron or hole spin resonance one returns to a random spin distribution which contains more singlets so that the recombination rate is enhanced. The pair concept is central because the spin orientation of the system as a whole remains random and it is only the orientation of the two spins in the same pair that is correlated.

To make an explicit calculation of the effect one must consider all spin configurations between the singlet and the triplet extremes. We use the usual vector representation in which to each spin quantum state (electron or hole) one associates a spin vector of length $\frac{1}{2}$ (in \hbar units) which has the property that its projections on axes x, y, z are equal to the quantum averages of S_x, S_y, S_z . In this representation one obtains the quantum average :

$$\langle \mathbf{S}_e \cdot \mathbf{S}_h \rangle = \frac{\cos \theta}{4} \quad (3)$$

where θ is the angle between electron and hole spin vectors and is the only parameter necessary to characterize the spin distribution for our purpose. For such a pair, the recombination probability per unit time can be expressed as

$$W_R(\theta) = W_S \langle \pi_S(\theta) \rangle \quad (4)$$

where W_S is the recombination rate for a pair in a pure singlet configuration. This assumes, for simplicity, that the triplet recombination is completely forbidden.

Using (1), (3) and (4), one obtains :

$$W_R(\theta) = W_S \frac{1 - \cos \theta}{4} \quad (5)$$

If the pairs with an angle between θ and $\theta + d\theta$ are created at the rate $c(\theta)$ and dissociate at a rate W_D [11], the steady state density of pairs with angle θ is given by detailed balance :

$$N(\theta) = \frac{c(\theta)}{W_R(\theta) + W_D} \quad (6)$$

In general $c(\theta)$, appearing in the usual rate equation [12], will depend on hole concentration p , electron concentration n and possibly on pair concentration $N(\theta)$. For simplicity and illustration purposes, we shall assume that the possible pair sites are weakly populated (which is certainly the case for an amorphous semiconductor with a large number of states in the gap) so that the creation rate is independent of the steady state concentration of the pair density $N(\theta)$. The pairs being created by capture from carriers with an isotropic spin distribution, it is reasonable to assume an isotropic distribution for $c(\theta)$ which then takes the form :

$$c(\theta) = \frac{C}{2} \sin \theta \quad (7)$$

where C is the total creation rate depending only on the concentrations n, p of injected carriers.

The variation of the density of pairs with angle θ takes the form :

$$N(\theta) = \frac{2 C \sin \theta}{4 W_D + W_S(1 - \cos \theta)}. \quad (8)$$

For comparison, we consider the case where the recombination rate W_R would be equal to the average value $W_S/4$, independent of the spin orientations. We then get the random distribution :

$$N_{\text{RAND}}(\theta) = \frac{2 C \sin \theta}{4 W_D + W_S}.$$

Figure 1 shows a plot of $N(\theta)/N_{\text{RAND}}(\theta)$ for various values of the ratio $\lambda = W_D/W_S$. As expected, when the dissociation W_D is not too fast compared to the

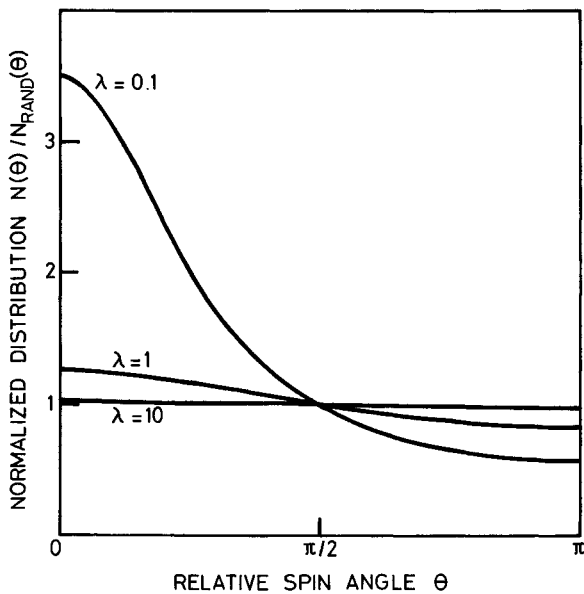


FIG. 1. — Steady state distribution of the angle θ between spins of the electron-hole pairs compared to a random distribution (see text), for different values of $\lambda = W_D/W_S$

$$\frac{N(\theta)}{N_{\text{RAND}}(\theta)} = \frac{1 + 4 \lambda}{1 + 4 \lambda - \cos \theta}.$$

singlet recombination rate W_S (i.e. λ not too large) the distribution is peaked at $\theta = 0$, showing a surplus of triplet orientations.

With this distribution, we are able now to calculate the magnitude of the spin-dependent effect on recombination. The total recombination rate is obtained by summing $N(\theta) W_R(\theta)$ over all possible values of θ :

$$R = \int_0^\pi N(\theta) W_R(\theta) d\theta. \quad (9)$$

Using (5) and (8) this gives, expressed as a function of $\lambda = W_D/W_S$:

$$R = C \left[1 - 2 \lambda \log \frac{1 + 2 \lambda}{2 \lambda} \right]. \quad (10)$$

Now the resonant saturation of either the electron or the hole spin [13], extrapolated to infinite microwave power, restores the spin-pair random distribution, and the pairs recombine at a rate given by the average of expression (5) :

$$\overline{W}_R = W_S/4.$$

The recombination rate is then simply

$$R_{\text{SAT}} = \frac{C}{1 + 4 \lambda}. \quad (11)$$

Thus in the present model the spin dependent recombination effect is simply due to the change of the recombination rate from R to R_{SAT} when one saturates the spin resonance line. The relative change

$$\frac{\Delta R}{R} = \frac{R - R_{\text{SAT}}}{R}$$

is plotted in figure 2 as a function of $\lambda = W_D/W_S$.

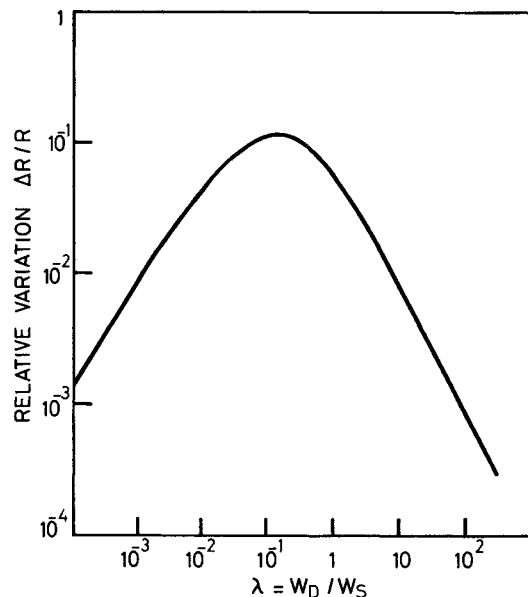


FIG. 2. — Relative variation of the recombination rate $\Delta R/R$ obtained by saturation of the ESR as a function of dissociation to singlet recombination rate ratio $\lambda = W_D/W_S$. For λ varying over 6 orders of magnitude, $\Delta R/R$ remains larger than 10^{-3} .

A maximum effect of the order of 10 % is obtained for $\lambda = 0.3$. For smaller values of $\lambda = W_D/W_S$ the dissociation probability is small so that the recombination rate is essentially equal to the pair creation rate C , i.e. spin independent. For large λ the pair lifetime is dominated by the dissociation process and the triplet enhancement in eq. (8) becomes small.

We have thus shown the possibility of relative variations of the recombination rate as high as 10 % upon application of a resonant microwave field. The actual effect will in fact be smaller because of a number of considerations omitted in the present simplified picture :

- Finite triplet recombination ;
- Distribution in λ values ;
- Spin relaxation processes in the pair state ;
- Incomplete saturation of the resonance ;
- Existence of competing recombination mechanisms that do not involve pairs.

Work is in progress to introduce these effects in the general description. Altogether they can lead to the experimentally observed value $\Delta R/R \lesssim 10^{-4}$.

Another omitted problem is the exchange interaction between an electron and a hole in a pair. If it is large compared to the difference of their Zeeman energies, the rf field will not change the angle θ . This implies that the overlap between the two wavefunctions must be small, but still large enough to allow a finite recombination probability. For carriers trapped

in localized states of sufficient depth, pairs having these properties can certainly exist.

The situation is different if one or both carriers are in shallow states. In this case, the Coulomb interaction may play a role, and a bound pair (exciton) can exist with large overlap, as envisaged by Pai and Enck [14] for chalcogenides and Engemann and Fischer [15] for silicon. If so, and if the mean free path is small, we may apply the classical analysis of Onsager [16] : thermal energy can separate the carriers from time to time up to a distance $e^2/\kappa kT$ without them subsequently becoming free. At this distance the exchange may be small enough to allow the rf field to change θ and thus increase the probability of recombination when the carriers return to the ground state of the pair.

A remarkable feature of the present theory is that it predicts a spin-dependent effect independent of the applied magnetic field in the first order of approximation. This has been verified in a preliminary experiment [17] where the spin-dependent photoconductivity has been measured on the same amorphous silicon sample at two resonance frequencies of 9.3 GHz and 1.9 GHz. Instead of a spin dependent effect varying like the square of the resonance field (a factor $(9.3/1.9)^2 = 24$ in this experiment) as predicted by the previous models [3, 6, 9], the same variation $\Delta R/R \simeq 0.5 \times 10^{-4}$ (extrapolated to complete saturation) has been obtained at the two frequencies, thus providing a crucial test for the present theory.

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