

# OPTICAL SPIN POLARIZATION IN MOLECULAR CRYSTALS

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## ABSTRACT

The subjects of this paper are two closely connected phenomena:

(1) The polarization of the electronic spin  $S$  of optically excited triplet states in molecular crystals, termed OEP.

(2) The polarization of nuclear spin  $I$  in molecular crystals due to their interaction with polarized triplet states and triplet excitons, termed ONP.

Section II deals with OEP; typical experimental results are presented with the example of naphthalene. The origin of this OEP is discussed; it is caused by symmetry selection rules for the population and depopulation of the three triplet levels.

ONP is treated in Section III. Experimental results are given for pure and doped crystals at room temperature as a function of the magnetic field  $H_0$  and its orientation with respect to the axes of the crystal. The results obtained in high magnetic field can be interpreted by transfer of OEP to the nuclear spins by hyperfine relaxation transitions analogous to the Overhauser effect. On the other hand, the relaxation interactions cannot be responsible for the large ONP observed in low fields around 100 G; a possible mechanism for explaining these results is based on selective population of nuclear substates.

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## I. INTRODUCTION

In this paper I would like to report on the polarization of electronic and nuclear spins by light. If one irradiates with light an aromatic monocrystal of for instance anthracene, which is placed in a magnetic field  $H_0$ , one observes considerable enhancement with respect to the static polarization of the nuclei. The largest enhancement factor measured so far at room temperature is about  $10^4$ . *Figure 1* shows the magnetization  $M \propto \langle I_z \rangle$  as a function of time, if the magnetic field  $H_0$  is reduced from a high value of 15 kG to 250 G, in the dark and for two light intensities. As can be seen, the magnetization with irradiation does not approach the equilibrium value for 250 G, but a much larger, in this case negative value. We shall see that this ONP originates from the interaction between the nuclear spins  $I$  of the protons and the electronic spins  $S$  of the optically excited paramagnetic triplet states, and we shall further see that the distribution of the electronic spins into the three triplet levels deviates strongly from the Boltzmann equilibrium, i.e. the electronic spins  $S$  exhibit a marked OEP.

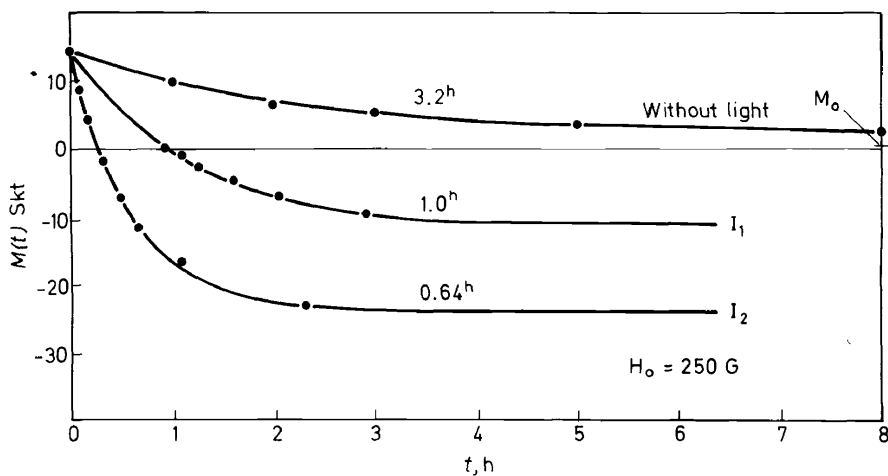


Figure 1. Magnetization as a function of time without light and for two different light intensities when reducing  $H_0$  at  $t = 0$  from 15 kG to 250 G.  $M_0$  = equilibrium magnetization without light at  $H_0 = 250$  G

In order to understand these observations we have first to remember some properties of triplet states, which we shall do with the example of naphthalene, Figure 2. Similarly to the most simple 2-electron system—the helium atom—molecules possess a triplet system in addition to a singlet term

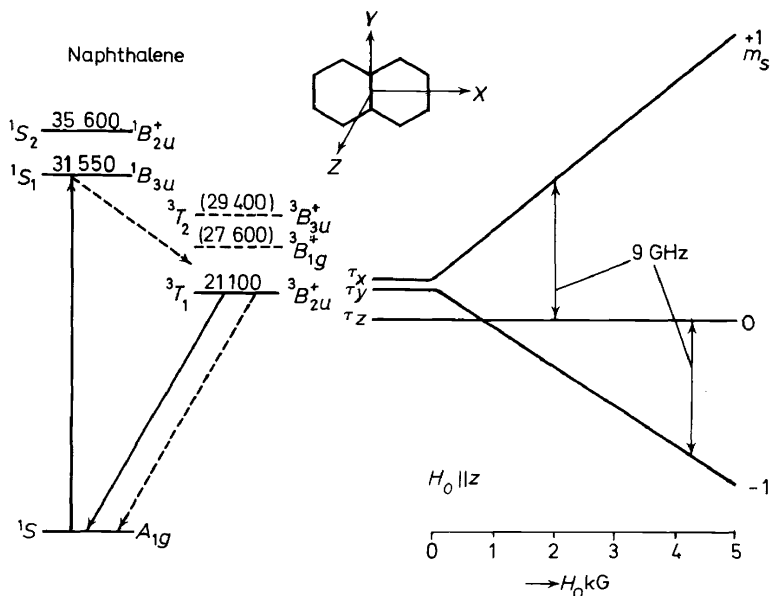


Figure 2. Excited states and triplet energy levels of naphthalene

system. Transitions between the two systems are 'spin forbidden', with the result that the lowest triplet state is a long-lived metastable state. In contrast to a free radical with one unpaired electron the two unpaired electrons of a triplet are, in addition to their Zeeman interaction with the external magnetic field  $H_0$ , dipole coupled to each other which results in the spin Hamiltonian:

$$\mathcal{H}_S = \mu_B H \cdot g \cdot S + DS_z^2 + E(S_x^2 - S_y^2) + S \cdot A \cdot I + \mu_k \cdot H \cdot g_k \cdot I \quad (1)$$

If we neglect the first hyperfine interaction term and consider the energy levels of the triplet state without external magnetic field  $H_0$ , we find zero-field splitting due to the dipole coupling, the magnitude of which is determined by  $D$  and  $E$ . We may imagine the meaning of the spin functions  $\tau_i$  as follows: the two electrons coupled to a spin  $S = 1$  are oriented with respect to the molecular frame in the absence of a magnetic field. However, *within* the molecules they are not oriented in certain directions but in planes, i.e. the spin functions  $S_z$  means that the spin  $S$  is oriented in the plane perpendicular to the  $z$ -direction, which in the case of naphthalene with  $D_{2h}$  symmetry is the molecular plane.

If we apply an external magnetic field  $H_0$ , e.g. parallel to the  $z$ -axis as in *Figure 2*, we obtain, in addition to the dipole interaction, the electronic Zeeman interaction and also the nuclear Zeeman term, which is much smaller and which we shall neglect here. It is obviously important for the behaviour of the triplet state whether we are in a high field range, where the Zeeman energy is large as compared to  $D$ ,  $\mu_B(H \cdot g \cdot S) \gg D$ , and  $m_S = 0, \pm 1$  is a good quantum number suitable for identification of the three triplet levels, or whether we are in low field,  $\mu_B(H \cdot g \cdot S) \ll D$ , where the states are determined by their spin functions  $\tau_i$ . The  $D$  value of naphthalene is about  $0.1 \text{ cm}^{-1}$ , hence the criterion of low field is fulfilled up to several hundred gauss, and the criterion of high field from several thousand gauss. As usual the situation is more complicated in the transition range.

Now let us consider the two effects mentioned in the beginning. Schworer and Wolf<sup>2</sup> showed in 1966 by esr measurements that the population of the three triplet levels is far from being equal, but obeys certain selection rules. The same is true for the depopulation. Other authors<sup>3</sup> had drawn similar conclusions from optical measurements at about the same time. Under certain conditions this selective population can result in a very marked electronic polarization (OEP), which I shall consider in Section II of this paper.

The hyperfine interaction between the nuclei  $I$  and the electrons  $S$  is described by the fourth term in the Hamiltonian. Its time dependent part is the most important mechanism for nuclear relaxation. If the population of the electronic levels deviates markedly from the Boltzmann equilibrium this relaxation interaction causes a dynamic polarization of the nuclei due to the Overhauser effect, which was discovered in 1953. We shall term this polarization, because of its origin from optical radiation, 'ONP', and I shall deal with it in Section III.

## II. OEP

In order to understand the OEP we have to consider the selection rule for

the population and depopulation of the different triplet sub-levels. In principle the transitions between the singlet and triplet systems are 'spin-forbidden'; however, this 'forbiddenness' can partially be lifted by admixture of some singlet character to a triplet state and vice versa. Such an admixture occurs especially by a spin orbit coupling operator, which, however, does not mix all singlet and triplet states, but only states of identical symmetry. The symmetry of a singlet state is completely determined by its orbital symmetry; in the case of naphthalene the first excited singlet state  $^1S_1$  is of  $B_{3u}$  symmetry. The symmetry of the triplet sub-levels, on the other hand, is given by the product of the orbital symmetry of the  $^3T_1$  state ( $B_{2u}$  in the case of naphthalene) with the symmetry of the respective triplet spin function, which is different for all three spin functions  $\tau_x$ ,  $\tau_y$ , and  $\tau_z$ . This can easily be seen if one remembers that the spin functions correspond to the orientations of spins in the three symmetry planes of the molecule, and that these three planes behave differently with respect to symmetry operations. The important consequence of this difference is that the symmetry condition of the admixture of the first singlet state is only fulfilled for one of the three triplet sub-levels. I do not intend to go into details of the three spin functions  $\tau_i$  of the naphthalene molecules which possess the symmetries  $B_{3g}$ ,  $B_{2g}$  and  $B_{1g}$  since the emphasis is to be on the principle of the selection rules. However, I should mention that this description is very simplified. In addition to the admixture of the first excited state, admixtures of higher excited states may not be negligible, or the admixture of a basically 'symmetry forbidden' electronic state can occur by a non-totally symmetric vibration, which complicates the theoretical calculations.

Both radiative transitions ( $^1S_0 - ^3T_1$  absorption and phosphorescence) and radiationless transitions between the singlet and the triplet system become possible by this mixture of states. It turns out that for the population the radiationless transitions are most efficient and hence the triplet states are

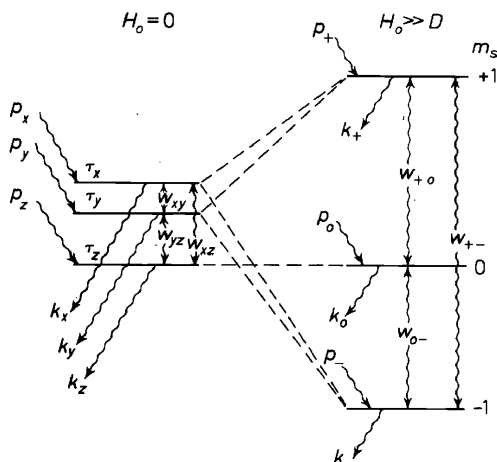


Figure 3. Rate constants of population, depopulation and relaxation in zero magnetic field and in high magnetic field

populated in most cases following the well-known Jablonski scheme by  $^1S_0 \rightarrow ^1S_1$  absorption and intersystem crossing.

We shall now consider the equilibrium population of the three triplet sub-levels  $\tau_i$  with this mechanism. It depends on the three rate constants  $p_i$  for the population and on the three rate constants  $k_i$  for the depopulation, Figure 3. For a complete description of the system, however, we must also consider the three rate constants  $w_{ij}$ , which measure the spin-lattice relaxation transitions between the three levels. The latter increases rapidly with increasing temperature, with the result that at room temperature the population does not deviate very much from the Boltzmann equilibrium, due to fast relaxation.

If we now apply a high magnetic field  $H_0$  as defined above, the population results, in analogy to zero field, from nine rate constants, where the rate constants  $p_i$  and  $k_i$  are linear combinations of the zero field constants, due to the mixture of states by the external magnetic field. In the general case, the three Zeeman levels characterized by the quantum numbers  $m_s = 0, \pm 1$  are linear combinations of all three zero field functions  $\tau_x$ ,  $\tau_y$  and  $\tau_z$ . In the special case  $H_0$  parallel to one of the three main axes, the middle level  $m_s = 0$  contains only the pure spin function corresponding to this axis, and the two

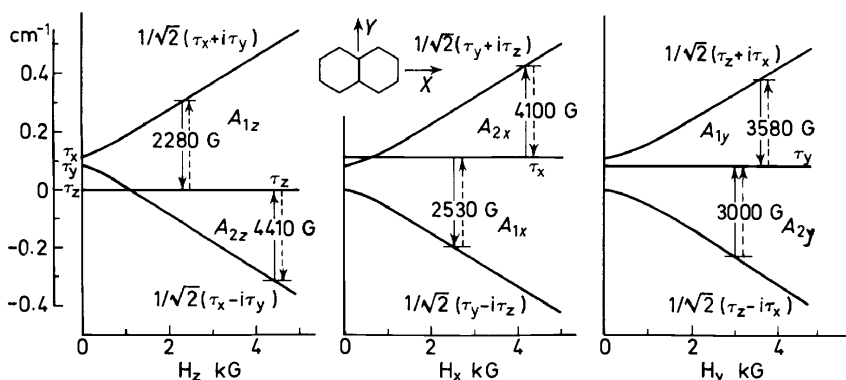


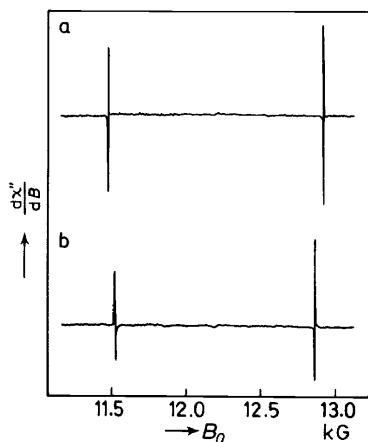
Figure 4. Energy levels, spin functions and esr transitions of naphthalene for  $H_0$  parallel to the main axes<sup>2</sup>

other levels  $m_s = \pm 1$  are linear combinations of the other zero field functions. If for instance  $H_0$  is parallel to  $z$  as in Figure 2, the state  $m_s = 0$  contains only the zero field function  $\tau_z$ , and the two states  $m_s = \pm 1$  are linear combinations of the other two zero field functions  $\tau_x$  and  $\tau_y$ . For  $H_0 \rightarrow \infty$  this mixture is complete, i.e. the coefficients of  $\tau_x$  and  $\tau_y$  are equal for  $m_s = +1$  and for  $m_s = -1$ ; hence the corresponding rate constants,  $p_+ = p_-$  and  $k_+ = k_-$ , are also equal, and correspondingly the populations are also equal,  $N^+ = N^-$ , i.e.  $\langle S_z \rangle = N^+ - N^- = 0$ , i.e. the OEP approaches zero for  $H_0 \rightarrow \infty$ . The degree of mixture in the usual magnetic fields achieved experimentally will be discussed later. Now we shall look at the experimental

results of Schworer and Sixl<sup>2</sup> for naphthalene at 4.2 K, where the relaxation is still sufficiently slow, *Figure 4*.

At a microwave frequency of about 9 GHz we observe in some cases absorption, as usual, and in some cases emission. The two levels which contain the spin function  $\tau_x$  are always found to be more populated than the others. It is impossible to deduce from such static measurements whether the steady state OEP is mainly due to the selection rules of the population or of the depopulation. However, an analysis of dynamic measurements shows that in the case of naphthalene the OEP originates from selective population of the  $\tau_x$  level. The depopulation rate from this level is also the largest and hence decreases the equilibrium value of the OEP, but the difference is less than for the population rates. In the case of other molecules, however, the reverse was also found, that is, that OEP is due to selective depopulation. At higher temperatures one observes absorption instead of emission as expected because of the increasing relaxation rates.

All these investigations are performed with isolated molecules, i.e. with naphthalene- $h_8$  in a heavy matrix of naphthalene- $d_8$ . The measurement of



*Figure 5.* ESR of triplet excitons in naphthalene<sup>4</sup>

triplet excitons, however, leads to analogous results, as shown in *Figure 5b* after Haarer and Wolf<sup>4</sup>, again with the example of naphthalene.

Since the excitons in naphthalene jump back and forth between the molecules in the two different orientations in the crystals one observes only two exchange-narrowed lines each of which results from averaging between two lines of differently oriented molecules. As can be seen from the phase of the esr absorption line one finds the usual absorption with one line and emission with the other, as well as with localized triplet states.

### III. ONP

Now we shall go on to deal with the ONP. In doing so we shall restrict ourselves to the high field case, where the electronic energy levels can be

described by the magnetic quantum number  $m_s$ , similar to the case of free radicals with spin  $S = \frac{1}{2}$ . Furthermore, we shall restrict ourselves to pure crystals with freely mobile triplet excitons. In this case we shall explain the ONP on the basis of relaxation interaction between the protons and the electrons by time dependent hfs interaction in analogy to the DNP by Overhauser effect. We shall start from the known theory of DNP in solutions of free radicals and discuss the modifications which are necessary for our case. One modification is that the time dependence of the hfs interaction is due to the migration of the excitons through the crystal. Measurements, which I have no space to discuss here, have shown that the correlation time  $\tau_c$  of this migration is of the order of several picoseconds, in other words, the excitation energy stays for a few picoseconds on one particular molecule and then jumps to the neighbour molecule<sup>3,6</sup>.

At this point it may be useful to remember the principle of DNP by Overhauser effect. We shall do so using the nomenclature of a recent review article<sup>7</sup>. The relative polarization  $P$ , i.e. the enhancement factor with respect to the polarization in the temperature equilibrium in the same magnetic field, is defined by

$$P = \frac{\langle I_z \rangle - I_0}{I_0} = \xi f \frac{S_0 - \langle S_z \rangle}{S_0} \frac{S_0}{I_0} \quad (2)$$

The coordinate system is chosen so that the  $z$  axis is parallel to  $H_0$ .  $\langle I_z \rangle$  is the expectation value of the nuclear polarization and  $I_0$  the same quantity in temperature equilibrium following Curie's law,  $I_0 \propto I(I+1)\gamma_1 H_0$ .

The important parameters in equation 2 are the coupling parameter  $\xi$ , the leakage factor  $f$  and the term  $(S_0 - \langle S_z \rangle)/S_0$  which measures the deviation of the electronic spins from Boltzmann equilibrium and is frequently termed the saturation parameter. All three parameters must be modified for our case of electronic spin  $S = 1$  and single crystals, rather than  $S = \frac{1}{2}$  and liquids as dealt with in ref. 7.

Let us first consider the coupling parameter  $\xi$  neglecting the constant factor  $I(I+1)/S(S+1)$ .  $\xi$  has different values depending on the nature of the coupling, scalar or dipolar. For pure scalar coupling  $\xi = -1$ . For dipolar coupling the spatial average of  $\xi = \frac{1}{2}$  in liquids (this holds only for the fast narrowing case  $\tau_c \cdot \omega_s \ll 1$ , which is, however, approximately true in our case with  $\tau_c$  values of several picoseconds). On the other hand, in a single crystal  $\xi = \xi(\theta)$ , where  $\theta$  is the angle between the connecting vector between nucleus and electron and the external field  $H_0$ <sup>8</sup>. A comparison of theory with the experimental results is complicated by the fact that in most aromatic crystals six or more values of the angle  $\theta$  for intramolecular interaction and many more for intermolecular interaction must be considered.

The second important modification concerns the  $\langle S_z \rangle$  value. In the DNP the deviation of  $\langle S_z \rangle$  from the equilibrium value  $S_0$  is effected by saturation of the esr transitions. Complete saturation corresponds to  $\langle S_z \rangle = 0$ , i.e.  $0 < \langle S_z \rangle \leq S_0$ . In our case of ONP,  $\langle S_z \rangle$  is given by the selective population and depopulation of the three triplet sub-levels and the relaxation rates between them. In contrast to the ordinary Overhauser effect this  $\langle S_z \rangle$ , due to optical irradiation, can be much larger than  $S_0$  and also negative, particularly in low field. For  $H_0 \rightarrow \infty$ ,  $\langle S_z \rangle$  approaches zero, because for an

infinitely high magnetic field  $H_0$  the admixture coefficients of the zero field spin states to the two states  $m_s = \pm 1$  are equal, and hence the populations of the latter are equal. We are interested in the value of  $\langle S_z \rangle$  in high fields which are not infinite but on the order of 2 to 20 kG. In order to find this  $\langle S_z \rangle$  we start from three rate equations with nine rate constants  $p_i$ ,  $k_i$ , and  $w_i$  mentioned above and obtain after some simplifications<sup>9</sup>

$$\frac{S_0 - \langle S_z \rangle}{S_0} = \left[ 1 + \frac{w_{ik}}{6k} \left( \frac{1}{k_i^r} + \frac{1}{k_k^r} \right) \right]^{-1} \left\{ 1 - \frac{N}{6(N_i^0 - N_k^0)} \left[ \left( \frac{1}{k_i^r} + \frac{1}{k_k^r} \right) \langle (p_i^r - p_k^r) + (k_k^r - k_i^r) \rangle \right] \right\} \quad (3)$$

The factor in the first bracket which we call 'life-time factor' contains basically the ratio of the relaxation rate to the rate constants of the depopulation (the reciprocal life-time)  $1/(1 + w/k)$ . If this ratio is large, i.e. the relaxation is fast, the life-time factor becomes small and the deviation of  $\langle S_z \rangle$  from  $S_0$  is small, too. On the other hand, if the ratio is small the life time factor approaches 1 for vanishing relaxation and  $\langle S_z \rangle$  is essentially determined by the expression in the brackets  $s_{ik}^*$  which we denote as 'reduced electronic polarization factor'. The mixing of states is already taken into account in the rate constants  $p_i$  and  $k_i$ , which are not the zero field constants, but which are different for each magnetic field and must be calculated for each field from the mixture of the zero field functions. Hence the bracket term  $s_{ik}^*$  is a measure for  $\langle S_z \rangle$  except of the life-time factor.

Let us now consider the particular molecule of phenazine with which most of our experiments in high field have been performed. The crystal structure is monoclinic, two molecules per unit cell. The term scheme and the triplet levels are shown in *Figure 6*. In contrast to naphthalene the  $^1S_1$  state

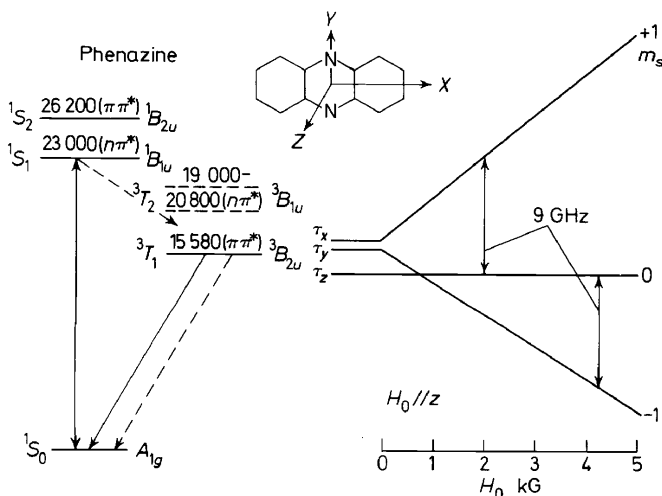


Figure 6. Excited states and triplet energy levels of phenazine



is an  $n-\pi^*$  term which is mixed very effectively by spin orbit interaction with the  $\pi-\pi^*$   ${}^3T_1$  state; hence one finds here experimentally the theoretically expected selectivity of the population,  $p_x \gg p_y, p_z$ <sup>10</sup>.

Preliminary computer calculations<sup>9</sup> using the numerical values of phenazine rendered the following result for the reduced electronic polarization factor  $s_{ik}^*$ :

(1) The very marked orientation dependence of  $s_{ij}^*$  is qualitatively similar for different  $H_0$  but decreases in magnitude with increasing field.

(2) The mixing of states is incomplete up to several tens of thousands gauss yielding values of  $s_{ik}^*$  at 11 kG, the highest field investigated experimentally, which are still several times as high as the static polarization in Boltzmann equilibrium for  $H_0$  parallel to the molecular axes and at least one order of magnitude higher for arbitrary directions of  $H_0$ . This result means also that the assumption that  $m_s$  is a good quantum number is not yet a good approximation even at fields as high as 11 kG.

Finally we must consider the leakage factor  $f$  which is defined by  $f = \rho / (\rho + w^0)$ , where  $\rho$  is the spin-lattice relaxation rate of the nuclear spins  $I$

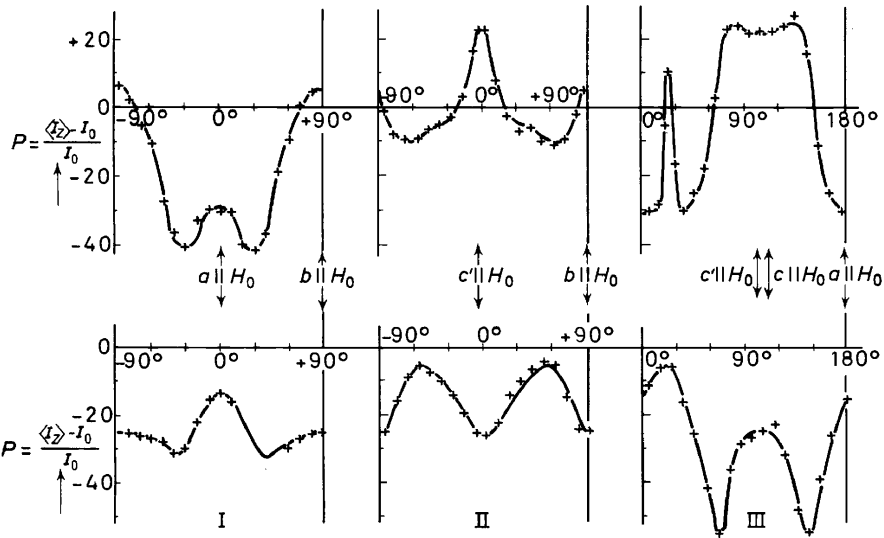


Figure 7. ONP of a phenazine crystal for 3.4 and 11 kG as a function of the orientation of  $H_0$  in the  $a,b$ -plane I, in the  $b,c$ -plane II, and in the  $a,c$ -plane III

due to their interaction with the electronic spins  $S$ , and  $w^0$  is their relaxation rate due to any other mechanism. Of course,  $\rho$  is proportional to the concentration of the paramagnetic spins which is in our case not a constant but proportional to the light intensity  $L$ . Hence  $f$  depends also on  $L$ , but for the high light intensities used in our experiment  $\rho \gg w^0$  and  $f$  approaches one.

Now I would like to show you a few results<sup>9,11</sup> obtained by Schuch with

phenazine single crystals at room temperature. For the experimental technique I refer you to refs. 9 and 11.

In *Figure 7* the relative polarization  $P$  at 3.4 and 11 kG is plotted as a function of the angle  $\phi$  between the crystalline axis and the  $H_0$  field in the  $a,b$ -plane, in the  $a,c$ -plane and in the  $b,c$ -plane, respectively. The rate constant of the polarization was determined to be  $3.3 \times 10^{-3}$  at 3.4 kG and  $1.1 \times 10^{-3}$  at 11 kG. The highest polarization  $p$  measured was of the order of about  $-50$ , corresponding to an absolute polarization  $p = (n^+ - n^-)/(n^+ + n^-)$  of about  $0.5 \times 10^{-4}$  at 3.4 kG and  $1.5 \times 10^{-4}$  at 11 kG.

The results can be summarized as follows: the ONP exhibits a marked anisotropy which is rather different in the two fields investigated. The sign of the polarization is negative in all directions at 11 kG.

We conclude from the fact that fairly large polarizations of the order of 50 are observed that the lifetime factor  $[1 + w/k]^{-1}$  cannot be too small; the much lower polarization in hydrocarbons like naphthalene and fluorine is probably due to much smaller lifetime factors. In this connection it seems to be important that in the case of phenazine, because of its crystalline structure, the excitons are one-dimensional, i.e. they move exclusively or at least predominantly along a row of translationally equivalent molecules, with the effect that their efficiency in relaxing the electronic spins  $S$  is strongly reduced. This was originally deduced from optical measurements<sup>12</sup> and is also plausible on the basis of the model of the crystal.

The electron-nuclear interaction is certainly mixed scalar and dipolar. The measured anisotropy is primarily due to the anisotropy of the electronic polarization, and also, to a much lesser extent, to the anisotropy of the coupling parameter  $\zeta$  for the dipolar part of the interaction. The negative sign found at 11 kG in all directions investigated seems to indicate, in combination with the sign of the reduced electronic polarization factor calculated for this field, a predominantly dipolar electron nuclear interaction. However, this conclusion must be taken with care, mainly because the assumption that  $m_s$  is a good quantum number turned out to be not sufficiently well justified at the highest field  $H_0 = 11$  kG investigated experimentally. Hence we are preparing at present measurements at fields of  $H_0 > 50$  kG using a superconducting magnet.

Finally I would like to show you some results in low field which are much less understood. One general observation is that much higher polarization is observed in doped crystals than in pure crystals. We have primarily investigated fluorene crystals, because fluorene possesses a convenient crystal structure (orthorhombic), comparatively short polarization times which facilitate the collecting of data, and finally because large polarizations occur in fluorene doped with  $10^{-4}$  to  $10^{-3}$  anthracene, phenazine or acridine. The absolute polarization  $p$  of fluorene with 0.1 per cent anthracene, phenazine and acridine, respectively, is plotted in *Figure 8* as a function of  $H_0$  for 2 or 3 different orientations with  $H_0$  parallel to the three main axes of the crystal. Note the very marked field dependence including several changes of sign in the range from 0 to 200 G, which behaves very differently in the three orientations. In *Figure 9* the orientation dependence of  $p$  on  $H_0$  is plotted for the same crystals in the two fields of 80 and 140 G, which shows the marked anisotropy even more clearly. A different ordinate is plotted on the

## OPTICAL SPIN POLARIZATION IN MOLECULAR CRYSTALS

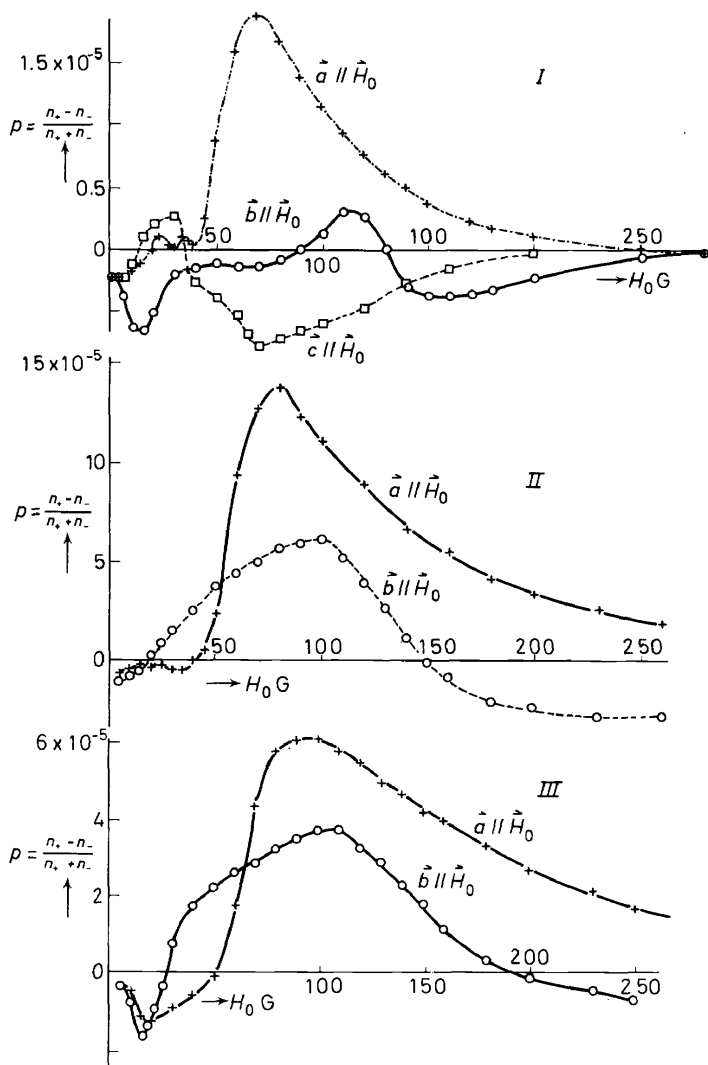


Figure 8. ONP of a fluorene crystal as a function of the magnetic field  $H_0$  parallel to the main axes of the crystal for different guest molecules: I = anthracene, II = acridine, III = phenazine, concentration always 0.1 per cent

right side for comparison, namely the magnetic field  $H_0$  in which the static polarization in Boltzmann equilibrium would be equal to the measured ONP. Note that the highest polarization measured at 80 G corresponds to a static polarization in the field of 800 kG, i.e. an enhancement of the polarization by light of a factor of 10 000.

I shall conclude with a few brief remarks concerning these low field results.

It would be tempting to think that the mechanisms discussed for the high field can also make an important contribution in low field, at least as long as  $m_I$  is a good quantum number; however, our calculations<sup>9</sup> show that this is not so; particularly the drastic field dependence observed in the field range below 200 G, including several sign changes, cannot be explained with these

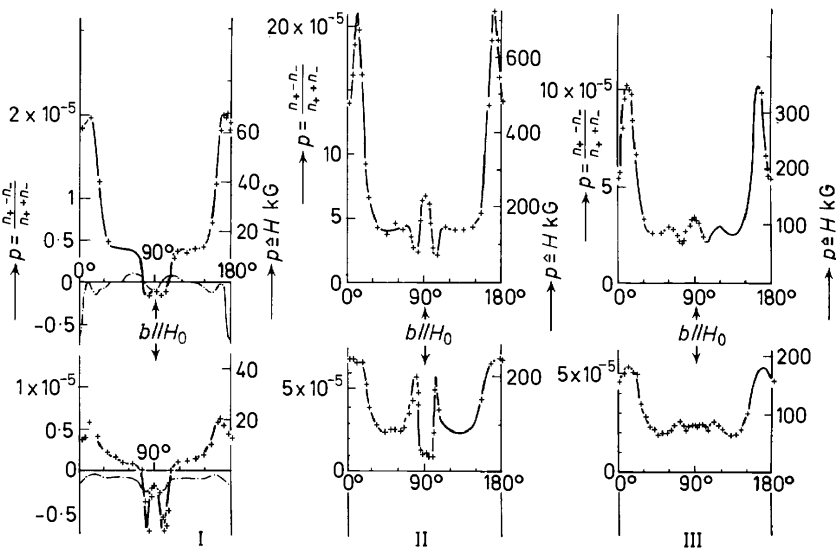


Figure 9. ONP of a fluorene crystal for  $H_0 = 80$  G (above) and 140 G (below) as a function of the orientation on the  $a,b$ -plane for different guest molecules: I = anthracene, II = acridine, III = phenazine, concentration always 0.1 per cent

mechanisms. It requires new mechanisms and we have just made a first step in this direction. In collaboration with Hans Colpa, who has spent some time with us in Heidelberg, we have shown with the simple example of two electrons and two protons that an unequal population of the three triplet levels due to the selection rules of spin orbit coupling can also lead, in combination with the hyperfine interaction, to a selective population of the nuclear substates<sup>13</sup>. These considerations, however, are still in a preliminary state.

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## OPTICAL SPIN POLARIZATION IN MOLECULAR CRYSTALS

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