

we write out the final results in the form of a drawing (the continuous curve). For comparison we have drawing the equilibrium Fermi function $f(x) = [e^{2x} + 1]^{-1}$ as a dashed curve; it is sufficiently close to the one found by us in the characteristic range $0 < x < 2$.

The authors are grateful to R. N. Gurzhi and the participants in the seminar organized by him for discussion of the work.

¹In this connection, one should recall the work of Shabanskiĭ,^[6] where an incorrect attempt was made to establish the possibility of such a simplification. This has already been pointed out in Ref. 3.

²This could actually be either a "dirty" film with $l < d$ (l is the free path length, d the film thickness) or a "clean" film ($l > d$) with diffuse scattering by the boundary.

³The word "impurity" is put in quotation marks since in the case of a "clean" film, we are speaking of scattering by the boundaries with a characteristic momentum relaxation time $\tau \sim d/v_F$, and the corresponding kinetic equation does not contain the term $v \cdot \nabla n_p$, which is necessary for calculation of the conductivity σ .

⁴For a "clean" film, it is given by the well known relation

$\sigma = (3/4)\sigma_0(d/l) \ln(l/d)$, where σ_0 is the conductivity of the bulk specimen.

⁵The analysis of the effect of the thermostat on the behavior of the distribution function in the case of an arbitrary relation between T_e and T ($0 < \gamma < \infty$) is connected with the account of the term $I^T(\xi, g)$, will be the purpose of a separate publication.

¹V. A. Shklovskii, *Fiz. Tverd. Tela* (Leningrad) **17**, 3076 (1975) [*Sov. Phys. Solid State* **17**, 2040 (1975)].

²M. I. Kaganov, I. M. Lifshitz, and L. V. Tanatarov, *Zh. Eksp. Teor. Fiz.* **31**, 232 (1956) [*Sov. Phys. JETP* **4**, 173 (1957)]; M. I. Kaganov and V. G. Peschanskiĭ, *Zh. Eksp. Teor. Fiz.* **33**, 1261 (1967) [*Sov. Phys. JETP* **61**, 970 (1958)].

³V. G. Volotskaya, L. E. Musienko, I. M. Dmitrenko, and Yu. V. Kalenkin, *Fiz. Nizk. Temp.* **2**, 500 (1976) [*Sov. J. Low Temp. Phys.* **2**, 248 (1976)].

⁴B. I. Davydov, *Zh. Eksp. Teor. Fiz.* **7**, 1069 (1937).

⁵E. Conwell, *Kinetic properties of semiconductors in strong electric fields* (Russ. transl.), Mir, 1970, p. 302.

⁶V. P. Shabanskiĭ, *Zh. Eksp. Teor. Fiz.* **31**, 657 (1956) [*Sov. Phys. JETP* **4**, (1957)].

⁷D. Pines, *Elementary Excitations in Solids* (Russian transl.), Mir, 1965, p. 331.

⁸J. Bardeen and D. Pines, *Phys. Rev.* **99**, 1140 (1955).

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Optical polarization of nuclei in molecular crystals at 4.2°K

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Polarization of hydrogen nuclei induced by unpolarized, near-ultraviolet light in molecular fluorene crystals with impurities is investigated at 4.2°K. Two characteristic peaks separated by a narrow gap, which have not been observed previously, are found in the dependence of the polarization on the external magnetic field intensity. The positions of the peaks are found to coincide with the regions of minimal distance between the magnetic sublevels of the triplet state of localized fluorene molecules. The effect is explained on the basis of the model of selective population and mixing of electron-nuclear triplet states. The calculations are in satisfactory agreement with the experiments and this uniquely defines the mechanism of optical polarization of nuclei at low temperatures.

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1. INTRODUCTION

About ten years ago, the phenomenon of optical polarization of nuclei (OPN) was discovered in molecular crystals by a group of German investigators.^[1] At room temperature (and all the experiments on OPN to date have been carried out under these conditions), an enhancement of nuclear polarization was obtained that was record-breaking in comparison with other methods, and the effect arose under the action of unpolarized light. This feature drew serious attention to OPN in molecular crystals and stimulated a whole series of researches devoted to the elucidation of its physical mechanism.^[2–8] At the present time, it is clear that OPN in molecular crystals is due to the nonequilibrium population of the electron spin sublevels that arises upon excitation of

phosphorescent triplet states of the molecules. Two specific mechanisms of transfer of polarization from the electron spins to the nuclear spins were proposed in Refs. 4, 5: a modification of the Overhauser effect in the migration of the excitation in the triplet exciton band of the matrix^[4] and selective population and depletion of the electron-nuclear magnetic sublevels of triplet molecules with account of the mixing of states by hyperfine interaction (HFI).^[5] In crystals with impurities, about which we shall speak below, the first mechanism is of little effect^[4]; so far as the second is concerned, although general considerations and calculated estimates indicate its usefulness,^[5,8] the most characteristic feature of this mechanism has not been observed experimentally up to the present. This feature is the sharp increase in nuclear polarization (predicted by the theory)

in regions of maximum approach (the so-called anticrossing i.e., mutual repulsion) of electron magnetic sublevels.^[5] The absence of this effect, the search for which has caused the expenditure of considerable effort,^[5,6] leaves open the question as to which of the excited molecules (impurity or matrix) serves as the source of polarization of the nuclei in the bulk of the sample. The experiments which we undertook at low temperatures had the aim of obtaining new information on the mechanism of OPN; as will be shown below, this aim has been accomplished to a significant extent.

2. EXPERIMENTAL CONDITIONS

The experiments were carried out on fluorene crystals ($C_{13}H_{10}$), which had earlier served as an object for the study of OPN. As an impurity, which facilitates the effective absorption of the pump light throughout the volume of the sample, we chose *o*-phenanthroline ($C_{12}H_6N_2$), which has a singlet-singlet absorption band edge near 350 nm.^[7] The techniques of cleaning, growing and doping the fluorene crystals were described in Ref. 8. In addition to the specially introduced *o*-phenanthroline (concentration ~0.1%), 5,6 benzindane ($C_{13}H_{12}$) was present in the samples and could not be removed by zone melting.^[9]

The experimental arrangement combined an NMR spectrometer of the *Q*-meter type at 14 MHz, which allowed us to record the NMR signal from the protons of the sample, and an ordinary EPR spectrometer, of the 3-cm range, which served to record the EPR spectra of optically excited triplet states. The optical pumping was provided by a DSh-500 lamp, provided with a set of filters which selected the light in the band 280–360 nm. All the experiments were carried out at 4.2°K; the samples, which had the shape of discs of diameter 8 mm and thickness 2–3 mm, were cooled directly by the liquid helium.

The EPR spectra of optically excited triplet states of molecules of *o*-phenanthroline and benzindane in fluorene crystals have been described in Ref. 8. In the present work, they were used for orientation of the sample in the external magnetic field H_0 and for control on the effectiveness of the optical pumping. Change in the spectral composition of the pump by means of filters, which eliminated the direct absorption of light by the benzindane molecules and fluorene, did not lead to a change in the relation between the EPR signals from the *o*-phenanthroline and benzindane molecules; this shows that the excitation of the triplet states of benzindane occurs mainly as a result of the transfer of energy from the *o*-phenanthroline molecules, which play the role of donors.^[8]

The time of nuclear spin-lattice relaxation T_{1n} , measured at $H_0 = 3.3$ kG and $T = 4.2$ °K, amounted to ~70 min in the investigated samples before their irradiation, and the dependence $T_{1n} \propto (H_0)^{3/4}$ was observed. After irradiation of the samples, the value of T_{1n} (in the absence of light) increased sharply, which is evidently explained by the coupling of the impurity paramagnetic molecules of oxygen in the course of a photochemical reaction, the rate of which depends on the magnetic field.^[10] This in-

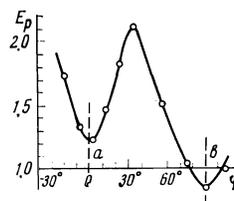


FIG. 1. Dependence of the enhancement of the polarization of the nuclei E_p on the angle φ between H_0 and the a axis of the fluorene crystal (H_0 lies in the ab plane).

teresting effect does not have any relation to the OPN, however, and is not considered in what follows.

The increase in the nuclear polarization E_p in the presence of optical pumping was measured by the ratio of the amplitude of the NMR signal of the protons of the sample to its equilibrium value in the field $H_0 = 3300$ Oe (the absolute value of the polarization $p = (n_+ - n_-) / (n_+ + n_-) = E_p p_0$, where n_+ and n_- are the populations of the lower and upper magnetic levels of the nucleus, and the equilibrium polarization is $p_0 = 8.4 \times 10^{-5}$).

3. RESULTS

When the pump light is turned on, the value of the NMR signal of the protons was seen to deviate from its equilibrium value (the OPN effect). At maximum intensity of the light, achievable in our experiments, the typical time of establishment of the stationary polarization amounted to ~20 min at $H_0 = 3300$ Oe and did not exceed this value at lower fields. All the data given below correspond to the steady state.

Figure 1 shows the dependence of E_p in the presence of optical pumping at $H_0 = 3300$ Oe on the angle φ between H_0 and the crystallographic axis a of fluorene in the ab plane. It is seen that the relative increase in the polarization of the nuclei is not large, but the absolute values of p have the same order as in OPN at room temperature.^[3,6] As also in Refs. 3, 6 the OPN effect is strongly anisotropic; it is seen in Fig. 1 that the experimental values of p correspond to the angles $\varphi = 0, 35$ and 90° . We recall that the z and y axes of the molecules of fluorene and benzindane lie in the ab plane and are turned relative to the a and b axes by the angles $\pm 35^\circ$, respectively (the signs $+$ and $-$ correspond to the two positions of the molecule in the unit cell), and the orientation of the *o*-phenanthroline molecules differs only in the exchange of y and z .^[8] Thus, the data of Fig. 1 do not allow us to find out which of the molecules mentioned is responsible for the polarization.

The study of the dependence of OPN on the value of H_0 gave more significant results. The graph of such a dependence for $\varphi = 15^\circ$ (φ is the angle between H_0 and the a axis of the crystal) is shown in Fig. 2b. It is seen that there are very characteristic features in the regions of ~500 and 950 Oe on the curve $p(H_0)$. These features consist of two maxima, separated by a narrow gap (because of its resemblance to the letter "M," we shall call them the *M* features in what follows). Up to now, such features have not been observed in any OPN experiment.

We have proposed that the *M* effect is connected with the presence of some kind of singularity in the behavior of the energy levels of the molecules responsible for the

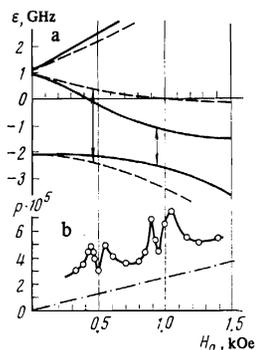


FIG. 2. a) Dependence of the energy ϵ of the electron magnetic sublevels of the triplets of the X collectors in the fluorene crystal at $\varphi = 15^\circ$ on the magnetic field H_0 (H_0 in the ab plane). The solid and dashed lines correspond to the two magnetic complexes. The arrows indicate the points of closest approach of the levels. b) Dependence of the polarization of the nuclei p on the field intensity H_0 at this same orientation. The dot-dash curve is the equilibrium polarization of the nuclei.

OPN, and the eigenvalues of the spin Hamiltonian of all the triplet centers present in our crystal are compared in Fig. 2b: *o*-phenanthroline, benzindane, and the molecules of the matrix (in the latter case, we have used both the parameter of the X traps, i.e., of localized triplet molecules of fluorene,^[11] and the parameters of the spin-Hamiltonian of the triplet excitons, averaged over the nonequivalent sites^[12]). Correlation was discovered only for the spectrum of the X traps, and the position of the *M* singularities coincided with the regions of maximum approach of the magnetic sublevels of each of the magnetic complexes (Fig. 2). This correlation was confirmed at other orientations of H_0 , in particular, at $H_0 \parallel z$ ($\varphi = 35^\circ$), when the approach of the levels was maximal and their mutual repulsion ("anticrossing") was due only to the hyperfine interaction. The experimental results for this case are shown in Fig. 4c (see below); it is seen that the region of the *M* effect here is significantly narrower (amounting to 35 Oe in comparison with the 220-250 Oe in Fig. 2b), and the enhancement of the polarization is greater than at other orientations.

As we have already pointed out, the possibility of enhancement of OPN in regions of anticrossing was considered in Ref. 5; however, the central gap observed by us was not predicted there. To explain its nature, we carried out a more detailed calculation for the case $H_0 \parallel z$.

4. CALCULATION OF OPN IN THE REGION OF MUTUAL REPULSION OF ENERGY LEVELS

Let us consider a molecule which undergoes a transition, under the action of the pump light, from the ground singlet state S_0 to the excited state S_1 and then experiences a nonradiative transition to the triplet phosphorescent state T_1 and, finally, returns to S_0 . We assume for simplicity that there is only one nuclear spin $I = \frac{1}{2}$ in the molecule (in fact, there are ten protons in the fluorene molecule, each of which has its HFI parameter^[13]; this circumstance will be taken into account later. Thus, in the states S_0 and S_1 there are two sublevels, "+" and

"-" corresponding to the orientations I along and counter to the field H_0 , and in the state T_1 , there are six electron-nuclear levels ($i = \text{number of the level, counting upwards}$). The designations for the probabilities of the transitions, which produce the population and destruction of the triplet levels, are shown in Fig. 3.

If we compare, in correspondence with the scheme of Fig. 3, the rate equations for population of all the levels of the considered system, assuming that optical pumping acts continuously between S_0 and S_1 without changing the nuclear spin, and that the spin-lattice relaxation in the system is unimportant, then the stationary solution for nuclear polarization in state S_0 takes the form

$$p = \left(\sum_{i=1}^6 \frac{W_i^+ V_i^- - W_i^- V_i^+}{W_i^+ + W_i^-} \right) \left[1 - \sum_{i=1}^6 \frac{W_i^+ (V_i^+ - V_i^-)}{W_i^+ + W_i^-} \right]^{-1}. \quad (1)$$

The probabilities W_i^\pm and V_i^\pm , entering into (1) and determining the OPN effect depend on the composition of the wave functions at the triplet levels. The spin Hamiltonian of the molecule in the state T_1 takes the form

$$\mathcal{H} = \beta_e H_0 g_e S + D(S_z^2 - 2/3) + E(S_x^2 - S_y^2) + SA I - g_N \beta_N H_0 I, \quad (2)$$

where $g_e, g_N, \beta_e, \beta_N$ are the g factors and the magnetic moments of the electron and nucleus, respectively; A is the HFI tensor; S is the electron spin ($S = 1$); D and E are parameters which determine the splitting of the electron levels of the triplet at $H_0 = 0$ and x, y, z are the principal axes of the molecule. We carry out the calculation only for $H_0 \parallel z$ and limit ourselves to that region of fields H_0 in which maximum approach of the electron levels occurs. Under these conditions, $g_e \beta_e H_0 \gg E$; it is therefore convenient to choose the basis functions in the form $|k, l\rangle$, where $k = -1, 0, +1$ are the projections of the spin S , and $l = +, -$ are the projections of the spin I in the H_0 direction. Then the eigenfunctions of the Hamiltonian (2) are written in the form

$$\Psi_i = \sum_{k,l} a_{ik} |k, l\rangle. \quad (3)$$

Using (3), we can find the expressions for the probabilities V_i^l :

$$V_i^l = \sum_k (a_{ik}^l)^2 v_k, \quad (4)$$

where

$$v_{-1} = v_{+1} = 1/2 (v_x + v_y), \quad v_0 = v_z. \quad (5)$$

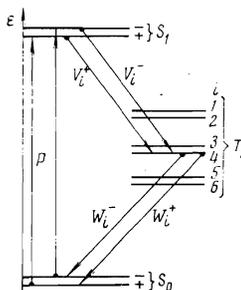


FIG. 3. Diagram of the energy levels of an aromatic molecule. P—optical pump. In order not to clutter the drawing, the transitions V_i^+ and W_i^+ are shown only for $i = 4$.

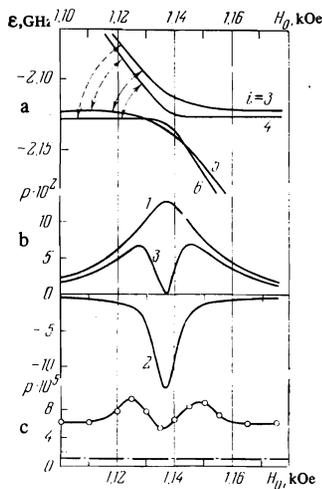


FIG. 4. a) Diagram of the four lowest electron-nuclear sub-levels of the triplet of the X trap in fluorine at $H_0 \parallel z$. The arrows indicate the pairs in which mixing of states occurs. In the figure, b and c are plots of the polarization p of the nuclei on the field H_0 at this same orientation. b) Theory (see text). c) Experiment. The dot-dash curve is the equilibrium value of the polarization.

and v_x, v_y, v_z are the experimentally measured rates of populating the states $|x\rangle, |y\rangle, |z\rangle$ of the triplet at $H_0 = 0$ (see, for example, Ref. 11). The expressions for W_i^\dagger and w_k are similar to (4), (5).

At $H_0 \parallel z$ and $g_e \beta_e H_0 \approx D$, the levels characterized by the functions $|-1, \pm\rangle$ and $|0, \pm\rangle$ come closer together (Fig. 4a). Calculation shows that in this case the state $|-1, +\rangle$ mixes only with $|0, -\rangle$, and $|-1, -\rangle$ only with $|0, +\rangle$ (the solid arrows in Fig. 4a). In this case, the composition of the corresponding mixed wave functions is characterized by the relations of the coefficients 1: $(\sqrt{m^2 + 1} - m)$ and 1: $(\sqrt{r^2 + 1} - r)$, where

$$m = \frac{2D - A_{zz} - 2(H+h)}{8(A_{xx} + A_{yy})}, \quad (6a)$$

$$r = \frac{2D + A_{zz} - 2(H-h)}{8(A_{xx} - A_{yy})}. \quad (6b)$$

Here A_{ij} are the elements of the HFI tensor, $H = g_e \beta_e H_0$, $h = g_N \beta_N H_0$. The parameters m and r characterize the degree of mixing of the indicated pairs of states: at $m = 0$ or $r = 0$, the mixing in the pair is complete, and at $|m|, |r| \gg 1$, it is absent. It is clear from (6) that m and r vanish, generally speaking, at different (although nearby) values of H_0 .

The expressions (6) are valid only upon coincidence of the HFI axes with the axes of the molecule; in the opposite case, the denominators of (6) take the form

$$8[(A_{zz} \pm A_{ww})^2 + A_{xy}^2]^{\frac{1}{2}}.$$

With account of (1)-(6), we finally obtain

$$p = \left[\frac{w_{-1} v_0 - w_0 v_{-1}}{w_{-1} + w_0} \left(\frac{1 - M^2}{1 - M^2 \Delta^2} - \frac{1 - R^2}{1 - R^2 \Delta^2} \right) \right] \left\{ 1 - \frac{v_{-1} + v_0}{w_{-1} + w_0} \right. \\ \times \left[\left(\frac{w_{-1}}{1 + M \Delta} - \frac{w_0}{1 + R \Delta} \right) \delta + \frac{2w_0 w_{-1}}{w_{-1} + w_0} \left(\frac{M^2}{1 - M^2 \Delta^2} + \frac{R^2}{1 - R^2 \Delta^2} \right) \right] \right\}^{-1}, \quad (7)$$

where

$$M^2 = \frac{m^2}{m^2 + 1}, \quad R^2 = \frac{r^2}{r^2 + 1}, \quad \Delta = \frac{w_{-1} - w_0}{w_{-1} + w_0}, \quad \delta = \frac{v_{-1} - v_0}{v_{-1} + v_0}.$$

Numerical calculation has been completed for the values

$v_x : v_y : v_z = 3 : 1 : 1$; $w_x : w_y : w_z = 1 : 8 : 1$ (we have used $\sum_k v_k = \sum_k w_k = 1$, $D = 3189$, $E = 90$ MHz^[11]) and the HFI parameters $A_{zz} = -0.9$ MHz, $A_{xx} = -11.3$ MHz, $A_{yy} = -5.7$ MHz, $A_{xy} = -3.8$ MHz, which were determined experimentally in Ref. 13 for protons 2 and 2' in the fluorene molecule. The result of the calculation is shown in Fig. 4b, curve 3. It is seen that the shape of the theoretical curve $p(H_0)$ has the typical M-shaped form, and the distance between the maxima and the depth of the gap is in excellent agreement with experiment (Fig. 4c).

We now make clear the physical meaning of the obtained result. In accord with the model applied in our calculation,^[5] positive polarization of the nuclei stems from the fact that the population of some i -th level of the triplet takes place predominantly from state $|S_{1, -}\rangle$ and phosphorescence from this same i -th level, predominantly to the state $|S_{0, +}\rangle$, i. e., the probabilities V_i^\dagger and W_i^\dagger are maximal (to obtain negative polarization, V_i^\dagger and W_i^\dagger must be the largest). It is clear that such a situation becomes possible only as a result of the mixing of electron-nuclear states containing different electron and nuclear functions. Far from the region of anticrossing, the levels 3, 4, 5, 6 are described by "pure" states and there is almost no OPN effect. In the approach of the levels, the pair 3, 5 (Fig. 4a) gives a positive polarization upon mixing, which reaches a maximum at $m = 0$ (curve 1 in Fig. 4b) and the pair 4, 6—negative, which is maximum at $r = 0$ (curve 2 in the same drawing). If both curves had identical width, the total result would be close to zero; however, because of the difference between (6a) and (6b), the region of negative polarization turns out to be narrower, which leads to the observed M singularity.

As has already been noted, the location of the extrema of curves 1 and 2 in Fig. 4b can differ somewhat, and then the M singularity will be asymmetric. Such a result is obtained, in particular, for protons 7 and 7' of the fluorene molecule.^[13] The result of the averaged curves of $p(H_0)$, which were obtained for all ten protons of fluorene, differs little from curve 3 in Fig. 4b.

It is seen from a comparison of Fig. 2 with Fig. 4c that the width of the M singularity increases sharply upon departure of H_0 from the magnetic axis. This phenomenon is explained by the fact that an additional mixing of the states arises in this case, due to the non-diagonal matrix elements of the electron Zeeman part of the Hamiltonian (2) (the dashed arrows in Fig. 4a). It can be shown that even at small departures of H_0 from the z axis ($1-3^\circ$), this mechanism of mixing becomes predominant.

5. DISCUSSION OF RESULTS

The clear similarity of the theoretical and experiment curves of $p(H_0)$ in the region of the M singularity leaves no doubt as to the correctness of the chosen OPN mechanism. However, the theoretically calculated absolute value of the quantity p turns out to be about 700 times larger than the theoretical. There are three possible reasons for this divergence.

a) A decrease in the polarization in the case $H_0 \parallel z$ can be produced by an imperfect crystal, which leads to a scatter in the orientation of the axis along the sample. The presence of such a scatter (mosaic) is confirmed by the fact that the EPR lines of the triplet molecules of benzindane undergo significant narrowing (from 30 to 24 Oe) as H_0 approaches the z axis. Estimates show that this corresponds to a disorientation of the z axis by $2.5-3^\circ$ which, as has already been pointed out, leads to an additional mixing of states and a departure from the calculated results. However, it is scarcely probable that this effect can completely explain such a great reduction in the value of p , the more so that the calculated width of the M singularity differs little from the experimental.

b) In the light fluxes used ($\sim 10^{16}$ quanta/sec), each molecule that makes a contribution to the OPN spends a major part of its time in the ground state and during this period, "leakage" of nuclear polarization due to spin-lattice relaxation of the protons can take place. Since all forms of internal motions are frozen at 4.2°K , the reason for the leakage can only be the paramagnetic impurities. Those of them which also exist in the non-irradiated sample, cannot play an important part, since the value of T_{1n} in the dark is much greater than in the light. This fact indicates that the decrease in illumination by a factor of two did not lead to a change in the stationary value of p , i. e., saturation was observed in the dependence on the light intensity. However, all this does not exclude leakage, due to optically excited paramagnetic impurities and, above all, to the triplet molecules of benzindane which possess a very short electron relaxation time T_{1e} (according to our data, less than 10^{-3} sec).

To test this assumption, we carried out a control experiment on a very carefully purified sample (110 passes through the molten zone), in which the concentration of benzindane was reduced by a factor of three (for the same content of *o*-phenanthroline). The measurements showed that this had practically no effect on the value of p ; consequently, the "leakage" of the nuclear polarization due to impurities of triplet molecules is unimportant.

c) Finally, the third reason for the weakening of the OPN effect could be spin-lattice relaxation in the triplet state. It is not difficult to show that in the limiting case, when a Boltzmann distribution can be established within the triplet lifetime τ over all six electron-nuclear sublevels, we get the following equality in place of (1):

$$p = -\frac{1}{2kT} \sum_{i=1}^6 \varepsilon_i (W_i^+ - W_i^-), \quad (8)$$

where ε_i is the energy of the i -th level. In the case $H_0 \parallel z$, it follows from (8) that

$$p = -\frac{1}{4kT} [A_{zz}w_1 - g_N\beta_n H_0(2w_0 - w_1)]. \quad (9)$$

This equation has no singularities in the region of mutual repulsion of the levels, and at $H_0 = 1130$ Oe, it yields $p \sim 10^{-5}$, which is smaller by an order of magnitude than the maximal experimental value.

Thus, the fast spin-lattice relaxation in the triplet state can completely eliminate the M singularity and in essence the entire OPN effect. It is evident that our case is intermediate: the appearance of the M singularity indicates a departure from the Boltzmann equilibrium, and the small value of p indicates the insignificance of this departure. The magnitude of the departure from equilibrium, and consequently the amplitude of the M singularity, is approximately proportional to $\exp(-\tau/T_{1e})$. Then, comparing the experimental and theoretical results (Figs. 4b, c) we find $\tau/T_{1e} = 7$, which is in satisfactory agreement with the experimental data for the X -traps in fluorene.^[11]

For triplet molecules of *o*-phenanthroline and benzindane, the ratio T_{1e}/τ is much smaller, which explains the absence of M singularities in the regions of repulsion of the levels of these molecules. We note that the EPR spectra that were observed of the molecules of *o*-phenanthroline and benzindane corresponded to the Boltzmann equilibrium at the electron levels of the triplets.

It is not completely clear why we did not succeed in observing the EPR spectrum of the X traps directly. It is possible that this is connected with the large value of T_{1e} , which leads to saturation of the HFI lines by the field. On the other hand, it is impossible to exclude totally the idea that the OPN effect is due, not to the X traps, but to mobile excitons of fluorene, which have the same EPR spectrum as the localized triplets of the molecule. Such a situation is possible only in the case in which the jumps of the excitons between nonequivalent sites in the cell are sufficiently rare (the value of the Davydov splitting is small); unfortunately, there are no corresponding data for fluorene at the present time.

Finally, the mechanism of population of the triplet levels of fluorene remains open. The light absorption in the singlet-singlet band of the molecules of the matrix is most significant in a thin layer at the irradiated surface, and such a mechanism of excitation of the triplets would lead to a dependence of the OPN on the thickness of the sample, which has not been observed. Transfer of the excitation from *o*-phenanthroline is most probable; however, the T_1 level of fluorene lies 1690 cm^{-1} higher than that for the *o*-phenanthroline, so that the ordinary mechanism of triplet-triplet transfers^[14] is not possible.

Thus, the M singularities observed in the present work in regions of closeness of the triplet sublevels represents the first reliable indication of the OPN mechanism predicted in Ref. 5, and allow us to attribute the effect with reliability to a contribution of the triplet states of the molecules of the matrix.

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¹G. Maier, U. Haeberlen, H. C. Wolf, and K. H. Hausser, Phys. Lett. 25A, 384 (1967).

²G. Maier and H. C. Wolf, Z. Naturforsch. 23a, 1068 (1968).

³K. H. Hausser, O. Lauer, H. Schuch, and D. Stehlik, Proc.

XVI congress AMPERE, Bucharest, 1970, p. 83.
⁴H. Schuch, D. Stehlik, and K. H. Hausser, Z. Naturforsch. 26a, 1944 (1971).
⁵J. P. Colpa, K. H. Hausen, and D. Stehlik, Z. Naturforsch. 26a, 1792 (1971).
⁶P. Lay, D. Stehlik, and K. H. Hausser, J. Magn. Reson. 15, 270 (1974).
⁷J. S. Brinen, D. D. Rosebrook, and R. C. Hirt, J. Phys. Chem. 67, 2651 (1963).
⁸S. K. Morshnev, Zh. Prikl. Spektrosk. 23, 428 (1975).
⁹E. A. Johnson, J. Chem. Soc. 994 (1962).

¹⁰V. A. Atsarkin and S. K. Morshnev, Pis'ma Zh. Eksp. Teor. Fiz. 22, 261 (1975) [JETP Lett. 22, 121 (1975)].
¹¹H. Sixl and H. C. Wolf, Z. Naturforsch. 27a, 198 (1972).
¹²H. Sternlicht and H. M. McConnell, J. Chem. Phys. 35, 1796 (1961).
¹³V. Zimmermann, M. Schwoerer, and H. C. Wolf, Chem. Phys. Lett. 31, 401 (1975).
¹⁴A. N. Terenin and V. L. Ermolaev, Dokl. Akad. Nauk SSSR 85, 547 (1952).

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Distribution of local magnetic moments in Mn over inequivalent lattice sites in quasibinary $(\text{Fe}_{1-x}\text{Mn}_x)_3\text{Al}$ alloys

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Nuclear spin echo and magnetic diffuse scattering of neutrons by Mn^{55} nuclei in quasibinary $(\text{Fe}_{1-x}\text{Mn}_x)_3\text{Al}$ alloys are investigated. Three regions of resonant absorption corresponding to three different positions of the Mn ions in the Fe_3Al lattice are observed. The moments of Mn at various sites are determined from the magnetic moments obtained by neutron diffraction and averaged over the lattice. The NMR and neutron-diffraction data indicate that Mn atoms with an antiferromagnetic orientation of the local magnetic moments appear when the Mn concentration in the alloy increases.

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Fe-Mn-Al alloys, just as Fe-Cr-Al alloys, have high electric resistivity ($\rho = 1.5-2 \Omega\text{-mm}^2/\text{m}$) at relatively high magnetization. The anomalies observed in the temperature dependence of the resistivity, particularly the presence of smeared out minima of ρ in wide temperature ranges,^[1] can be due to the specific character of the electronic structure of these alloys and to singularities of the behavior of the local magnetic moments in them. The most important circumstance is that in these systems exchange interactions of both the ferro- and anti-ferromagnetic type take place, and leads to appreciable changes in the local characteristics when the atomic environment is varied.

A particularly acute problem is the determination of the local magnetic moments of the manganese and iron atoms ($\mu(\text{Mn})$ and $\mu(\text{Fe})$) in these alloys. However, neutron-diffraction methods yield only local magnetic moments of all the alloy components averaged over the lattice, and do not make it possible to investigate the distribution of the moments over the non-equivalent lattice sites and to ascertain the role of the atomic environment. At the same time, methods of investigating hyperfine interactions, and especially methods of measuring the nuclear spin echo, have exceptionally high resolving power and measurement accuracy, but it is quite difficult or impossible to determine the absolute values of the local magnetic moments. Naturally, optimal re-

sults can be obtained by combining these methods.

We have investigated the magnetic diffuse scattering of neutrons and nuclear spin echo on the nuclei Mn^{55} in the quasi-binary alloys $(\text{Fe}_{1-x}\text{Mn}_x)_3\text{Al}$. The neutron-diffraction investigations were carried out at the Central Institute of the Solid State Physics and Metallurgy and the Central Institute for Nuclear Research of the Academy of Sciences of the German Democratic Republic in Dresden, while the nuclear spin echo was investigated at the Moscow State University. The samples for the measurements were smelted in an induction furnace with strong cooling. The quenched ingots were reduced in ball grinders to a powder with particle dimensions not larger than $50 \mu\text{m}$. The concentrations of the manganese and the aluminum in the investigated samples are listed in Table I.

The nuclear spin echo on the Mn^{55} nuclei was measured with a spectrometer operating in a wide frequency band, using pulses of $1 \mu\text{sec}$ duration and with $15 \mu\text{sec}$

TABLE I.

Sample No.	C(Mn), at.%	C(Al), at.%	$\bar{\mu}$, μ_B	$\bar{\mu}$ (Fe), μ_B	$\bar{\mu}$ (Mn), μ_B
1	3.4	24.4	1.37	2.0	2.0
2	7.0	24.9	1.18	1.7	1.7
3	9.4	24.9	1.06	1.7	0.7
4	13.9	25.5	0.89	1.5	0.7