Electric-dipole spin transition of the neutral acceptor $\mathrm{Mn}_{\mathrm{Ga}}^{0}$ in GaAs

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(Submitted 27 November 1991)
Pis'ma Zh. Eksp. Teor. Fiz. **55**, No. 2, 108–112 (25 January 1992)

The intensity of the spin-absorption lines of the $\mathrm{Mn}_{\mathrm{Ga}}^{0}$ center ($\mathrm{Mn}^{2+} + h$) in the $\vec{H}_1$ and $\vec{E}_1$ components of the microwave field has been studied as a function of the direction of the external magnetic field $\vec{H}_0$ in Mn-doped *p*-GaAs crystals. This behavior was studied both experimentally and theoretically. The spin-resonance spectra are governed by electric dipole transitions, not magnetic dipole transitions.

Centers of two types have been identified in ESR studies of Mn-doped GaAs crystals:[1–3] a neutral acceptor Mn^0, which consists of a weakly localized hole with five 3d core electrons ($\mathrm{Mn}^{2+} + h$, total spin $F = 1$), involved in an exchange interaction; and an ionized acceptor Mn^- (Mn^{2+}, $S = 5/2$). It was assumed in those studies that the ESR spectra which were recorded were caused by magnetic dipole transitions. However, several pieces of evidence-the angular distribution of the intensity of the ESR lines observed for the Mn^0 center at low values of the crystal-field constant,[2] the comparable intensities of the ESR lines for the transitions $\Delta M_F = 1$ and $\Delta M_F = 2$ (Refs. 1 and 2), and the fact (which we have established) that the concentration of centers N_{Mn^0} determined from the ESR spectra with the help of a reference sample can be at least an order of magnitude greater than the concentrations N_{Mn^0} determined by other methods—all indicate that the spin resonance might be due to electric-dipole spin transitions.[4] In this letter we are reporting an effort to identify the spin transitions of Mn^0 in *p*-type GaAs.

The ESR measurements were carried out over the temperature interval 4.2–100 K on a Varian E-12 rf spectrometer in the *X* band, with a modulation of the magnetic field at 100 kHz. The GaAs crystals had been grown by the Czochralski method under a B_2O_3 layer; Mn had been added to the melt. The concentration N_{Mn} was found by spark mass spectrometry and by Hall-effect measurements. The values lay in the range 10^{16}–10^{18} cm^{-3}. The oriented test samples had dimensions of $2\times2\times8$ mm and were placed in an H_{011} cylindrical resonator, either at an antinode of the component $\vec{H}_1$ (at the center of the resonator) or at an antinode of the component $\vec{E}_1$ (half the radius of the resonator at half-height), where, according to experimental estimates, the $\vec{H}_1$ amplitude is lower than that at the center of the resonator by nearly three orders of magnitude.

Figure 1 shows spin-absorption spectra at the antinodes of the $\vec{H}_1$ and $\vec{E}_1$ compo-

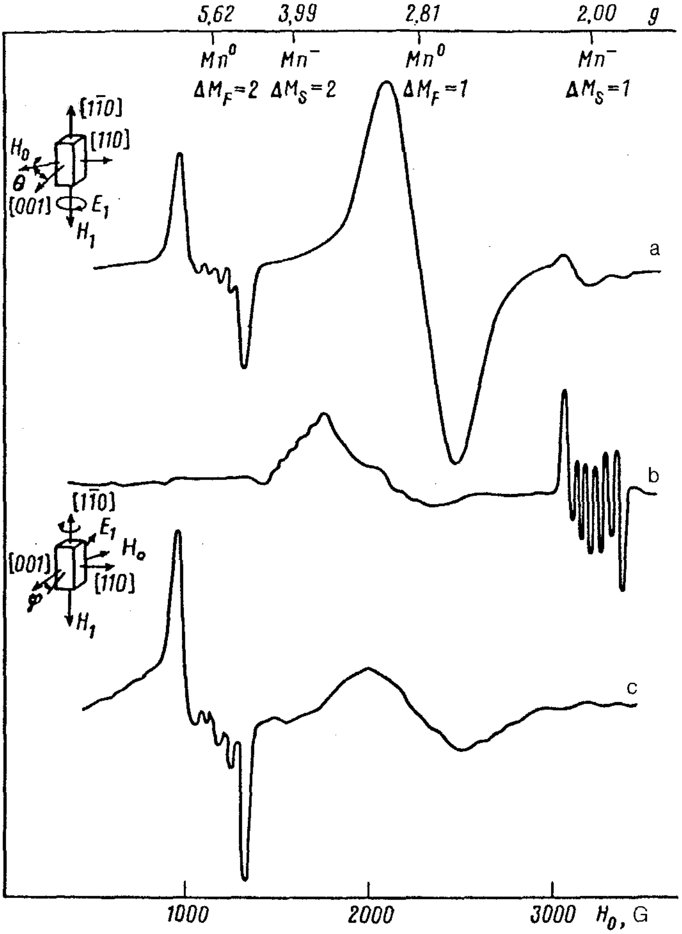

FIG. 1. Spin-absorption spectra of GaAs⟨Mn⟩. a—H_1 spectrum, $T = 4.2$ K, $\theta = (\vec{H}_0, [001]) = 0°$, $N_{\mathrm{Mn}} = 5 \times 10^{17}$ cm^{-3}; b—H spectrum, $T = 20$ K, $\theta = 35°$, $N_{\mathrm{Mn}} = 5 \times 10^{16}$ cm^{-3}; c—E_1 spectrum, $T = 4.2$ K, $\varphi = k(\vec{E}_1, [001]) = 70°$, $\vec{H}_0 \perp \vec{E}_1$, $N_{\mathrm{Mn}} = 5 \times 10^{17}$ cm^{-3}.

nents of the microwave field; we will be referring to these spectra as the "H_1" and "E_1" spectra. The observed H_1 spectrum of Mn^0 and Mn^- in GaAs is similar to that reported in Refs. 1 and 2. The minimum width of the Mn^0 line ($\Delta M_F = 1$) in the orientation $\vec{H}_0 \| [100]$ was $\Delta H_{pp} = 380$ G for some of the samples. In other words, in these cases it was approximately equal to the distance between the two outermost peaks of the hyperfine components of the Mn^0 line ($\Delta M_F = 2$). For this line, the hyperfine constant is $A = 62$ G, and we have $\Delta H_{pp}^{hf} = 50$ G. Above 11 K, the H_1 spectra of the Mn^0 line disappear, and it becomes possible to detect a line with $g = 3.990 \pm 0.005$ (Fig. 1b). In the samples with the low Mn^0 concentration, it is possible to resolve six components of this line ($A = 56$ G). The fact that the hyperfine constants are the same for the lines with $g = 2.000$ and $g = 3.990$ and also the fact that

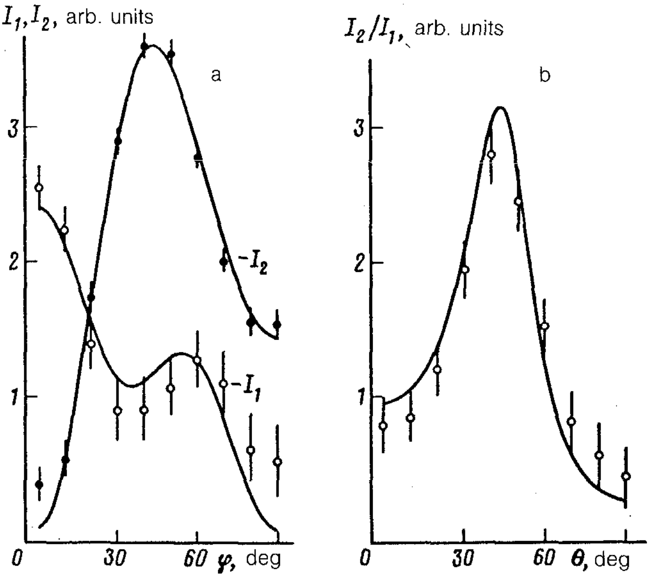

FIG. 2. Angular distribution of the total intensity of the spin-absorption signals of Mn^0 in GaAs at $T = 4.2$ K with $N_{Mn} = 5\times 10^{17}$ cm^{-3}. The solid lines are theoretical, calculated from expressions (7) and (8) for the experimental geometry shown in the insets in Fig. 1. a: E_1 spectrum, $I_1 \approx F_1(\vec{e},\vec{h}) = \cos^2\varphi(1 - 3\sin^2\varphi\cos 2\varphi)$, $I_2 \approx F_2(\vec{e},\vec{h}) = (1/4)\sin^2\varphi(1 + 5\cos^2\varphi + 6\cos^4\varphi)$. b: H_1 spectrum, $I_2/I_1 \approx F_2(\vec{e},\vec{h})/F_1(\vec{e},\vec{h}) = (1/8)[1 + 3\cos^2\theta(1 + \sin^2\theta)]/(1/2)[1 - (3/4)\sin^2 2\theta]$.

the second line lies at a field approximately half the field corresponding to the first line show that these lines belong to transitions with $\Delta M_S = 1$ and $\Delta M_S = 2$ of the Mn^- center.

The E_1 spectra have been recorded for the Mn^0 center ($\Delta M_F = 1.2$) and also for the Mn^- center ($\Delta M_S = 2$) for the first time in III-V crystals, to the best of our knowledge. For the Mn^0 center we observed a change in the total intensity of the absorption signals I_1 and I_2, which correspond to the transitions $\Delta M_F = 1$ and $\Delta M_F = 2$ when the orientations of the crystal axes with respect to the direction of $\vec{H}_0$ (in the H_1 spectra) or of $\vec{E}_1$ and $\vec{H}_0$ (in the E_1 spectra) were changed (Fig. 2).

To describe the observed effects, we consider a model of the $Mn^{2+} + h$ center which corresponds to point symmetry group T_d. The perturbation operator which determines the microwave absorption in the crystallographic coordinate system X, Y, Z is[4]

$$V(t) = V_{E_1}(t) + V_{H_1}(t), \tag{1}$$

$$V_{E_1}(t) = \alpha[E_{1x}(t)\{S_yS_z\} + E_{1y}(t)\{S_zS_x\} + E_{1z}(t)\{S_xS_y\}], \tag{2}$$

$$V_{H1}(t) = g\mu_B\vec{H}_1(t)\vec{S}. \tag{3}$$

Here $\vec{E}_1(t) = \vec{E}_1\sin\omega t$, $\vec{H}_1(t) = \vec{H}_1\cos\omega t$ are the electric and magnetic components of the microwave field, with frequency ω, in the resonator. Corresponding to these field components are the electric dipole interaction in (2) and the magnetic dipole interaction in (3), which are determined by the constants α and $g\mu_B$; here the operator $\vec{S}$ represents the effective spin of the ground state of the center. Since the Zeeman interaction, described by the spin Hamiltonian $H = g\mu_B \vec{H}_0 \vec{S}$, outweighs the other interactions in these experiments, the probabilities for transitions between magnetic sublevels are determined by $|M_{M,M'}|^2$, the matrix elements of operator (1) calculated between the eigenvectors $|M\rangle$ of the operator $S_{z'}$, where z' is along the direction of $\vec{H}_0$. Evaluating the matrix elements of the electric-dipole spin transitions and of the magnetic-dipole transitions, we find

$$|M^E_{M,M-2}|^2 = \frac{1}{4}\alpha^2 E_1^2 (S_+^2)^2_{M,M-2} F_2(\vec{e},\vec{h}), \tag{4}$$

$$|M^E_{M,M-1}|^2 = \frac{1}{4}\alpha^2 E_1^2 (M - \frac{1}{2})^2 (S_+)^2_{M,M-1} F_1(\vec{e},\vec{h}), \tag{5}$$

$$|M^H_{M,M-1}|^2 = \frac{1}{16} g^2 \mu_B^2 H_1^2 (S_+)^2_{M,M-1}, \tag{6}$$

where $S_+ = S_x + iS_y$. For the electric-dipole spin transition, the dependence on the directions $\vec{e} = \vec{E}_1/|\vec{E}_1|$ and $\vec{h} = \vec{H}_0/|\vec{H}_0|$ is given by

$$F_1(\vec{e},\vec{h}) = 1 - [e_x^2(h_x^2 + 4h_y^2)]_{\text{cp}} + 2[e_x e_y h_x h_y (1 - 4h_z^2)]_{\text{cp}}, \tag{7}$$

$$F_2(\vec{e},\vec{h}) = [e_x^2(h_x^2 + h_y^2 h_z^2)]_{\text{cp}} - 2[e_x e_y h_x h_y (h_x^2 + h_y^2)]_{\text{cp}}, \tag{8}$$

where $[\ldots]_{cp}$ represents the sum of three terms which are generated through a cyclic permutation of the indices x, y, z. The probabilities for a spin resonance corresponding to transitions $M \to M - 1$ contain, along with contributions (5) and (6), their interference term, $M^{E,H}_{M,M-1}$, which is unimportant in the case at hand. According to (7) and (8), the electric-dipole spin transitions with selection rules 2 and $\Delta M_S = 1$ are characterized by an angular dependence, while the "allowed" magnetic dipole transitions are not. The "forbidden" magnetic dipole transitions ($\Delta M_S = 2$) are not manifested in our experiments. As we see in Fig. 2, the theoretical curves of $F_1(\vec{e},\vec{h})$ and $F_2(\vec{e},\vec{h})$ give a good description of the experimental behavior at the antinodes of both the electric and magnetic components of the microwave field.

To find a quantitative estimate of the probabilities for electric-dipole spin transitions, we placed a reference sample in the resonator, along with a GaAs⟨Mn⟩ test sample in the form of an eight-sided prism. This reference sample was a CdS crystal, in which the ESR specrum of shallow donors has been observed,[6] with $g_R = 1.774$ and with paramagnetic centers in a number $N_H = 6 \times 10^{14}$. We compared the overall intensities of the ESR spectrum of the reference sample, I^H_{1R}, for which the electric-dipole spin transitions are unimportant, and I^E_{1H} of the H_1 spectrum of Mn^0 ($\Delta M_F = 1$), which is due to electric-dipole transitions. The parameter α was estimated from the following expression (which is in atomic units):

$$|\alpha| = g_{\text{R}} \frac{\sqrt{2}}{137} \frac{\rho}{r_0} \left[\frac{I^E_{1H} N_H}{I^H_{1\text{R}} N_E} \right]^{1/2}. \tag{9}$$

Expression (9) was derived by ignoring the effect of the sample on the field distribution in the H_{011} resonator (near the geometric center, $\vec{H}_1$ is at a maximum and is essentially constant, while $|\vec{E}_1|$ is proportional to the radius), using expressions (5) and (6).

Expression (9) assumes that the sample is cylindrical with a radius of r_0; here $\rho = [(3.832/R)^2 + (\pi/L)^2]^{-1/2} \approx 0.5$ cm is the geometric factor of a resonator of radius R and height L, and $N_E = 6\times 10^{15}$ is the number of Mn^0 centers in the sample, estimated from Hall-effect measurements. Substituting these values along with $r_0 = 0.12$ cm into (9), we find $|\alpha| \approx 1$ a.u. This figure is significantly larger than the known values; for Mn^+ in Si, for example, is smaller by two orders of magnitude.[7] Nevertheless, this is not an unexpected result for the $\mathrm{Mn}^{2+} + h$ center: According to an estimate in Ref. 5, the probabilities for electric-dipole spin transitions for a hole localized at an acceptor in a III-V compound can be greater than the probabilities for magnetic dipole transitions by six orders of magnitude.

It can be concluded from these results that the "ESR spectrum" of the Mn^0 center is governed by electric-dipole spin transitions. In comparison with those transitions, magnetic dipole transitions are essentially unseen, even under the conditions most favorable for them. The observation of electric-dipole spin transitions at the center of the resonator stems from the high probability for these transitions and from the nonzero value of $|\vec{E}_1|$ in a sample of finite size.

[1] J. Schneider, U. Kaufmann, W. Wilkening *et al.*, Phys. Rev. Lett. **59**, 240 (1987).

[2] V. F. Masterov, K. F. Shtel'makh, and M. N. Barbashov, Fiz. Tekh. Poluprovodn. **22**, 654 (1988) [Sov. Phys. Semicond. **22**, 408 (1988)].

[3] N. S. Averkiev, A. A. Gutkin, O. G. Krasikova *et al.*, Fiz. Tekh. Poluprovodn. **23**, 73 (1989) [Sov. Phys. Semicond. **23**, 44 (1989)].

[4] M. D. Glinchuk, V. G. Grachev, M. F. Deĭgen *et al.*, *Electrical Effects in Radio-Frequency Spectroscopy*, Nauka, Moscow, 1981.

[5] É. I. Rashba and V. I. Sheka, Fiz. Tverd. Tela (Leningrad) **6**, 576 (1964) [Sov. Phys. Solid State **6**, 451 (1964)].

[6] V. Ya. Bratus', I. M. Zaritskiĭ, S. G. Pekar' *et al.*, Fiz. Tekh. Poluprovodn. **14**, 1339 (1980) [Sov. Phys. Semicond. **14**, 790 (1980)].

[7] G. H. Ludwig and F. S. Ham, Phys. Rev. Lett. **8**, 210 (1962).

Translated by D. Parsons