Giant intensity of magnetic dipole spin transitions in semimagnetic Van Vleck semiconductors

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A resonant intensification of the effective dynamic g-factor occurs in the semimagnetic Van Vleck semiconductor $A^2_{1-x}Fe_xB^6$ at frequencies close to the resonant frequencies of a spin-orbit multiplet of Fe^{2+} ions. This g-factor determines the intensity of magnetic dipole spin transitions of band electrons.

Recent experimental and theoretical research[1–3] on the spin resonance of free electrons and of electrons bound at shallow donors in semimagnetic semiconductors with the general formula $A^2_{1-x}Mn_xB^6$, which are characterized by an orientational paramagnetism of Mn^{2+} ions ($3d^5$ shell), have established that the primary mechanism for such transitions is an electric dipole spin (composite) resonance.[4] This conclusion follows from the calculation of Ref. 5 and 3, where it was shown, by different methods, that the exchange interaction of an electron with Mn^{2+} ions, which is responsible for the giant spin splitting,[6] causes only a negligible change in the dynamic g-factor $\tilde{g}$ of an electron. It turns out to be on the same order of magnitude as in an ordinary semiconductor: $\tilde{g} = g_c - g_i$ (g_c is the band g-factor of a conduction electron, and $g_i \approx 2$ is that of an Mn^{2+} ion). It determines the low intensity of the magnetic dipole transitions (ESR) [along with the electric-dipole spin (composite) resonance].

In this letter we show that in the new class of semimagnetic semiconductors $A^2_{1-x}Fe_xB^6$, where the Fe^{2+} ions ($3d^6$ shell) exhibit a polarization (Van Vleck) paramagnetism,[7–10] there should be a substantial intensification of the ESR. This result is conveniently demonstrated on the basis of the representation of an effective field[6] $\mathbf{G}_{\text{eff}}$ which is acting on the spin of an electron in a semimagnetic semiconductor;

$$\mathbf{G}_{eff} = g_c\mu\mathbf{H} + \mathbf{G} = g_c\mu\mathbf{H} - Jx\langle\mathbf{S}\rangle. \tag{1}$$

Here $\mathbf{H}$ is the external magnetic field, J is the magnitude of the exchange interaction of an electron with impurities ($\approx$0.2–0.4 eV), and $\langle\mathbf{S}\rangle$ is the expectation value of the spin of a magnetic impurity. The iron ions are in the lowest-lying singlet state, A_1, i.e., in a state which is nonmagnetic at $\mathbf{H} = 0$. An average spin is induced by the field $\mathbf{H}$ as a result of a mixing by the Zeeman-energy operator of this singlet with magnetic states excited by the magnitude of the spin-orbit splitting $\Delta\epsilon \approx 1$–2 meV. For semimagnetic semiconductors with a cubic lattice in a static field $\mathbf{H}_0 \| [001]\mathbf{z}$, the expectation values of the components of the spin operator ($S = 2$) are given by[9] ($\hbar = 1$)

$$\langle S_z\rangle = -\frac{4\omega_0}{\sqrt{\Delta\epsilon^2 + 4\omega_0^2}}, \quad \langle S_y\rangle = \langle S_x\rangle = 0, \tag{2}$$

where $\omega_0 = g_0 \mu H_0$, and $g_0 \approx 2$.

Let us consider the perturbation of a semimagnetic semiconductor by an electromagnetic wave of circular polarization (σ^+ or σ^-). We assume that the wave is of such a nature that its magnetic component satisfies $\mathbf{H}_1(t) \perp \mathbf{H}_0$. If we also restrict the discussion to fields which are not too strong, H_0, $H_0 \ll \Delta\epsilon / g_0 \mu$, we find $\langle S_z \rangle = -4\omega_0 / \Delta\epsilon$ for an arbitrary orientation of $\mathbf{H}_0$ with respect to the crystallographic axes. This conclusion agrees with (2) and allows us to introduce, with the help of (1), a static isotropic g-factor which determines the giant spin splitting ω_s of the electron levels:

$$\bar{g} = g_c + \frac{4Jx}{\Delta\epsilon} g_0, \quad \omega_s = |\bar{g}| \mu H_0. \tag{3}$$

In the calculation of the transverse components $\langle S_\pm \rangle$, $S_\pm = S_x \pm i S_y$, it is sufficient to consider the coupling of the singlet A_1 by the perturbation operator

$$V^\pm = \frac{1}{2} g_0 \mu H_1 (S_- e^{\pm i\omega t} + S_+ e^{\mp i\omega t}) \tag{4}$$

with only the first excited triplet, T_1, which corresponds to an energy $\Delta\epsilon + (1/2) M\omega_0$ ($M = 0, \pm 1$). As a result, we find

$$\langle S_+ \rangle = -4 g_0 \mu H_1 \frac{\Delta\epsilon}{\Delta\epsilon^2 - (\omega \mp \frac{1}{2}\omega_0)^2} e^{\pm i\omega t}; \quad \langle S_- \rangle = \langle S_+ \rangle^*. \tag{5}$$

Substituting (5) into (1), we find the following expression for the dynamic g-factor of a band electron in a Van Vleck semimagnetic semiconductor:

$$\tilde{g}_\perp^I = g_c + \frac{4Jx\Delta\epsilon}{\Delta\epsilon^2 - (\omega \mp \frac{1}{2}\omega_0)^2} g_0. \tag{6}$$

The superscript on $\tilde{g}_\perp$ specifies the sign of the circular polarization of the field $\mathbf{H}_1(t)$. For a hexagonal material, $\tilde{g}_\perp$ is given by a similar expression. This result makes it possible to (for example) determine the intensity of a spin magnetic resonance of band electrons in a Van Vleck semimagnetic semiconductor, which is proportional to the square of $\tilde{g}_\perp$. The sign of the circular polarization in (6) is the same as the sign of $\bar{g}$ in (3) in this case, and ω is the same as the giant spin splitting ω_c of the conduction band in the field H_0.

The basic approximation used in the derivation of (6) is ignoring the magnetic-polaron effects. This approximation made it possible to introduce effective field (1). The magnetic-polaron correction to the energies is given in order of magnitude by[10] $E_{\text{mp}} = (Jx)^2 / (\bar{N} |\omega_g - \Delta\epsilon|)$, where $\bar{N} \gg 1$ is a characteristic value of the number of magnetic impurities with which an electron interacts. In general, it is necessary to satisfy the inequalities

$$\omega_s, |\omega_s - \Delta\epsilon| \gg \max\{E_{\text{mp}}, \tau^{-1}\}, \tag{7}$$

where τ is the relaxation time of the electron spin.

Up to this point, we have been discussing a spin resonance of an electron in which there is no change in the state of the subsystem of the magnetic impurities. We should point out that the effective-field method is not adequate for analyzing magnetic dipole transitions in the case of a pump energy $\omega > \Delta\epsilon$, even if conditions (7) hold. In this case there may be transitions at combinational frequencies, i.e., transitions in the course of which the spin resonance of an electron is accompanied by the excitation of one of the magnetic impurities. In the case under consideration here, $\omega_0 \ll \Delta\epsilon$, the most intense of this class of transitions is that with an energy $\omega = \omega_s + \Delta\epsilon$ (one of the impurities is excited to a state with an energy $\Delta\epsilon$ from the triplet T_1). Under conditions (7), the wave functions of this system can be represented in a multiplicative form, and a simple calculation shows that the intensity of this resonance is determined by the matrix element

$$M_{cr} = -\frac{Jx}{\sqrt{2}}\left(\frac{1}{(\omega \mp \frac{1}{2}\omega_0) - \Delta\epsilon} - \frac{1}{(\omega \mp \frac{1}{2}\omega_0)}\right) g_0 \mu H_1 . \qquad (8)$$

Returning to the case of a pure spin resonance, we note that the large dynamic g-factor, $\tilde{g} \sim 100$, causes the intensity of the paramagnetic resonance of an electron to become comparable to the intensity of the electric-dipole spin (composite) resonance even in hexagonal materials, in which the latter is most apparent. The observation of a donor-electron ESR would be facilitated not only by a large value of $\tilde{g}$ but also by the absence of spin fluctuations.[8] In the case of orientational semimagnetic semiconductors, spin fluctuations broaden the spin splitting of an electron, $\Delta\omega_s \approx JxS/\bar{N}^{1/2}$. The broadening is greater than the ordinary broadening for an ESR frequency, $\sim 10^{10}$ Hz. It thus becomes impossible to realize an ESR in such systems. In the case of Van Vleck semimagnetic semiconductors, the linewidth is determined by Gaussian fluctuations of the local impurity concentration, which lead to fluctuations of the effective g-factor in (3). As a result, with decreasing observation frequency $\omega = \omega_s$ there is a proportionate decrease in the width (at the half-intensity level) of the spin resonance: $\Delta\omega_s/\omega_s = 2.35/\bar{N}^{1/2}$. For a Coulomb center (with an electron orbital radius a), we would have $\bar{N} = 8\pi n a^3$ here, where n is the number of Fe^{2+} ions per unit volume.

As an example we consider the ESR of shallow donors in $Zn_{0.98}Fe_{0.02}Se$ ($\Delta\epsilon = 1.8$ meV, $J = 220$ meV). We then have $\bar{g} \approx 20$; i.e., at an observation frequency of 10^{10} Hz the ESR line would be expected to lie at a field $H_0 = 360$ G, and the width of this line would be expected to be $\Delta H_0 = \Delta\omega_s/(\bar{g}\mu) = 57$ G. Its integral intensity would be more than two orders of magnitude greater than that of the ESR of the same number of shallow donors in a nonmagnetic semiconductor.

[1] R. Stepniewski, Solid State Commun. **58**, 19 (1986).
[2] M. Dobrowolska *et al.*, Phys. Rev. B **29**, 6652 (1984).
[3] Yu. G. Rubo *et al.*, Zh. Eksp. Teor. Fiz. **95**, 1880 (1989) [Sov. Phys. JETP **68**, 1087 (1989)].
[4] É. I. Rashba, Usp. Fiz. Nauk **84**, 557 (1964) [Sov. Phys. Usp. **7**, 823 (1964)].
[5] S. M. Ryabchenko and Yu. G. Semenov, Phys. Status Solid (b) **134**, 281 (1986).
[6] S. M. Ryabchenko, Izv. Akad. Nauk SSSR Ser. Fiz. **46**, 440 (1982).
[7] A. Twardowski *et al.*, J. Crystal Growth **72**, 401 (1985).
[8] Yu. G. Semenov, Izv. Akad. Nauk SSSR. Ser. Fiz. **52**, 507 (1988).
[9] Yu. G. Semenov, Fiz. Tekh. Poluprovodn. **21**, 1802 (1987) [Sov. Phys. Semicond. **21**, 1092 (1987)].
[10] D. Scalbert *et al.*, Phys. Rev. Lett. **62**, 2865 (1989).

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