RAMAN SCATTERING DUE TO THE MAGNON-SPIN FLIP OF THE CONDUCTION ELECTRONS IN FERROMAGNETIC SEMICONDUCTORS

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Using the s–d model, it is shown that, the new Raman scattering processes called the magnon-spin flip of a conduction electron excitations can occur. For typical values of the s–d exchange integral the order of magnitude of the extinction coefficient for such processes is found to be 10^{-9}–10^{-11} cm^{-1} sr^{-1}. It is also shown that the analysis of the dependence of the energy of the magnon-spin flip excitation on the external magnetic field makes it possible to determine the value and sign of the s–d exchange integral and as well as the g factor for conduction electrons.

Introduction

The available literature [1–7] is lacking in interpretations and predictions of possible anomalies of the Raman processes in magnetic semiconductors. A direct consequence of such a situation in theoretical knowledge, is the inability to interpret the one and two magnon Raman spectrum in magnetic semiconductors on the basis of the insulator model [1, 2] as well as the inability to use Raman spectroscopy for investigating the conduction band and the interactions between magnons, and the spins of conductions electrons and photons. On the other hand, these interactions play an important role in the transport phenomena peculiar to magnetic semiconductors such as: the magnon drag of conduction electron as predicted by Sugihara in 1972 [8] and anomalies of the thermoelectric power associated with the magnetic ordering [9]. The latter has been investigated by many authors. Therefore, after making possible the direct interpretation of the new phenomena in Raman spectroscopy of elementary excitation in the magnetic semiconductor, we will present the calculation of the excinction coefficient for the processes connected with the generation of the magnon-spin flip of a conduction electron excitation.

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1. Quantum model of a ferromagnetic semiconductor interacting with a field of electromagnetic radiation

From a number of theoretical and experimental papers [8, 9, 11, 13, 17] it is concluded that one can rather successfully predict the physical phenomena as well as interpret the experimental data for magnetic semiconductors resorting to the model which takes into account the exchange interactions between the conduction electrons and the system of magnetically ordered spins of valence band electrons. In our further consideration, according to the usual terminology, such a model will be called the *s–d* model. The Hamiltonian for a magnetic semiconductor when considering the *s–d* exchange interactions and the applied homogeneous constant magnetic field can be written in the following form [8, 9, 11, 12, 17]:

$$H = H_0+H_m+H_{s-d}+H_{e-r}. \tag{1.1}$$

The operator H_0, describing the system of unperturbed electrons of the conduction and valence bands, has the following form

$$H_e = \sum_{kms} E_{kms}c^+_{kms}c_{kms}, \tag{1.2}$$

where $c_{k,m,s}$, $c^+_{k,m,s}$ denote the annihilation and creation operators of an electron with wave-vector $\boldsymbol{k}$ and spin s in band m. The value of the energy $E_{k,m,s}$ is defined as follows

$$E_{kcs} = E_{kc}+sg_cH_z, \tag{1.3a}$$

$$E_{k,v,s} = E_{k,v}, \tag{1.3b}$$

where $E_{k,m}$ is the energy of an electron with the wave-vector $\boldsymbol{k}$ in the Bloch state of the m-th band in the absence of an external magnetic field. It should be noted that for the valence electrons, the part of their energy dependent on external magnetic field was introduced to the second term of the Hamiltonian (1.1) describing the energy of the localized spins. The second term of the Hamiltonian (1.1) takes the following form

$$H^{(m)}_m = \sum_q \hbar\omega_q f^+_q f_q, \tag{1.4}$$

where f^+_q and f_q denote the creation and annihilation operators, respectively for magnons with wave-vector $\boldsymbol{q}$ and energy

$$\hbar\omega_q = -g_v|\mu_B|H_zNS-N_zJS^2+\sum_q [2J_zS(1-D_q)+g_v|\mu_B|H_z], \tag{1.4a}$$

$$D_q = z^{-1}\sum_{\langle m\rangle} e^{i\cdot q(R_m-R_n)}. \tag{1.4b}$$

The symbol $\langle m\rangle$ below summation denotes that the sum is limited to the nearest neighbours of the spin S_n at the site $\boldsymbol{R}_n$. S is the value of the localized spin, whereas N is number of crystal lattice sites.

The s–d Hamiltonian H_{s-d}, for a ferromagnet in the second-quantization representation, is given by the following expression.

$$H^{(f)}_{s-d} = -\left(\frac{2S}{N}\right)^{1/2} \sum_{k,k'q} J_{s-d}(k, k')\delta(k' - k + q)$$

$$\times (c^{+}_{k,c,+}c_{k',c-}f_{q} + c_{k',c,-}c_{k,c,+}f^{+}_{q})$$

$$+ \frac{1}{N} \sum_{k,k',q,q'} J_{s-d}(k, k')\delta(k' - k + q' - q)\,(c^{+}_{k,c,-}c_{k',c,-} - c^{+}_{k,c,+}c_{k',c,+})$$

$$-2S \sum_{k,s} J_{s-d}(k, k)\delta_{s,-1/2}c^{+}_{k,c,s}c_{k,c,s}. \tag{1.5}$$

The last term of the Hamiltonian (1.1) gives rise to the interaction between the electron system and the electromagnetic field. It can be rewritten, making use of the creation and annihilation operators of photons, in the following form

$$H_{e-r} = \left(\frac{2\pi e^2 \hbar}{m^2 \cdot \varepsilon \cdot V}\right)^{1/2} \sum_{lks} \left[\frac{1}{(\omega_l)^{1/2}} u_l\right.$$

$$\left.(p_{k+lm,\,k,m'}c^{+}_{k+l,m,s}c_{k,m',s}a_l + p_{k,m,\,k'm'}c^{+}_{k-l,m,s}c_{k,m',s}a^{+}_l)\right], \tag{1.6}$$

where

$$p_{k,m,\,k'm'} = \langle k, m, s|p|k', m', s\rangle \tag{1.6a}$$

denote the matrix elements of the momentum operator calculated in the Bloch function system $|k, m, s\rangle$. a^{+}_l, and a_l are the creation and annihilation operators of photons with wave vector l, energy $\hbar\omega_l$ and polarization u_l, respectively. Having transformed the Hamiltonian of the system to the second-quantization representation, we can proceed to discuss the Raman light scattering on magnetic elementary excitations in ferromagnetic semiconductors.

2. *Raman process associated with the generation of an elementary excitation of the type: magnon-spin flip of a conduction electron*

Recent experimental investigations allow on to come to the surprising conclusion that the extinction coefficients for the one and two-particle Raman effects [3, 25] have the same order of magnitude [3, 4, 20, 22]. The reason for this phenomena is either the appearence of the resonance interaction between the elementary excitations which gives rise, to e. g., the creation of plasmon-phonon and phonon-plasmon-cyclotron pairs [20, 22] or some other interactions responsible for the two-particle Raman effect stronger than that for single modes [3, 4]. In our considerations we will show that, in magnetic semiconductors, we should expect the occurrence of Raman effect associated with the generation of a new type of two-particle elementary excitation consisting of magnon and spin flip of conduction electron. First, we will present the calculations of the extinction coefficient for such processes in ferromagnetic semiconductors as they are less complicated.

In the case of Raman effect, the differential extinction coefficient is defined as a fraction of the incident photons inelastically scattered per unit path per unit solid angle. Denoting the extinction coefficient by h, we obtain

$$h = \frac{\partial^2}{\partial\Omega\partial X}\left(\frac{N_2}{N_1}\right), \tag{2.1}$$

where N_1 and N_2 are the numbers of the incident and scattered photons per unit time per 1 cm^2, respectively. X is the width of the sample, and Ω is the solid angle.

The ratio N_2/N_1 can be written in a form allowing direct transformation to quantum quantities, as follows

$$\frac{N_2}{N_1} = \frac{W(t)\varepsilon^{1/2}}{N_1 tc}. \tag{2.2}$$

$W(t)$ in Eq. (2.2) is the probability of the annihilation to the moment t of the incident photon possessing a given polarization and wave vector, with the simultaneous creation of the scattered photon, ε is the dielectric constant for the incident light.

Resorting to the quantum field theory [24], we can express $W(t)$ in the following form:

$$W(t) = \langle b|U(-\infty, t)\,|a\rangle, \tag{2.3}$$

$$U(-\infty, t) = \sum_n (-1)^n \int^{t} dt_1 \int^{t_1} dt_2 \ldots \int^{t_{n-1}} dt_n H'(t_1) \ldots H'(t_n), \tag{2.4}$$

where $H = H_{s-d} + H_{e-r}$ denotes the time-dependent non-diagonal term of the Hamiltonian in the interaction representation, i. e. the sum of the operators of the interactions between all the elementary excitations occurring in the system. $|a\rangle$, $|b\rangle$ stand for the product of the unperturbed states of photons, electrons and magnons. Concerning the necessity of the annihilation of the photon appearing with the simultaneous creation of the scattered photon and the excitation of the type: magnon-spin flip of a conduction electron, the non-zero contribution to $W(t)$ is obtained in the third order of the perturbation calculus. Resorting to Eqs (2.1), (2.3) and (2.4) we can express $W(t)$ in the form

$$W(t) = \sum_{\substack{k,k'q\\ l_2}} \Bigg| \sum_{c,d} \frac{\langle n_{l_1}-1;\, n_{l_2}+1;\, n_q+1;\, n_{k,c+} = 0;\, n_{k',c-} = 1|H'|c\rangle}{(E_c-E_0)\,(E_d-E_0)}$$
$$\times \langle c|H'|d\rangle\, \langle d|H'|n_{k',c,-} = 0;\, n_{k,c,+} = 1;\, n_q;\, n_{l_1},\, n_{l_2}\rangle\Bigg|^2$$
$$\times\, \delta\left(\hbar\omega_{l_1} - \hbar\omega_{l_2} - \hbar\omega_q + \frac{E_{k',c-} - E_{k,c,+}}{\hbar}\right), \tag{2.5}$$

where E_0 and E_c, E_d denote values of the energy in the initial and intermediate states, respectively. c, d are the unperturbed states of the system under consideration and n_{l_1}, n_{l_2}, n_q, $n_{k,c+}$, $n_{k,c-}$ denote the occupation numbers for the photons incident and scattered, the magnons with the wave vector $\boldsymbol{q}$ and conduction electrons in the Bloch states $|\boldsymbol{k}, c, +\rangle$, $|\boldsymbol{k}, c, -\rangle$, respectively. The quantities $\hbar\omega_{l_1}$, $\hbar\omega_{l_2}$, $\hbar\omega_q$, $E_{k,c+}$, $E_{k,c-}$ are the energies of these particles ordered in an analogical way.

In our further considerations, similarly to other authors [1–6], [20–26], we will restrict ourselves to the spontaneous Raman effect and we will consequently perform the calculations for the low temperature region. We can then assume that in the initial state n_{l_2}, and n_q are equal to zero. Moreover, in order to simplify the calculations we will take into account the strong magnetic polarization of conduction band via the s–d interaction

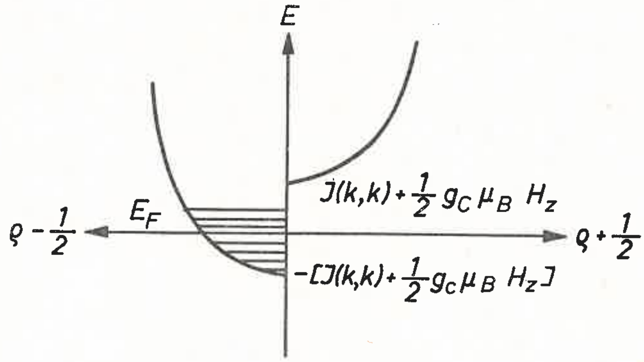

Fig. 1. Decoupling of the energy levels of conduction electrons due to the s–d interaction $\varrho-\frac{1}{2}$ and $\varrho+\frac{1}{2}$ denote the density of conduction band states for the spin $s = -\frac{1}{2}$ and $+\frac{1}{2}$, respectively. H_z stands for the static homogeneous external magnetic field, E_F denotes the Fermi level

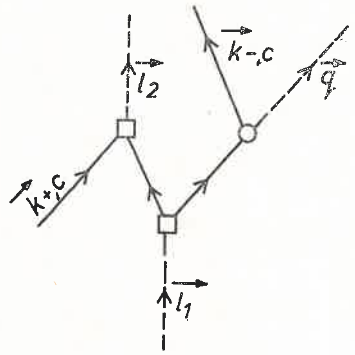

Fig. 2. Illustration of the scattering processes giving rise to the Raman absorption associated with the magnon-spin flip excitation

[11, 12, 17]. As a consequence of such a polarization, at small concentrations of conduction electrons, we observe either the band with the spin $+1/2$ or $-1/2$ in accordance to the sign of the s–d exchange integral.

The scheme of occupation of the conduction band is given in Fig. 1. Careful analysis of the scattering processes shows that the contribution to $W(t)$ is due to the scattering processes shown in Fig. 2.

A typical example of the products of the matrix elements, corresponding to the scheme in Fig. 2, can be analytically written in the following form

$$\frac{u_{l_1} p_{k-l_2,v;k,c} J_{s-d}(k'k'+q) u_{l_2} p_{k'+q,c,k-l_2,v}}{(E_{k',c,-} - E_{k'+q-l_1,v,+} + \hbar\omega_q - \hbar\omega_{l_1})(E_{k'+q,c,+} - E_{k'+q-l_1,v+} - \hbar\omega_{\,1})} n_{k,c,+}(1-n_{k',c,-})^{1/2}, \tag{2.6}$$

(the schemes of all the scattering processes can be obtained by permutation of the localization of the operators H_{s-d} and H_{e-r} at the vertices of the diagram as well as by consideration of the two possible spin orientations in operators).

Thus we obtain 12 matrix elements corresponding to the Raman processes of light scattering on the two-particle elementary excitations of the type: magnon spin flip of a conduction electron. In our further considerations we will resort to the fact that the difference between the width of the energy gap E_g and the energy of incident photons is considerably larger then the s–d exchange integral (in many experiments $E_g - \hbar\omega_{l_1} = E_{k,c} - E_{k,v} - \hbar\omega_{l_1}$ is of the order of 0.5–1 eV, whereas the exchange integral estimated due to transport phenomena is of the order of 0.01–0.1 eV [8, 9, 13, 17].

The above simplifications allow one to represent $W(t)$ for the Raman light scattering on the magnon with the simultaneous spin flip of a conduction electron, in the following way

$$W(t) = \frac{B}{\omega_{l_1}^2} \sum_{q,l_2,k} \left| \frac{u_{l_2} p_{k-q,v,k-q,c} u_{l_1} p_{k-q,c,k-q,v}}{E_g - \hbar\omega_{l_2}} \; \frac{J_{s-d}(k-q,k)(1-n_{k',c-})^{1/2} n_{k,c,+}^{1/2}}{\hbar\omega_q + E_{k-q,c,-} - E_{k,c,+}} \right|^2$$

$$\times\, \delta(\hbar\omega_{l_1} - \hbar\omega_{l_2} - \hbar\omega_q + E_{k,c,+} - E_{k-q,c,-}), \tag{2.7}$$

where

$$B = \frac{8\pi^2 h e^4}{\varepsilon^2 \cdot V^2 \cdot m^4}. \tag{2.7a}$$

Due to Eq. (2.7) we obtain the differential extinction coefficient in the following form:

$$\frac{d^2 h}{d\omega d\Omega} = \frac{e^4}{m^4 c^4 V} \sum_{q,k} \left[\frac{\overline{u_{l_2} p_{k-q,v,k-q,c} u_{l_1} p_{k-q,c,k-q,v}}}{(E_g - \hbar\omega_{l_2})(\hbar\omega_q + E_{k-q,c,-} - E_{k,c,+})} \right.$$

$$\left. \times J_{s-d}(k, k-q) \cdot n_{k,c,+}^{1/2} (1-n_{k',c,-})^{1/2} \right]^2$$

$$\times\, \delta\left(\omega_{l_1} - \omega_{l_2} - \omega_q - \frac{E_{k-q,c,-} - E_{k,c,+}}{\hbar}\right), \tag{2.8}$$

where the solid line over the product of the matrix elements means that we make use of the approximation of the weak dependence of this product on wave vectors $\boldsymbol{l}_1$, $\boldsymbol{l}_2$ and $\boldsymbol{q}$ which is usual in qualitative estimations [1–7], [20–23], [26].

3. Conclusions and discussion of the results

Careful analysis of the form of Eq. (2.8) points to the possibility of further simplifications as well as the formulation of the following conclusions:

a. On expressing the energy denominator in the parabolic band approximation as follows

$$\hbar\omega_q + \frac{\hbar^2}{2m}(q^2 - 2\boldsymbol{k}\cdot\boldsymbol{q})$$

and noting that $|\boldsymbol{k}| \ll k_B$, where k_B denotes maximum value of the wave vector in the Brillouin zone we obtain a factor of the order

$$\left|\frac{2\cdot J(\boldsymbol{k}, \boldsymbol{k}-\boldsymbol{q})m}{\hbar^2 q^2}\right|^2$$

strongly reducing the probability of the generation of the magnons with larger value of wave vectors. Therefore, we can conclude that in the Raman processes, involving magnon and spin flip of a conduction electron excitation, are generated only by magnons from the center of the Brillouin zone for which the following condition is satisfied

$$\frac{\hbar^2 q^2}{2m} \leqslant J_{s-d}(\boldsymbol{k}, \boldsymbol{k}-\boldsymbol{q}).$$

Using the typical value of the *s–d* exchange integral [7–17], i. e.

$$J_{s-d}(\boldsymbol{k}, \boldsymbol{k}-\boldsymbol{q}) \approx 0.01-0.1\ \text{eV},$$

and assuming the width of the conduction band to be of the order of 1 eV,

$$q \leqslant 0.3k_B.$$

b. Due to above mentioned restriction of the order of magnitude of the magnon wave vector and the energy conservation rule expressed by the Dirac delta in Eq. (2.8) the maximum of the Raman absorption occurs near the following value of absorbed energy

$$\hbar\omega = \hbar(\omega_{l_1} - \omega_{l_2}) \approx \hbar\omega_q + 2SJ(\boldsymbol{k}, \boldsymbol{k}-\boldsymbol{q}).$$

c. Eq. (2.8) allows one to estimate the value of the extinction coefficient. On assuming, similarly to Loudon [27] in the case of the phonon processes, that

$$E_g - \hbar\omega_{l_2} \approx 0.5-1.0\ \text{eV},$$

$$|p_{k,v;k,c}| \approx 3 \cdot 10^{-20} \frac{\text{g cm}}{\text{s}}, \quad S = \tfrac{1}{2}$$

$$\frac{J_{s-d}(k, k-q)}{\hbar\omega_q + E_{k-q,c,-} - E_{k,c,+}} \approx 1$$

and taking into account that magnons from approximately about 1/10 of the Brillouin zone take part in these processes, we obtain the following value of the extinction coefficient for concentrations of conduction electrons of the order of 10^{16} cm^{-3}

$$\frac{\partial^2 h}{\partial\Omega\partial\omega} \approx 10^{-9} - 10^{-11}\ \text{cm}^{-1}\ \text{sr}^{-1}.$$

It can be concluded here that the excinction coefficient for the Raman absorption associated with the generation of the elementary excitation pair of the type: magnon-spin flip of a conduction electron is of the same order as that in the one and two-magnon Raman effect in insulators [1–7].

d. The analysis of our calculations indicates also that the occurrence of the considered processes in ferromagnetic semiconductors are limited to materials exhibiting a negative value of the *s–d* exchange integral, i. e. the antiparallel orientation of the spins of conduction electrons and those localized at crystal lattice sites. In general, this condition can be concluded from the form of the operator $H_{s\text{-}d}$ which gives rise to the appearance in Eqs (2.7) and (2.8) of the following factor

$$n_{k,c,+}(1 - n_{k',c,-}).$$

Such a factor, at full polarization of the localized spins shown in Fig. 1, differs from zero only for an antiparallel orientation of the localized spins and those of the conduction electrons.

e. The main data of interest are provided for studying the shift of the Raman absorption maximum in an external magnetic field. From Eq. (2.8) it can be concluded that the change of the frequency corresponding to the maximal absorption, is given by

$$(g_v - g_c)\mu_B H_z$$

where g_v and g_c denote the giromagnetic factors of valence and conduction electrons, respectively. The simultaneous measurement of a shift of the absorption maximum in the magnetic field for the Raman effect of the type: the magnon-spin flip of a conduction electron and for the one-magnon Raman processes [1–7] allows on to determine g_c–g_v and g_v, i. e. values of the both giromagnetic factors.

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