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The sum rule for the luminescence of semiconductors doped with transition metal impurities

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Abstract. A theory of two complementing luminescence lines observed in some $A_{II}B_{VI}$ semiconductors doped with transition metal impurities is proposed. The first line is known to be attributable to an intracentre transition; the second line appears as a result of a second-order process of interference between radiative and non-radiative transitions with participation of the d shells of the impurity atoms. A detailed calculation of the intensity of such a process is presented. It is shown that the specific resonance can make this second-order process quite strong if the impurity-phonon coupling is strong enough. The possibility of observing pairs of complementing lines in various $A_{II}B_{VI}$ and $A_{III}B_V$ systems is discussed. Some unresolved problems associated with the effect are also touched upon.

1. Introduction

Several years ago Broser and collaborators published a striking experimental observation in the luminescence spectrum of $A_{II}B_{VI}$ semiconductors doped with transition metal impurities (for ZnS:Cu see Broser *et al* 1988; for ZnS:Ni and CdS:Cu see Hoffmann *et al* 1988). The effect observed in these papers was called the 'sum rule', since the energies $h\nu_1$ and $h\nu_2$ of two zero-phonon lines in the luminescence spectrum summed to the forbidden energy gap, i.e

$$h\nu_1 + h\nu_2 = E_g. \quad (1)$$

One of these lines, $h\nu_1$, belongs to the so-called infrared band. For ZnS:Cu it corresponds to the emission of a photon with an energy $h\nu_1 = 0.858$ eV, and is due to the intracentre transitions between two states of the Cu impurity appearing when the 2D state of the d shell is split by the cubic crystal field (point group T_d). The split states in terms of the many-electron configuration are $^2T_2(t_2^5e^4)$, the ground state, and $^2E(t_2^6e^3)$, the first excited state (see, for example, Ballhausen 1962) with an energy difference

$$\Delta E \equiv 10D_q = E(^2E(t_2^6e^3)) - E(^2T(t_2^5e^4)) = h\nu_1. \quad (2)$$

This splitting is caused mainly by the crystal field of the host atoms surrounding the d impurity. There is also a covalent renormalization of ΔE due to a hybridization of the d functions with the band Bloch states (Kikoin and Fleurov 1979). It is quite clear that this splitting is mainly an internal impurity property, and is not connected with the width of the forbidden energy gap.

This is the reason why the existence of a second line complementing the $h\nu_1$ line to the forbidden energy gap (1) is so surprising. The second line in the case of ZnS:Cu is found in the blue part of the spectrum, and is due to the emission of photons with an energy $h\nu_2 = 2.965$ eV. This zero phonon line together with its phonon satellites is observed at low temperatures (around 4–6 K) and disappears above 30 K. There are reasons to believe that this line is really connected to the transition metal impurity, rather than to an unidentified defect. This point of view is also supported by the fact that pairs of complementing lines are observed in several systems. We would expect that the observation of this line reflects intrinsic properties of the transition metal impurities in semiconductors and try to explain the ‘sum rule’ using this line of argument. The problem is that, if our knowledge of the electronic structure of this system is correct, there are no dipole (first-order) transitions producing the necessary photon. That is why an attempt was made (Dahan and Fleurov 1992) to find a second-order process allowing for the complementary line. That paper showed that an interference between radiative and non-radiative transitions, and a peculiar resonance which may take place in such systems, considerably enhance the intensity of the complementing line. Therefore the generally very weak second-order process is nevertheless observed.

The aim of the present paper is to present a detailed description of the mechanism only briefly outlined in Dahan and Fleurov (1992), and to perform the calculations allowing one to estimate the intensity of the complementing line. The mechanism producing this line is described in section 2. The calculations are carried out in section 3, where the important role of Jahn–Teller distortions is emphasized. Section 4 presents a discussion of the results.

2. The origin of the complementing line

The process to be considered is the recombination of an electron–hole pair via a transition metal impurity. This pair is created by external irradiation. Both the electron and the hole thermalize rapidly, and the energy of the pair nearly equals the forbidden energy gap E_g . Most probably, this pair is bound to the impurity and produces as a result a narrow zero-phonon line. We are looking for a second-order process in which a photon is emitted with energy $h\nu_2 = E_g - 10Dq$. The initial state of the system contains the energy of the valence band with a hole, $E_v(N - 1)$, and the conduction band energy with one electron, $E_c(1)$; N is the total number of electrons in the bands. It is clear that $E_c(1) + E_v(N - 1) = E_g + E_b$, where $E_b = E_c(0) + E_v(N)$ is the energy of the band electrons in the ground state. The transition metal impurity is in its ground state, which in the case of ZnS:Cu is the state ${}^2T_2(t_2^5e^4)$ with nine electrons in the d shell, i.e. the initial-state energy is

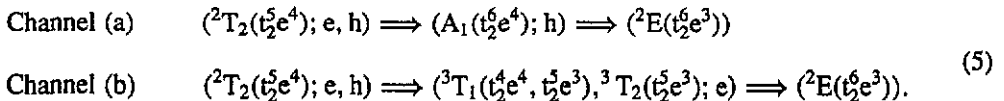
$$E_{\text{in}} = E_b + E_g + E({}^2T_2) + E_{\text{ph,in}} \quad (3)$$

where $E_{\text{ph,in}}$ is the energy of the phonon system.

In order to obtain the $h\nu_2$ line the final state must be a state in which there is no electron–hole pair in the bands and with the transition metal impurity in the excited state ${}^2E(t_2^6e^3)$, i.e. its energy is

$$E_f = E_b + E({}^2E) + E_{\text{ph,f}} \quad (4)$$

There are two possible channels leading from state (3) to state (4), as expressed by the following reactions:



In channel (a) the electron from the conduction band is at the first stage, captured by the Cu atom converting the nine-electron atomic state ${}^2T_2(t_2^5e^4)$ into the ten-electron atomic state $A_1(t_2^6e^4)$; the valence hole for the moment remains free. The intermediate state is

$$E_{\text{int,a}} = E_b + E_g - E_c + E(A_1) + E_{\text{ph,a}}. \quad (6)$$

At the second stage the free hole is captured by the Cu atom and its ten-electron state becomes again a nine-electron state. The capture of the hole means the removal of an electron from the filled shell $A_1(t_2^6e^4)$. If the electron is removed in the t_2 state we arrive at the desired final state, with the energy as given in (4).

Channel (b) gives us another possibility of arriving at the same final state. First, the free hole is captured creating two possible intermediate states ${}^3T_1(e^4t_2^4, e^3t_2^5)$ and ${}^3T_2(e^3t_2^5)$ with energies

$$\begin{aligned} E_{\text{int,b1}} &= E_b + E_g - E_h + E({}^3T_1) + E_{\text{ph,b1}} \\ E_{\text{int,b2}} &= E_b + E_g - E_h + E({}^3T_2) + E_{\text{ph,b2}}. \end{aligned} \quad (7)$$

After that, the electron remaining in the conduction band is captured to produce the desired final configuration of the d shell.

Channels (a) and (b) both provide the possibility of a transition with the desired energy change. What remains is to verify that the rate of the above two-stage process is large enough to account for the experimental data.

We have two types of interaction at our disposal which may cause transitions between the various electronic states. The radiative transitions are due to the interaction

$$\mathcal{R} = -\frac{e}{mc} \sum_i \hat{P}_i \cdot A \quad (8)$$

of the electrons with an electromagnetic field A . The term \hat{P}_i is the momentum operator of the i th electron. There are also non-radiative transitions due to the non-adiabaticity operator

$$\mathcal{L} = \frac{\hbar^2}{M} \sum_j \langle \Psi_{\mu'} | \frac{\partial}{\partial R_j} | \Psi_{\mu} \rangle \frac{\partial}{\partial R_j} \quad (9)$$

where R_j is the coordinate of the j th atom and M is its mass. The functions Ψ_{μ} are the electronic parts of the wavefunctions of the states described above. The free differential operator $\partial/\partial R_j$ in equation (9) is supposed to act on the phonon part of the wavefunctions.

These two types of interaction, \mathcal{L} and \mathcal{R} , produce three possible second-order processes.

(i) The second-order dipole process (\mathcal{R}^2) produces two photons, $h\nu'_2$ and $h\nu''_2$, whose sum energy is

$$h\nu_2 = h\nu'_2 + h\nu''_2.$$

It is clear that a broad spectrum rather than a sharp line appears, and therefore this process is not of interest to us.

(ii) Second-order non-adiabatic processes (\mathcal{L}^2) do not produce any photons and do not contribute to the luminescence spectrum.

(iii) Only the interference 'radiative-non-radiative' transitions (\mathcal{LR}) produce the necessary photon $h\nu_2$. The intensity of this line will be calculated in the next section.

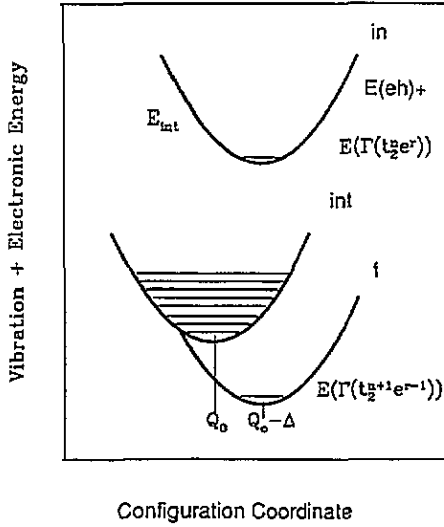


Figure 1. A scheme for the configurational coordinates for the second-order transition; Q is the local phonon coordinate, Δ is the Jahn-Teller displacement.

3. Transition rate of the complementing line

The complementing line $h\nu_2$ appears due to the above second-order process, whose rate can be calculated under the following assumptions. No phonons are excited in the initial state, since the temperature is low and we believe that the phonon relaxation is more rapid than the recombination of the electron-hole pairs. The final state is also not excited vibronically, since the calculation is done for the zero phonon line. As for the intermediate states, there are no restrictions concerning their possible vibronic excitations (figure 1) and the corresponding summation is to be carried out. We are also interested in a single photon process, which in second order only appears due to an interference between the radiative and non-radiative transitions. The corresponding rate is

$$W_{if}^{(2)} = \frac{2\pi}{\hbar} \delta(E_{in} - E_f - h\nu) \left| \sum_{int} \left(\frac{\langle \Phi_f | \mathcal{R} | \Phi_{int} \rangle \langle \Phi_{int} | \mathcal{L} | \Phi_{in} \rangle}{\Delta E_e + \Delta E_{ph} + i\Gamma_{ph}/2} + \frac{\langle \Phi_f | \mathcal{L} | \Phi_{int} \rangle \langle \Phi_{int} | \mathcal{R} | \Phi_{in} \rangle}{\Delta E_e + \Delta E_{ph} - h\nu + i\Gamma_{ph}/2} \right) \right|^2. \quad (10)$$

Here we use the standard adiabatic representation for the wavefunction Φ as a product of an electronic wavefunction, Ψ , and a nuclear wavefunction, χ , that is $\Phi(\{\mathbf{r}\}, \{\mathbf{R}\}) = \Psi(\{\mathbf{r}\}; \{\mathbf{R}\}) \chi(\{\mathbf{R}\})$. The term $\Delta E_e = E_{in,e} - E_{int,e}$ is the change in the electronic energy of the whole system due to the transition from the initial to an intermediate state. The term $\Delta E_{ph} = E_{ph,in} - E_{ph,int}$ is the corresponding change in the phonon energy. The summation over the intermediate states in (10) includes a summation over all possible phonon configurations of each intermediate electronic state. It is clear that one can always find a phonon configuration that makes the real part of one of the denominators in (10) equal to zero. These configurations produce the most important contributions to the probability per unit time $W_{if}^{(2)}$, and therefore its calculation demands a proper account be taken of the broadening Γ_{ph} of the vibronically excited intermediate states.

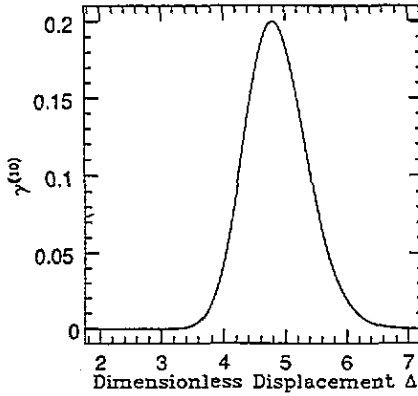


Figure 2. The contribution of channel (a) to the transition rate of the zero phonon line in the blue band as compared to the radiative transition rate plotted against the dimensionless displacement, Δ , for ZnS:Cu.

The transition rate (10) now becomes

$$W_{if}^{(2)} = \frac{2\pi}{\hbar} \left| \sum_{\text{int}} \left(\frac{\langle \Psi_f | \mathcal{R} | \Psi_{\text{int}} \rangle \langle \Psi_{\text{int}} | \mathcal{L}^{(e)} | \Psi_{\text{in}} \rangle F_{f,\text{int}} S_{\text{int},\text{in}}}{\delta E^{(8)} - \Delta E_{\text{ph}} - i\Gamma/2} + \frac{\langle \Psi_f | \mathcal{L}^{(e)} | \Psi_{\text{int}} \rangle \langle \Psi_{\text{int}} | \mathcal{R} | \Psi_{\text{in}} \rangle S_{f,\text{int}} F_{\text{int},\text{in}}}{\delta E^{(10)} - \Delta E_{\text{ph}} - i\Gamma/2} \right) \right|^2 \delta(E_g - \Delta E - h\nu_2) \quad (11)$$

where $S_{f,\text{int}}$ and $F_{\text{int},\text{in}}$ are the following overlap integrals:

$$F_{\text{int},\text{in}} = \langle \chi_{\text{int}}(\mathbf{R}) | \chi_{\text{in}}(\mathbf{R}) \rangle \quad S_{f,\text{int}} = \langle \chi_f(\mathbf{R}) | \mathcal{L}^{(l)} | \chi_{\text{int}}(\mathbf{R}) \rangle. \quad (12)$$

The upper indices l or e in the operators

$$\mathcal{L}^{(l)} = \sum_j \frac{i\hbar}{\sqrt{M}} \frac{\partial^{(l)}}{\partial \mathbf{R}_j} \quad \mathcal{L}^{(e)} = - \sum_j \frac{i\hbar}{\sqrt{M}} \frac{\partial^{(e)}}{\partial \mathbf{R}_j}$$

denote that the corresponding operator acts either on the vibronic or on the electronic part of the wavefunction, respectively.

The energy differences between the initial and the intermediate electronic states in the denominators (10) in the case of ZnS:Cu are

$$\delta E^{(10)} = \Delta E_c^{(10)} - h\nu = E_g - E^{(10)}(T_2) - h\nu \quad (13)$$

for channel (a), and

$$\delta E^{(8)} = \Delta E_c^{(8)} = E(^2T_2) \quad (14)$$

for channel (b), where $E(d^9) - E(d^8) = E(^2T_2)$ and $E^{(10)}(^2T_2) = E(d^{10}) - E(d^9)$ is the ionization energy of the tenth t_2 electron of the Cu^+ atom d shell. The photon energy $h\nu$ either appears or does not appear in the denominator in (11) depending on the order of the action of the interaction operators \mathcal{R} and \mathcal{L} , and in principle both channels must be taken into account. However, only those two channels which give the largest contribution are kept in the transition rate (11).

3.1. Vibrational wavefunctions

In order to calculate of the probability per unit time $W_{if}^{(2)}$ we have to formulate a model approach to be used for the vibronic wavefunctions. It is convenient to treat this process using the configuration coordinates (see figure 1). For the sake of simplicity, we assume that the vibronic frequencies do not change in the different electronic states:

$$\omega_{in}^{\Gamma} = \omega_{int}^{\Gamma} = \omega_i^{\Gamma}. \quad (15)$$

Here Γ denotes the irreducible representation of the point group to which the corresponding vibrations belong.

In the case of a tightly bound impurity atom we would expect the important interactions to be those with nearest neighbours. For T_d symmetry there are four nearest neighbours that give rise to the following vibrational modes:

$$\Gamma_v = A_1 + E + 2T_2. \quad (16)$$

The charge transfers from d^9 to d^{10} or to d^8 electronic configurations give rise to intermediate states with highly excited vibrational degrees of freedom. This happens due to a strong change of the Jahn–Teller displacement (figure 1). Therefore, the principal part of the vibrational energy is concentrated in the corresponding Jahn–Teller vibrational mode, which means that this mode plays the role of the accepting mode in the transition process.

The harmonic approximation for the vibrational wavefunctions are

$$\chi_{\mu}(\mathbf{Q}) = \prod_{\Gamma\gamma} \chi_{\mu\Gamma\gamma}^n(\mathcal{Q}_{\Gamma\gamma}) \quad E_{\mu\Gamma} = \sum_{\Gamma} (n + \frac{1}{2})\hbar\omega_{\Gamma\mu} + E_{\mu} \quad (17)$$

where E_{μ} is the electronic energy. The eigenfunction of the harmonic oscillator is

$$\chi_{\mu\Gamma\gamma}^n(\xi) = \left(\frac{\alpha_{\Gamma\mu}}{\sqrt{\pi}2^n n!} \right)^{1/2} H_n(\xi) \exp(-\frac{1}{2}\xi^2) \quad (18)$$

where $H_n(\xi)$ is the n th Hermite polynomial, and

$$\xi = \alpha_{\Gamma\mu} \mathcal{Q}_{\Gamma\gamma} \quad \alpha_{\Gamma\mu} = \sqrt{\frac{M\omega_{\Gamma\mu}}{\hbar}}.$$

For both channels the process ends in a state having electronic E symmetry. This means that its Jahn–Teller mode also has E symmetry. Therefore, a multiphonon transition from the intermediate to the final state is allowed only if a mode with $\Gamma = E$ in the intermediate state is excited. The first overlap integral in (12) is then

$$F_{int,in}(n\Delta) = \langle \chi_{int}(\mathbf{Q}_{int}) | \chi_{in}(\mathbf{Q}_{in}) \rangle \\ = \langle \chi_{intE\mu}^{(n)}(\mathcal{Q}_{E\mu}) | \chi_{inE\mu}^{(0)}(\mathcal{Q}_{E\mu} - \Delta) \rangle \prod_{\Gamma'\mu'} \langle \chi_{int\Gamma'\mu'}^{(n')} | \chi_{in\Gamma'\mu'}^{(n')} \rangle. \quad (19)$$

The operators $\mathcal{L}^{(e)}$ and $\mathcal{L}^{(i)}$ are parts of the kinetic energy operator, which is why they must have the same symmetry. An analysis of the electronic matrix element (see section 3.3)

shows that $\mathcal{L}_{T_2}^{(e)}$ makes a finite contribution. Therefore calculating the second overlap integral in (12)

$$\begin{aligned} S_{f,\text{int}}(n\Delta) &= \langle \chi_f(Q_f) | \mathcal{L}^{(l)} | \chi_{\text{int}}(Q_{\text{int}}) \rangle \\ &= \langle \chi_{fT_2\mu'}^{(n')} | \frac{\partial}{\partial Q_{T_2\mu'}} | \chi_{\text{int},T_2\mu'}^{(n'\pm 1)} \rangle \langle \chi_{fE\mu}^{(0)}(Q_{E\mu} - \Delta) | \chi_{\text{int},E\mu}^{(n)}(Q_{E\mu}) \rangle \\ &\quad \times \prod_{\Gamma''\mu''} \langle \chi_f^{(n'')} | \chi_{\text{int}}^{(n'')} \rangle \end{aligned} \quad (20)$$

we also keep only the vibrational mode with T_2 symmetry. Here

$$\Delta = (Q_{\text{int}\Gamma\gamma} - Q_{\Gamma\gamma})\alpha$$

is the dimensionless displacement between different electronic states for the accepting E mode above. Contributions from all the other modes are represented by the product over Γ'' and μ'' . Assuming that the electronic transition causes only the vibronic excitation of the accepting mode one gets (see, for example, Englman 1979)

$$F_{\text{int},\text{in}}(n\Delta) = e^{-\Delta^2/4} \left(\frac{\Delta}{2}\right)^n \frac{1}{\sqrt{n!}} 2^{n/2} (-1)^n \quad (21)$$

$$S_{f,\text{int}}(n\Delta) \cong e^{-\Delta^2/4} \left(\frac{\Delta}{2}\right)^n \frac{1}{\sqrt{n!}} 2^{n/2} (-1)^n \alpha = F_{\text{int},\text{in}}(n\Delta)\alpha \quad (22)$$

where α appears because of the differentiation in the first term in (20) and $(F_{\text{int},\text{in}})^2$ is the Franck-Condon factor. Inserting the vibrational and electronic terms into the probability per unit time one arrives at the equation

$$W_{\text{if}}^{(2)} = \frac{2\pi}{\hbar} \sum_{j\alpha} |L_{\alpha,\text{int}}^{(j)} P_{\text{int},\beta}^{(j)}|^2 V(\delta E^{(j)}, \Delta) \delta(E_g - \Delta E - \hbar\nu) \quad (23)$$

where $L_{\alpha,\text{int}}^{(j)} P_{\text{int},\beta}^{(j)}$ are defined by (46) and (48); α and β denote either the initial or final state depending on the channel. The term

$$V(\delta E, \Delta) = \frac{\hbar^4 e^{-\Delta^2} \alpha^2}{M^2} \left| \sum_{n=0}^{\infty} \left(\frac{\Delta^2}{2}\right)^n \{n! [(\delta E - \hbar\omega n) - \frac{1}{2}i\Gamma_{\text{ph}}]\}^{-1} \right|^2 \quad (24)$$

contains differing parameters for different channels. The superscripts (10) and (8) are suppressed in order to avoid an overly complicated notation.

3.2. Transition rate dependence on $\Delta^2/2$

The Stirling approximation is now used in (24) and the summation over n is substituted by an integration over the variable $x = \hbar\omega n$:

$$V = \frac{\hbar^4 \alpha^2}{\pi M^2 \hbar\omega} \left| \int_0^{\infty} \exp\left[-\frac{1}{\Delta^2} \left(\frac{x}{\hbar\omega} - \frac{\Delta^2}{2}\right)^2\right] \left[\sqrt{x}(\delta E - x - \frac{1}{2}i\Gamma_{\text{ph}})\right] dx \right|^2 \quad (25)$$

In order to calculate the integral in (25) the new variable $x = y^2$ is introduced. The subintegral function becomes even, and one may extend the limits of integration to $(-\infty, \infty)$. Closing the contour and calculating the pole contribution one arrives at

$$V = \frac{\alpha^2 \hbar^4}{M^2 \delta E \hbar \omega} \exp \left[-\frac{2}{\Delta^2} \left(\frac{\delta E}{\hbar \omega} - \frac{\Delta^2}{2} \right)^2 \right]. \quad (26)$$

Using this result the probability per unit time (23) can be represented as

$$W_{if}^{(2)} = \frac{2\pi}{\hbar} \sum_j |P_{int,\beta}^{(j)} \mathcal{L}_{\alpha,int}^{(j)}|^2 \frac{\alpha^2 \hbar^4}{M^2 (\hbar \omega)^2} \times \frac{\hbar \omega}{\delta E^{(j)}} \exp \left[-\frac{2}{\Delta^2} \left(\frac{\delta E^{(j)}}{\hbar \omega} - \frac{\Delta^2}{2} \right)^2 \right] \delta(E_g - \Delta E - \hbar \nu). \quad (27)$$

In order to get the transition rate of the process, (27) is integrated over all possible photon states:

$$R^{(2)} = \int W_{if}^{(2)}(\hbar \nu) \rho(\hbar \nu) \delta(E_g - \Delta E - \hbar \nu) d(\hbar \nu). \quad (28)$$

Performing the integration in (28) and using the relation

$$P_{AB} = -2\pi i m v_{AB} x_{AB} \quad (29)$$

connecting the matrix elements of the momentum and coordinate operators one arrives at the radiation intensity

$$I^{(2)} = \hbar \nu R^{(2)} = \frac{e^2 \pi^2 \nu^2}{c^3} \sum_j \nu_j^2 |x_{int,\beta}^{(j)} \mathcal{L}_{\alpha,int}^{(j)}|^2 V(\delta E^{(j)}, \Delta) \quad (30)$$

where

$$\nu_{10} = \frac{1}{\hbar} (E_g - E^{(10)}(2T_2)) \quad \nu_8 = \frac{1}{\hbar} E^{(9)}(E).$$

The intensity (30) is to be compared with that of the first-order process

$$I^{(1)} = \frac{4e^2 \pi^2 \nu^4}{c^3} |x_{if}|^2 \quad (31)$$

producing the red line ν_1 . Assuming that the coordinate matrix elements are more or less the same, one estimates the ratio of the intensities to be

$$\gamma = \frac{I^{(2)}}{I^{(1)}} = \left(\frac{\nu_2}{\nu_1} \right)^2 \sum_j \left(\frac{\nu_j}{\nu_1} \right)^2 \gamma^{(j)} \quad (32)$$

where

$$\gamma^{(j)} = A^{(j)} \frac{\hbar \omega}{\delta E^{(j)}} \exp \left[-\frac{2}{\Delta^2} \left(\frac{\delta E^{(j)}}{\hbar \omega} - \frac{\Delta^2}{2} \right)^2 \right].$$

The $A^{(j)}$ are dimensionless parameters representing the electronic part of the matrix elements. A detailed discussion of how these parameters are calculated for the multielectron d shells of the transition metal impurities is presented in the next section. The most important fact for us here is that each parameter $A^{(j)}$ is of the order of unity, which allows us to estimate the ratio (32) of the intensities.

The contribution $\gamma^{(10)}$ to the ratio (32) due to channel (a) is shown in figure 2 as a function of the dimensionless Jahn–Teller displacement Δ . This function has a well pronounced maximum in the range $4 \leq \Delta \leq 6$. Another contribution is due to channel (b), which has a similar behaviour; $\gamma^{(10)}$ in figure 2 is calculated assuming $\omega = 338.6 \text{ cm}^{-1}$, which corresponds to the longitudinal optical (LO) mode (Germer 1983). The proper frequency to be used here is that of the localized phonon, which is expected to be below the LO mode. This, however, will not change the essentials of the result. Therefore we may conclude that the resonance described above compensates for the smallness of the squared Franck–Condon factor and makes the transition rate, $I^{(2)}$, comparable to the ordinary radiative transition rate, $I^{(1)}$.

3.3. The electronic part of the transition rate

In this section we calculate the dimensionless parameter $A^{(j)}$ (32), defined as

$$A^{(j)} = \sum_{\alpha\beta} \left| \frac{A_{\alpha\beta}^{(j)}}{x_{i,f}} \right|^2 \frac{\alpha^2 \hbar^4}{M^2 (\hbar\omega)^2} \quad (33)$$

where

$$A_{\alpha\beta}^{(j)} = \sum_{\text{int}} \langle \Psi_\alpha | \mathcal{L}^{(e)} | \Psi_{\text{int}} \rangle \langle \Psi_{\text{int}} | \mathbf{X} | \Psi_\beta \rangle \quad (34)$$

is the matrix elements of the dipole transition appearing in (31).

We start by calculating the matrix elements of the operators $\mathcal{L}^{(e)}$ and \hat{R} acting on the electronic wavefunctions. The latter are chosen according to the model described in Kikoin and Fleurov (1979), where the single-electron wavefunctions are represented as superpositions of the atomic d functions, $\psi_{\Gamma\mu}$, and the Bloch functions, ψ_{ka} . The localized electrons are described by the function

$$\tilde{\psi}_{\Gamma\mu} = \frac{1}{\sqrt{(1+M')}} \left(\psi_{\Gamma\mu} - \sum_{ka} \frac{g_{ka}^{\Gamma\mu}}{E_{ka} - E_i} \psi_{ka} \right) \quad (35)$$

while the band-electron functions

$$\tilde{\psi}_{ka} = \psi_{ka} + \frac{1}{\sqrt{(1+M')}} \frac{g_{ka}^\mu}{E_{ka} - E_i} \left(\frac{1 - \sqrt{(1+M')}}{M'} \sum_{k'a'} \frac{g_{k'a'}^\mu}{E_{k'a'} - E_i} \psi_{k'a'} - \psi_{\Gamma\mu} \right) \quad (36)$$

are distorted due to the presence of the impurity. Here

$$M' = - \left. \frac{dM(E)}{dE} \right|_{E=E_i}$$

where

$$M(E_i) = \sum_{ka} \frac{|g_{ka}^{\Gamma\mu}|^2}{E_i - E_{ka}} \quad g_{ka}^{\Gamma\mu} = \langle ka | U_c | \Gamma\mu \rangle$$

and

$$E_i = E_{\Gamma\mu} + M(E_i).$$

Multielectron wavefunctions for various configurations d^n are constructed in accordance with the standard Racah algebra and using the conventional scheme of the strong crystal field (Satoru *et al* 1970):

$$\Psi_{i\Gamma M}(d^n) = \sum_{\Gamma'M'} \sum_{\gamma\mu} G_{\Gamma'M'}^{\Gamma M} C_{\Gamma'M'\gamma\mu}^{\Gamma M} \Psi_{i\Gamma'M'}(d^{n-1}) \psi_{i\gamma\mu}. \quad (37)$$

Here $G_{\Gamma'M'}^{\Gamma M}$ are seniority numbers and $C_{\Gamma'M'\gamma\mu}^{\Gamma M}$ are Clebsch–Gordan coefficients. The n th electron energy is defined as

$$E_{i\gamma} = E_{\Gamma_n} - E_{\Gamma_{n-1}}$$

where E_{Γ_n} is the multielectron energy for the ion d^n in the cubic crystal field, and $\gamma = e$ or t_2 . The spin variables are suppressed, since no interaction involving spins is considered in this paper.

The electronic wavefunction of the system in the initial state is

$$\Psi_{in\Lambda} = \hat{A} \sum_{M'\lambda'} C_{T_2M'\lambda'}^{\Lambda} \Psi_{T_2M'}(d^9) \psi_{\lambda'}^{(h)} \psi_c^{(e)} \quad (38)$$

where $M = \xi, \eta, \zeta$, \hat{A} is the antisymmetrization operator. For channel (a), the electronic wavefunction of the system in the intermediate state is

$$\begin{aligned} \Psi_{int_2M} &= \hat{A} \Psi_{A_1e_1}(d^{10}) \psi_{T_2M}^{(h)} = \hat{A} \left(\sum_{\mu} G_{T_2}^{A_1} \frac{1}{\sqrt{3}} \Psi_{T_2\mu}(d^9) \psi_{t_2\mu} \right. \\ &\quad \left. + \sum_{\gamma} G_E^{A_1} \frac{1}{\sqrt{2}} \Psi_{E\gamma}(d^9) \psi_{e\gamma} \right) \psi_{T_2M}^{(h)} \end{aligned} \quad (39)$$

where $\gamma = u, v$ and $M, \mu = \xi, \eta, \zeta$. The wavefunction of the final state of the system is

$$\Psi_{f\Gamma M} = \Psi_{EM}(d^9). \quad (40)$$

Using the above wavefunctions one can calculate the matrix elements of the operators \mathcal{R} and \mathcal{L} :

$$A_{(f, in)}^{(10)} = \sum_{M\gamma} \frac{1}{\sqrt{2}} G_E^{A_1} \langle k\nu M | \sum_{\Gamma'M'} \frac{\partial}{\partial Q_{\Gamma'M'}} | e\gamma \rangle \frac{1}{\sqrt{3}} \sum_{\mu\lambda'} G_{T_2}^{A_1} C_{t_2\mu\lambda'}^{\Lambda} (t_2\mu | X | kc) \quad (41)$$

where $|kc\rangle$ is the Bloch wavefunction of a conduction band electron. The non-adiabaticity operator is represented using the normal coordinates $Q_{\Gamma\gamma}$. Substituting the relevant part of

the distorted Bloch-electron wavefunction $\tilde{\psi}_{k\nu\lambda}$ (36) into (41) the non-adiabaticity matrix element becomes

$$\langle \Psi_f | \mathcal{L}^{(e)} | \Psi_{\text{int}} \rangle = \frac{1}{\sqrt{2}} \sum_{\Gamma' M' \gamma} G_E^{A_1} \frac{1}{(1+M')^{1/2}} \left\langle \frac{g_{k\nu M}^{e\gamma'}}{E_{k\nu} - E_c} \Psi_{e\gamma'} \left| \frac{\partial}{\partial Q_{\Gamma' M'}} \right| e\gamma \right\rangle. \quad (42)$$

The term $g_{k\nu M}^{e\gamma'}$ is the hybridization matrix element of the impurity potential, which can be expanded in powers of the atomic displacement Q .

The Jahn–Teller part of the Hamiltonian of the system in the linear approximation is

$$H_{JT} = \sum_{\Gamma\gamma} V_{\Gamma\gamma}(r) Q_{\Gamma\gamma} \quad (43)$$

where

$$V_{\Gamma\gamma}(r) = \left. \frac{\partial V(r)}{\partial Q_{\Gamma\gamma}} \right|_{Q=0}.$$

Using (43) in the calculation of the matrix element (42), one gets

$$\langle \Psi_f | \mathcal{L}^{(e)} | \Psi_{\text{int}} \rangle = \frac{1}{\sqrt{2}} \sum_{\Gamma' M' \gamma} G_E^{A_1} \frac{1}{(1+M')^{1/2}} \frac{\langle k\nu M | V_{\Gamma' M'} | e\gamma \rangle}{E_{k\nu} - E_c}. \quad (44)$$

The hole is usually captured from the top of the valence band ($k=0$) which transforms according to the irreducible representation Γ_{15} (or T_2). The electron wavefunction in the final state transforms according to the irreducible representation Γ_{12} (or E). Therefore, the matrix element of the Jahn–Teller potential $V_{\Gamma' M'}$ (43) is non-zero only if it transforms according to one of the irreducible representations appearing in the direct product $(\Gamma_{15} \times \Gamma_{12}) = \Gamma_{15} + \Gamma_{25} \equiv T_2 + T_1$. Since the atomic displacement Q_{T_1} does not exist among the vibrational modes of the tetrahedral lattice (which will be discussed later), the only term which is kept in the sum over Γ' in (44) is the term with $\Gamma' = T_2$.

Therefore, (44) becomes

$$\langle \Psi_f | \mathcal{L}^{(e)} | \Psi_{\text{int}} \rangle = \frac{1}{(1+M')^{1/2}} \frac{\langle k\nu | V_{T_2} | e \rangle}{E_{k\nu} - E_c} \sum_{M\gamma} \frac{G_E^{A_1}}{\sqrt{6}} C_{T_2 M e\gamma}^{T_2 M}. \quad (45)$$

So (41) is now

$$\begin{aligned} A_{(\Lambda)}^{(10)} &= \frac{1}{(1+M')^{1/2}} \frac{\langle k\nu | V_{T_2} | e \rangle}{E_{k\nu} - E_c} \sum_{M\gamma} \frac{G_E^{A_1}}{\sqrt{6}} C_{T_2 M e\gamma}^{T_2 M} \\ &\times \left(-\frac{e}{mc} \right) \sum_i \langle t_2 | X_i | kc \rangle \sum_{\mu\lambda'} \frac{G_{T_2}^{A_1}}{3} C_{(2\mu\lambda')}^{\Lambda}. \end{aligned} \quad (46)$$

For the case of channel (b) the intermediate electronic wavefunctions are

$$\Psi_{\text{int}_1 M} = \hat{A} \Psi_{T_1 M} (d^8) \psi_c^{(e)} \quad \Psi_{\text{int}_2 M} = \hat{A} \Psi_{T_2 M} (d^8) \psi_c^{(e)}.$$

Calculating the matrix elements of the radiative and non-radiative transition the initial- and the final-state wavefunctions of the impurity are chosen to be of the form

$$\begin{aligned}\Psi_{T_2M}(d^9) &= a_1 \Psi_{3T_1}(e^3 t_2^5) \Psi_e + a_2 \Psi_{3T_2}(e^3 t_2^5) \Psi_e \\ \Psi_{EM}(d^9) &= b_1 \Psi_{3A_2}(e^2 t_2^6) \Psi_e + b_2 \Psi_{3T_2}(e^3 t_2^5) \Psi_{t_2} + b_3 \Psi_{3T_1}(e^3 t_2^5) \Psi_{t_2}\end{aligned}$$

where a_i and b_i are the appropriate Clebsch–Gordan coefficients.

Thus the non-zero matrix elements for channel (b) are

$$\begin{aligned}A_{(f,\text{in})}^{(8)} &= \langle {}^3T_2(e^3 t_2^5) t_2 | X | T_2(d^8), kc \rangle \langle kc, {}^3T_2(e^3 t_2^5) | \mathcal{L}^{(e)} | {}^3T_2(e^3 t_2^5), \Psi_e, kh, kc \rangle \\ &+ \langle {}^3T_1(e^3 t_2^5) t_2 | X | T_1(d^8), kc \rangle \langle kc, {}^3T_1(e^3 t_2^5) | \mathcal{L}^{(e)} | {}^3T_1(e^3 t_2^5), \Psi_e, kh, kc \rangle. \quad (47)\end{aligned}$$

The electronic coefficient $A_{(f,\text{in})}^{(8)}$ contains two terms:

$$A_{(f,\text{in})}^{(8)} = A_{1(f,\text{in})}^{(8)} + A_{2(f,\text{in})}^{(8)}$$

where

$$\begin{aligned}A_{1(M''\Lambda)}^{(8)} &= \left(-\frac{e}{mc}\right) \sum_i \langle t_2 | X_i | kc \rangle \sum_M \frac{G_{3T_2M}^{EM''}}{\sqrt{3}} C_{3T_2M t_2 M}^{EM''} \\ &\times \frac{1}{(1+M')^{1/2}} \frac{\langle kv | V_{T_2} | e \rangle}{E_{kv} - E_e} \sum_{y'} \frac{G_{T_2M}^{T_2M}}{\sqrt{3}} (C_{T_2M e y'}^{T_2M})^2 C_{T_2M T_2 M}^\Lambda \\ A_{2(M''\Lambda)}^{(8)} &= \left(-\frac{e}{mc}\right) \sum_i \langle t_2 | X_i | kc \rangle \sum_{M_y} \frac{G_{3T_1M}^{EM''}}{\sqrt{3}} C_{3T_1M t_2 y}^{EM''} \\ &\times \frac{1}{(1+M')^{1/2}} \frac{\langle kv | V_{T_2} | e \rangle}{E_{kv} - E_e} \sum_{M'\Gamma_{y'}} \frac{G_{T_1M}^{T_2M'}}{\sqrt{3}} C_{T_1M e y'}^{T_2M'} C_{T_2M' T_2 \Gamma}^\Lambda\end{aligned} \quad (48)$$

Using the results obtained in this section, the coefficient $A^{(j)}$ (33) in equation (32) is estimated. Its most important part, connected with the covalent renormalization of the Jahn–Teller coupling, is written as

$$\left| \frac{\langle kv | V_{T_2} | e \rangle}{E_{kv} - E_e} \right|^2 = \frac{1}{a^2} \left| \frac{g_v^e(t_2)}{\Delta E} \right|^2.$$

Here

$$\Delta E = E_v - E_e$$

and

$$g_v^e(t_2) = \langle 0v | V(r) | e \rangle$$

is the hybridization parameter whose k dependence is neglected; a is of the order of the zero-point vibration of the mode responsible for the Jahn–Teller distortion.

Using the above expressions the dimensionless parameter $A^{(j)}$ becomes

$$A^{(j)} = \frac{1}{a^2} \left| \frac{g_v^c(t_2)}{\Delta E} \right|^2 \frac{1}{2(1+M')} \frac{\alpha^2 \hbar^4}{M^2 (\hbar\omega)^2} |C^{(j)}(\text{CG})|^2 \quad (49)$$

$$C^{(10)}(\text{CG}) = \sum_{M\gamma} \frac{G_B^{A_1}}{\sqrt{6}} C_{T_2 M \epsilon\gamma}^{T_2 M} \sum_{\mu\lambda'} \frac{G_{T_2}^{A_1}}{3} C_{t_2 \mu\lambda'}^\Lambda \quad (50)$$

$$C^{(8)}(\text{CG}) = \sum_M \frac{G_{T_2 M}^{EM''}}{\sqrt{3}} C_{T_2 M t_2 M}^{EM''} \sum_{\gamma'} \frac{G_{T_2 M}^{T_2 M}}{\sqrt{3}} (C_{T_2 M \epsilon\gamma'}^{T_2 M})^2 C_{T_2 M T_2 M}^\Lambda \\ + \sum_{M\gamma} \frac{G_{T_1 M}^{EM''}}{\sqrt{3}} C_{T_1 M t_2 \gamma}^{EM''} \sum_{M'\Gamma\gamma'} \frac{G_{T_1 M'}^{T_2 M'}}{\sqrt{3}} C_{T_1 M' \epsilon\gamma'}^{T_2 M'} C_{T_2 M' T_2 \Gamma}^\Lambda$$

The mass operator $M(E)$ is estimated, assuming again a constant hybridization parameter:

$$M(E) = |g_v^c(t_2)|^2 \sum_k \frac{1}{E_k - E_c} \quad (51)$$

The summation over k is now transformed to an integration, and the semi-elliptical model density of states

$$S(E) = \frac{1}{\pi D} \left[1 - \left(\frac{E}{D} \right)^2 \right]^{1/2} \quad (52)$$

is used (where $2D$ is the bandwidth). Then

$$M(E_c) = |g_v^c(t_2)|^2 \frac{2}{\pi D} \int_{-D}^D S(E) \frac{1}{E - E_c} dE = \frac{|g_v^c(t_2)|^2}{D} R(E_c) \quad (53)$$

where

$$R(\varepsilon) = \begin{cases} 2\varepsilon & |\varepsilon| < 1 \\ 2[\varepsilon + (\varepsilon^2 - 1)^{1/2}]^{-1} & \varepsilon > 1 \quad \varepsilon = E_c/D \\ 2[\varepsilon - (\varepsilon^2 - 1)^{1/2}]^{-1} & \varepsilon < -1. \end{cases} \quad (54)$$

Differentiating (53) over E in the region $|E| < |D|$ one gets

$$M' = \frac{|g_v^c(t_2)|^2}{D^2} \frac{1 + \varepsilon}{[\varepsilon + (\varepsilon^2 - 1)^{1/2}]^2}$$

Now we have the details to estimate the dimensionless parameter $A^{(j)}$ (32) using (49) with the above electronics details and with specific values connected to our example (ZnS:Cu). Substituting in (49) $\alpha = \sqrt{M\omega/\hbar} \sim 1/a$, taking into account that $V \sim 1 \text{ eV} - 2 \text{ eV}$ for ZnS:Cu and $D \sim 1.5 \text{ eV}$, and that the Clebsch-Gordan coefficient $C^{(j)}(\text{CG})$ is estimated to be of the order of one, $A^{(j)}$ becomes

$$A^{(j)} \sim 1.$$

There are reasons to believe that this estimate will also hold also for various other systems.

4. Discussion

This paper presents a detailed theoretical consideration of the 'sum rule' observed in the luminescence spectra of several semiconductors doped by transition metal impurities. In essence, the theory uses the multielectron structure of the d shells of the impurities. Only a peculiar interplay of the transitions between various multielectron states has allowed us to find the processes responsible for the lines whose energies complement each other to the forbidden energy gap of the host semiconductor.

Another important point is the necessity of a rather strong impurity-phonon coupling and, hence, a rather strong Jahn-Teller effect. It is only under this condition that we are able to understand why the second-order process producing the complementing line is not negligibly weak. Here an important part is played by the hybridization between the d state and band states which leads to the 'swallowing' of the localized state. Then the d-electron wavefunctions have enhanced radii and can efficiently interact with the lattice.

The most important precondition for the appearance of the complementing luminescence line as described above is as follows: *the multielectron structure of the atomic shell must participate in the creation of the deep levels*. Such a structure is typical of transition metal impurities. Therefore we may expect that every transition metal impurity should produce two luminescence lines, one corresponding to the intrashell transition (with energy $10Dq$) and the other complementing the first one to the energy gap. Moreover, there is no specific intrashell transition which is better than the others. One may expect that any line corresponding to a transition between two states of the d shell would have also a complementing line.

In order to check this assumption we have made a search of the experimental literature and found several examples of such pairs of lines (see table 1).

Table 1. Complementing lines for different intracentre transitions.

System	Type of transition	$h\nu_1$ (eV)	$h\nu_2$ (eV)	Ref.	$h\nu_1 + h\nu_2$ (eV)	Energy gap (eV)
ZnSe:Cr	$^5T_2 - ^5E$	0.68	2.05	a	2.73	2.82
ZnSe:Co	$^4A_2 - ^4T_2$	0.409	2.4328	b	2.841	2.82
ZnS:Ni ¹⁺	$^2T_2 - ^2E$	0.438		c		
			3.3897	d	3.828	3.85
ZnS:Ni ²⁺	$^2T_2 - ^2E$	1.5124	2.3332	e	3.845	3.85
ZnS:Fe ²⁺	$^3T_1 - ^5E$	1.25		f		
			2.61	g	3.86	3.85
CdS:Ni ²⁺	$^3T_1 - ^3T_2$	0.487		h		
			2.19	i	2.67	2.58
CdSe:Ni ²⁺	$^3T_1 - ^3T_2$	0.52		j		
			1.35	k	1.87	1.84
GaAs:Co ²⁺	$^4T_1(F) - ^4A_2(F)$	0.97		l		
			0.49	m, n	1.46	1.52
GaAs:Cr ²⁺	$^5A_2 - ^5E$	0.84		o		
			0.68	p, q	1.52	1.52
GaP:Ni ²⁺	$^3T_1 - ^3T_2$	0.8		r		
			1.5	s	2.3	2.35

a: Grebe *et al* 1976; b: Robbins *et al* 1980; c: Roussos *et al* 1983; d: Sokolov *et al* 1982; e: Hoffmann *et al* 1988; f: Skworonski *et al* 1981; g: Zimmerman and Boyn 1983; h: Pappalardo and Deitz 1961; i: Kazanski and Ryzkin 1971; j: Baranovski and Langer 1971; k: Buhmann *et al* 1981; l: Baranowski *et al* 1967; m: Kornilov *et al* 1974; n: Ennen *et al* 1980; o: Eaves *et al* 1981; p: Ulrici and Kleinert 1985; q: Koschel *et al* 1976; r: Jezewski *et al* 1987; s: Abagyan *et al* 1976.

This is an extended version of the table published in Dahan and Fleurov (1992). It contains data for several systems (first column) for various intracentre transitions (second

column). The notation standard for the crystal field theory Ballhausen (1962) is used to denote the states of the d shell. The authors of the papers referred to in the table either attributed the lines (presented here as complementing lines) to charge transfer processes or did not comment upon them at all. There are also examples where the intracentre transitions are observed in one paper while the complementing lines are found in another paper.

We believe that it would be very interesting to make a better experimental check of the pairs of lines presented above, as well as to look for other possible pairs in various systems. In addition to the entries in the table in Dahan and Fleurov (1992), this table contains three examples of the complementing pairs in $A_{III}B_V$ host semiconductors. It is quite clear from the considerations presented above that there should be no principal difference between the $A_{II}B_{VI}$ and $A_{III}B_V$ systems, except perhaps for the numerical values of the parameters in the theory. We understand that all these pairs of complementing lines cannot be considered as a real proof of the universality of the sum rule. These can be treated only as indirect evidence in favour of such universality. Direct evidence (for or against) can be produced only by specially designed experiments.

Although situation as it is described here is encouraging, there are still some important problems to be solved. One of them is briefly touched upon here. The important feature of the model presented in this paper is that the final state of the complementing second-order process is electronically excited. This fact does not present any problems as long as we consider the luminescence. It means, however, that one would not expect an observation of the complementing line in the absorption spectra. In this case the electronically excited state must serve as the initial state of the process and its extremely low occupation at low temperatures would make the intensity of the complementing line extremely weak. Nevertheless, the experiment says that this line is observed.

This fact is a challenge to the theory and must be properly addressed. We believe that the strong phonon-impurity interaction (the strong Jahn-Teller effect) may lead to self-localization of the impurity in the excited state. The relaxation of this state will then be coupled to a slow motion of the impurity atom and will be characterized by a very long lifetime, which can help resolve the inconsistency in the theory mentioned above. This approach resembles in some respects metastable states for double centres, discussed by Kagan and Kikoin (1980) and Kikoin *et al* (1986) in order to explain anomalous properties (for example, the large relaxation time for doped narrow-gap semiconductors). A detailed discussion of this problem, and of the experimental facts which can support such a model in our case, will be published elsewhere.

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