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Abstract

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PHYSICS

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POLARIZATION OF LUMINESCENCE UPON EXCITATION BY POLARIZED AND NATURAL LIGHT

Between the values of the degree of polarization obtained upon excitation by polarized and by natural light there exists a simple relation, established by S. I. Vavilov and V. L. Levshin ([1]):

$$P_n = \frac{P_p}{2 - P_p}, \tag{1}$$

where P_n is the degree of polarization upon excitation by natural light, and P_p upon excitation by polarized light. Formula (1) was obtained for observation at an angle $\pi/2$ to the direction of the exciting light. For observation at an angle $\chi \neq \pi/2$ (Fig. 1), straightforward calculations give

$$P_n = P_p \frac{1 - \cos^2 \chi}{2 - P_p \sin^2 \chi}, \tag{2}$$

from which it follows that, when observing in a direction parallel to the exciting beam of light ($\chi = 0$), P_n is always equal to zero, independently of the absolute value of P_p. At $\chi = \pi/2$, formula (2) becomes (1).

Fig. 1. Scheme for observing the polarized luminescence of isotropic solutions.

In practice the most important case is observation normal to the direction of the exciting light ($\chi = \pi/2$). Accordingly, everything set forth below refers to this particular case.

A careful consideration of the limits of applicability of the Levshin–Vavilov formula (1) shows that it is valid only for isotropic media and for the case in which absorption and emission are dipolar in character. For crystals, as well as for other multipoles and their combinations, this formula, as will be shown, has a different form.

In the present communication isotropic solutions and crystals of cubic syngony are considered. Crystals of other syngonies are not considered, since it is known that, as a result of intermolecular migration of energy in the crystal, the observed degree of polarization does not depend on the state of polarization of the exciting light (^{2}). The calculations are carried out for electric (e) and magnetic (m) dipoles, electric quadrupoles (q), and electric (σ_e) and magnetic (σ_m) circular oscillators.

1. As is known, the dependence of the degree of polarization of isotropic solutions on the angle η (Fig. 1) between the electric vector of the exciting light and the axis Oz is different for different multipoles (^{4}). If the degree of polarization does not reach 50%, then in the particular case $\chi = \pi/2$ this dependence is described by the formulas (^{5,6}) given in Table 1.

To obtain the value of the degree of polarization upon excitation by natural light, it is obviously necessary to sum over all values of the angle

Table 1

Absorption	Emission: e	Emission: q	Emission: m	Emission: σ_e	Emission: σ_m
e	$P = P_0 \frac{\cos^2\eta}{1 - P_0 \sin^2\eta}$	$P = P_0 \frac{\cos^2\eta}{1 + P_0 \sin^2\eta}$	$P = P_0 \frac{\cos^2\eta}{1 - P_0 \sin^2\eta}$	$P = P_0 \frac{\cos^2\eta}{1 + P_0 \sin^2\eta}$	$P = P_0 \frac{\cos^2\eta}{1 + P_0 \sin^2\eta}$
q	$P = -P_0 \frac{\sin^2\eta}{1 + P_0 \cos^2\eta}$	$P = P_0 \frac{\sin^2\eta}{1 - P_0 \cos^2\eta}$	–	–	–
m	$P = P_0 \frac{\sin^2\eta}{1 - P_0 \cos^2\eta}$	–	$P = -P_0 \frac{\sin^2\eta}{1 - P_0 \cos^2\eta}$	$P = P_0 \frac{\sin^2\eta}{1 + P_0 \cos^2\eta}$	$P = P_0 \frac{\sin^2\eta}{1 + P_0 \cos^2\eta}$
σ_e	$P = -P_0 \frac{\cos^2\eta}{1 + P_0 \sin^2\eta}$	–	$P = P_0 \frac{\cos^2\eta}{1 + P_0 \sin^2\eta}$	$P = P_0 \frac{\cos^2\eta}{1 - P_0 \sin^2\eta}$	$P = P_0 \frac{\cos^2\eta}{1 - P_0 \sin^2\eta}$
σ_m	$P = -P_0 \frac{\sin^2\eta}{1 + P_0 \cos^2\eta}$	–	$P = P_0 \frac{\sin^2\eta}{1 + P_0 \cos^2\eta}$	$P = P_0 \frac{\sin^2\eta}{1 - P_0 \cos^2\eta}$	$P = P_0 \frac{\sin^2\eta}{1 - P_0 \cos^2\eta}$

Table 2

	Emission:	Emission:	Emission:	Emission:	Emission:	Emission:	Emission:	Emission:	Emission:	Emission:	Emission:
Absorption	e	e	q	q	m	m	σ_e	σ_e	σ_m	σ_m	η
e	1	$P_n =$ $\frac{P_p}{2-P_p}$	$\frac{1}{2}$	$P_n =$ $\frac{P_p}{2+P_p}$	$-\frac{1}{2}$	$P_n =$ $-\frac{P_p}{2-P_p}$	-1	$P_n =$ $-\frac{P_p}{2+P_p}$	$-\frac{1}{3}$	$P_n =$ $-\frac{P_p}{2+P_p}$	$\frac{1}{3}$
q	$\frac{1}{2}$	$P_n =$ $-\frac{P_p}{2+P_p}$	$\frac{1}{2}$	$P_n =$ $-\frac{P_p}{2-P_p}$	–	–	–	–	–	–	$\frac{\pi}{2}$
m		$P_n =$ $\frac{P_p}{2-P_p}$	–	–	-1	$P_n =$ $-2\frac{P_p}{2-P_p}$	-1	$P_n =$ $-\frac{P_p}{2+P_p}$	1	$P_n =$ $-\frac{P_p}{2+P_p}$	$\frac{1}{3}$
σ_e	-1	$P_n =$ $-\frac{P_p}{2+P_p}$	–	–	1	$P_n =$ $\frac{P_p}{2+P_p}$	$\frac{1}{3}$	$P_n =$ $\frac{P_p}{2-P_p}$	$\frac{1}{3}$	$P_n =$ $-\frac{P_p}{2-P_p}$	$-\frac{1}{3}$
σ_m	-1	$P_n =$ $-\frac{P_p}{2+P_p}$	–	–	1	$P_n =$ $\frac{P_p}{2+P_p}$	$\frac{1}{3}$	$P_n =$ $\frac{P_p}{2-P_p}$	$\frac{1}{3}$	$P_n =$ $-\frac{P_p}{2-P_p}$	$-\frac{1}{3}$

according to the formula for adding polarizations

$$P_n = \sum_i P_{pi} I_i \Big/ \sum_i I_i. \tag{3}$$

Since the angle η varies continuously from 0 to π, the summation should be replaced by integration. Formula (3), in expanded form in accordance with Fig. 1, has the form:

$$P_n = \int_0^\pi \frac{I_z - I_x}{I_z + I_x}(I_z + I_x)\,d\eta \Big/ \int_0^\pi (I_z + I_x)\,d\eta = \int_0^\pi (I_z - I_x)\,d\eta \Big/ \int_0^\pi (I_z + I_x)\,d\eta. \tag{4}$$

To obtain formulas relating P_p and P_n, it is sufficient to calculate the integrals in the numerator and denominator of these formulas (for the results see Table 2).

As is seen from the table, the formulas for different combinations of multipoles differ noticeably. In these formulas the absolute value of P_p is taken. In addition, the last column of Table 2 gives the values of the angle η at which P_p must be measured. The formulas obtained can in many cases serve for a simple determination, from two measurements, of the nature of the elementary emitter.

Fig. 2. Observation scheme for polarized luminescence of crystals of cubic syngony, if the elementary oscillators are oriented: a –along 3G4; b –along 4G3; c –along (6G2)

Figure 2: Fig. 2. Observation scheme for polarized luminescence of crystals of cubic syngony, if the elementary oscillators are oriented: a –along 3G4; b –along 4G3; c –along (6G2)

2. Formulas expressing the relation between the observed values of the degree of polarization upon excitation by natural and polarized light are of particular interest in the case of crystals of cubic syngony. This is connected with the fact that, in the given case, P. P. Feofilov (3) succeeded in observing emitters of different multipolarity: electric and magnetic dipoles and circular oscillators.

Fig. 2. Scheme for observing polarized luminescence of crystals of cubic syngony, if the elementary oscillators are oriented: a –along $3G_4$; b –along $4G_3$; c –along $(6G_2)$.

The calculation in the case of crystals is carried out in a manner completely analogous to the case of isotropic solutions. Certain special features are connected with the fact that here the absorption and emission oscillators are not arranged chaotically, but are oriented in a definite way with respect to the symmetry elements of the crystal. In this connection the calculation should be performed for three cases, when the absorption and emission oscillators are located along axes of the fourth $3G_4$, third $4G_3$, and second $6G_2$ orders. Excitation and observation are carried out according to the scheme of Fig. 2, which is the most convenient from the practical point of view.

Oscillators oriented along axes of the fourth order (Fig. 2a). In this case formulas are obtained that are analogous to those pertaining to the case of isotropic solutions (Table 2), with the only difference that the absolute values of the degree of polarization in these two cases differ strongly. The values of the limiting degree of polarization for crystals are given in the upper left corner of the cells of Table 2, and for solutions—in the right.

Oscillators oriented along axes of the third order (Fig. 2b). The symmetry of the arrangement of the oscillators in this case is such that, for all multipoles and their combinations, the observed degree of polarization upon excitation by natural light is equal to zero, whereas upon excitation by polarized light P_p is not equal to zero and is different for oscillators of different multipolarity; consequently, the study of polarized luminescence upon excitation by natural light cannot be carried out.

Oscillators oriented along axes of the second order (Fig. 2c). The main feature of the case of second-order axes is that here two different values of the degree of polarization P_p are obtained depending on the excitation conditions: vertical oscillations of the electric vector of the exciting light correspond to one value of P_p, horizontal oscillations to another. In this connection, two series of formulas are obtained, given in Tables 3 and 4. Table 3 contains formulas corresponding–

Table 3

Absorption	Emission: e	Emission: m	Emission: σ_e	Emission: σ_m
e	$^{3}/_{7}$ $P_n = \frac{P_p}{3-2P_p}$	$-^{3}/_{7}$ $P_n = -\frac{P_p}{3-2P_p}$	$-^{3}/_{13}$ $P_n = -\frac{P_p}{3+2P_p}$	$^{3}/_{1}$ $P_n = \frac{P_p}{3+2P_p}$
m	$-^{1}/_{3}$ $P_n = -\frac{P_p}{1+2P_p}$	$^{1}/_{3}$ $P_n = \frac{P_p}{1+2P_p}$	$^{1}/_{13}$ $P_n = \frac{P_p}{1-2P_p}$	$-^{1}/_{3}$ $P_n = -\frac{P_p}{1-2P_p}$
σ_e	$-^{1}/_{3}$ $P_n = -\frac{P_p}{3+2P_p}$	$^{1}/_{3}$ $P_n = \frac{P_p}{3+2P_p}$	$^{8}/_{23}$ $P_n = \frac{P_p}{3-2P_p}$	$-^{8}/_{23}$ $P_n = -\frac{P_p}{3-2P_p}$
σ_m	$^{1}/_{13}$ $P_n = \frac{P_p}{1-2P_p}$	$-^{1}/_{13}$ $P_n = -\frac{P_p}{1-2P_p}$	$-^{1}/_{19}$ $P_n = -\frac{P_p}{1+2P_p}$	$^{1}/_{19}$ $P_n = \frac{P_p}{1+2P_p}$

Table 4

Absorption	Emission: e	Emission: m	Emission: σ_e	Emission: σ_m
e	$-^{1}/_{3}$ $P_n = \frac{P_p}{1+2P_p}$	$^{1}/_{3}$ $P_n = -\frac{P_p}{1+2P_p}$	$^{1}/_{113}$ $P_n = -\frac{P_p}{1-2P_p}$	$-^{1}/_{13}$ $P_n = \frac{P_p}{1-2P_p}$
m	$^{3}/_{7}$ $P_n = \frac{P_p}{3-2P_p}$	$-^{8}/_{7}$ $P_n = -\frac{P_p}{3-2P_p}$	$-^{1}/_{3}$ $P_n = -\frac{P_p}{3+2P_p}$	$^{1}/_{3}$ $P_n = \frac{P_p}{3-2P_p}$
σ_e	$^{1}/_{13}$ $P_n = -\frac{P_p}{1-2P_p}$	$-{}'/_{1}$ $P_n = \frac{P_p}{1-2P_p}$	$-^{1}/_{19}$ $P_n = \frac{P_p}{1+2P_p}$	$^{1}/_{19}$ $P_n = -\frac{P_p}{1+2P_p}$
σ_m	$P_n = -\frac{P_p}{3+2P_p}$	$^{1}/_{3}$ $P_n = \frac{P_p}{3+2P_p}$	$^{3}/_{23}$ $P_n = \frac{P_p}{3-2P_p}$	$-^{3}/_{2}$ $P_n = -\frac{P_p}{3-2P_p}$

···corresponding to excitation by polarized light with vertical ($\eta = 0$) oscillations of the electric vector; in Table 4 ($\eta = \pi/2$), with horizontal oscillations.

Sometimes, in order to excite polarized luminescence, one has to use natural light with some admixture of polarized light (for example, light that has passed through a spectral instrument). Naturally, the formulas derived are not applicable in such a case. If the degree of polarization of the exciting light P_0 is known, then for dipole absorption and emission of isotropic solutions it is not difficult to obtain the formula

$$P_p = \frac{2P_{\cdot\cdot}}{P_0(1-P_{\cdot\cdot})+(1+P_{\cdot\cdot})}, \tag{5}$$

which relates the degree of polarization of luminescence under excitation by polarized light P_p and by partially polarized light $P_{\cdot\cdot}$ with the degree of polarization of the exciting light P_0. Analogous formulas may be obtained for other multipoles and crystals.

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