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On the theory of the optical activity of crystals

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On the theory of the optical activity of crystals

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In the last time we can meet with the more intensive interest in rotatory power of crystals. This revival was caused first of all by the fact that in the last years relatively a great deal of experimental data were assembled partly by the crystals optically known partly the rotatory power was proved by any other crystals (for ex. by the selen crystals) where the existence of this phenomenon was not yet provided. Besides this there could be found some indications on the dependence concerning optical activity of crystals on the heat and pressure.

The experimental results obtained in present time have then evoked a new interest in the theoretical derivation of formulae with the aid of which may be described the rotatory power in the sufficiently large spectral region. Some authors try to derive these formulae by the means of the exciton theory, the others are using in their theories the models of coupled oscillators.

In this work the author has tried to generalize by means of the model of coupled oscillators the relations gained till now for the dispersion of rotatory power and on the basis of the quantum-mechanical consideration with respect to the damping he came to the expression where as special cases all the most important and earlier derived relations for rotatory power of crystals are involved.

In order to judge in what measure our equation then other ones, we shall show at least in the short summary the most important of them.

I. Formulae for rotatory dispersion of crystals

For the description of rotatory dispersion of crystals there exist in the present time a lot of formulae. Most of them are empirical ones containing the greater or the less number of constants.

The first formula describing the rotatory dispersion of crystals which was theoretically derived by means of the microscopic theory is Drude's formula

$$\varrho = \sum_i \frac{K_i}{\lambda^2 - \lambda_i^2} \tag{I,1}$$

where ϱ is the rotatory power (in degrees/ mm of crystals thickness), K_i is the constant, which is characteristic to the wave-length of the absorption λ_i (in micrometers).

The summation in this case is made over all "i", of the characteristic wave-lengths of the crystal absorption.

The formula (I,1) is available for description of the rotatory power in the ultraviolet region for α-quartz, cinnabar, benzil and sodium chlorate[1].

This author[2] has shown however that all the experimental data obtained in the visible region till to the ultraviolet region may by described by means of the more general formula in the form of

$$\varrho = \sum_i \frac{K_i \lambda^2}{(\lambda^2 - \lambda_i^2)^2} \tag{I,2}$$

which is quadratic with respect to te λ_i.

Even when the formula (I,2) was originally derived for the crystals with the space group of the symmetry D_3^4 or D_3^6 it was used successfully for describing the rotatory dispersion of another crystals belonging to the other group of symmetry (β-quartz, ethylene diaminosulphate)[3]. The same authors[4] have shown later that in the case of the crystals of sodium bromate and sodium uranylacetate the formula (I,1) appears to be more useful. In the year 1964 Kizel and al.[3] have obtained the curve of the rotatory dispersion of benzil and found that it is the superposition of Chandrasekhar's and Drude's curves. In the measuring regions there can be found Cotton's effect and for this reason the curve is then asymmetric with respect to the characteristic wave-length. This means that the part of the curve was corresponding to Drude's formula (I,1).

In this correspondence it is very suitable to mention one formula which was given in the year 1933 by Born and Göppert-Mayer[5]. This formula has the form

$$\varrho = \sum_i \frac{K_i^{(1)}}{\lambda^2 - \lambda_i^2} + \frac{K_i^{(2)}\lambda^2}{(\lambda^2 - \lambda_i^2)^2} + \sum_j \frac{K_j^{(1)}}{\lambda^2 - \lambda_j^2} + \frac{K_j^{(2)}\lambda^2}{(\lambda^2 - \lambda_j^2)^2} \tag{I,3}$$

where the index "i" is valid in the visible and ultraviolet and the index "j" in the infrared region. The formula (I,3) is relatively general as well, it may be shown however that in the case $K_i^{(1)} = 0$ it can be reduced in (I,2), in the case $K_i^{(2)} = 0$ then in the Drudes' formula (I,1).

As for practical use of this formula it seems that it can be truly used only in the case of benzil.

In the year 1964 the situation appeared that the rotatory dispersion of crystals was described by means of various formulae with greater or less accuracy.

Deriving his formula (I,2) Chandrasekhar had used the model of coupled oscillators. His derivation appears to have the classical form taking no account of the damping. In his theory Chandrasekhar takes for granted that the oscillators strengths in the case of both modes of vibration are the same. It is necessary then to mention that the concept of the oscillator strengthes has in his classical theory only a pure formal character, because it is impossible to express it on basis of the classical calculation in an explicit form. In the case of an individual characterictic wave-length he came then to the expression

$$\varrho = \frac{\pi}{\lambda}(n_l - n_r) = \frac{K\lambda^2}{(\lambda^2 - \lambda_0^2)^2},$$

$$K = \frac{Ne^4\lambda_0^4 f^2 \sin\Theta \cos\Theta}{2\pi m^2 d^2 c^4} \tag{I,4}$$

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The classical generalization of Chandrasekhar's formula (I,4) even in the case of damping was made on basis of a model of coupled oscillator by Vyšín[6] who came to the relation

$$\varrho = Bw^2 \left\{ \frac{1}{\omega_2^2 + 2ig_2\omega - \omega^2} - \frac{1}{\omega_1^2 + 2ig_1\omega - \omega^2} \right\},$$

$$B = \pi N f e^2 \frac{(\alpha^2 + \beta^2)}{2mc^2} \, l \sin \Theta \qquad\qquad (I,5)$$

In his work the author had shown also that after a modification and repartition of a real and imaginary parts in the relation (I,5) we may obtain the equation

$$Re\varrho = B\omega^2 \left\{ \frac{\omega_2^2 - \omega^2}{(\omega_2^2 - \omega^2)^2 + 4g_1^2\omega^2} - \frac{\omega_1^2 - \omega^2}{(\omega_1^2 - \omega^2)^2 + 4g_1^2\omega^2} \right\}$$

$$Im\varrho = B\omega^2 \left\{ \frac{2g_1\omega}{(\omega_1^2 - \omega^2)^2 + 4g_1^2\omega^2} - \frac{2g_2\omega}{(\omega_2^2 - \omega^2)^2 + 4g_2^2\omega^2} \right\} \qquad (I,6)$$

The first equation describes the dispersion of the rotatory power, the second one the circular dichroism.

The equation (I,5) is then evidently more general then the equation (I,2) since in the case of $\omega_{1,2}^2 \gg \omega^2$, that means in the spectral region sufficiently distant from the absorption where the damping is not evident we can obtain Chandrasekhar's equation (I,2) from the equation (I,5) as a special case.

The same author[7] in the year 1966 had derived the equation of the rotatory dispersion of crystals in the quantum-mechanical way. In this work he used also the model of coupled oscillators and had shown among others that the presumption of the equivalence of oscillator strengths for both normal modes of vibration must not be fulfilled in any time.

He provided in his theory that these oscillator strengths are different. He has not taken in account the damping and had come to the expression

$$\varrho = \frac{\pi N e^2 (\alpha^2 + \beta^2) \, \mathrm{d} \sin \Theta \varepsilon \, (f_{q2} + f_{q1}) \, \lambda_0^4}{2mc^4} \cdot \frac{\lambda^2}{(\lambda^2 - \lambda_0^2)^2} +$$

$$+ \frac{\pi N e^2 (\alpha^2 + \beta^2) \, \mathrm{d} \sin \Theta \, (f_{q2} - f_{q1})}{mc^2} \cdot \frac{1}{\lambda^2 - \lambda_0^2} \qquad (I,7)$$

This formula involves, as we can see, a quadratic and a linear member with respect to the characteristic wave-length λ_0.

In the case that the oscillator strengths of both modes of vibrations are equivalent the author is then passing to Chandrasekhar's formula (I,2) and presuming at the same time the little binding among the oscillators (in this case it can be namely ommited sometimes the quadratic member towards the linear member) in Drude's formulae (I,1).

The linear member of the expression (I,7) is suitable for the description of the rotatory dispersion of sodium bromate and sodium uranylacetate. In the case of benzil it is evidently necessary to use the two members of the forgoing formula.

II. Generalization of the theory

In the present work there is shown the quantum-mechanical description of the dispersion concerning the rotatory power of crystals with regard to the damping.

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By this evaluation we are going out again from a model of coupled oscillators, presuming that for the two normal modes of vibration the oscillator strengthes as so as the damping are different. The evaluation is then made on the basis of the results of the Chandrasekhar and Vyšín works and it is in substance the further development and generalization of Vyšín's[7] work.

If we should like generalize the that is preceding formulae for rotatory dispersion for the case of resonance, that is for the case where the frequency of light on the crystal is confused with one of the characteristic frequencies, it is necessary to involve by the calculation the life time of the excited states of the oscillators. This life time can be, according Davydov[9] formally included in this way that we are overgoing to the complex energies, that is we are making the transformation

$$E_k \to E_k - \frac{i}{2} \Gamma_k \hbar \tag{II,1}$$

where Γ_k^{-1} means the life time of the k-th excited state.

The Schrödinger equation for the two coupled oscillators can be then written in the normal coordinates in the following way

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \psi_{1n}}{\partial q_1^2} + \frac{m\omega_1^2}{2} q_1^2 \psi_{1n} + R_{q1}^{\varkappa} q_1 \psi_{1n} - \frac{\hbar^2}{2m} \frac{\partial^2 \psi_{2n}}{\partial q_2^2} + \frac{m\omega_2^2}{2} q_2^2 \psi_{2n} +$$

$$+ R_{q2}^{\varkappa} q_2 \psi_{2n} = \left(E_{1n} - \frac{i}{2} \Gamma_{1n} \hbar\right) \psi_{1n} + \left(E_{2n} - \frac{i}{2} \Gamma_{2n} \hbar\right) \psi_{2n} \tag{II,2}$$

Applying normal coordinates the original frequency will be then split in the two adjacent frequencies ω_1 and ω_2 and we obtain then two normal modes of vibration. The linearly polarized light wave propagating along the optical axis of the crystal, will be then split in the two circularly polarized waves. The force of the incident light wave on the coupled oscillator can be expressed in the normal coordinates using the expression [7]

$$R_{q\eta}^{\varkappa} = (a_{q\eta}^{\varkappa}) e \mathscr{E}_0 \cos(\omega t + \sigma) = (a_{q\eta}^{\varkappa}) \frac{e \mathscr{E}_0}{2} (e^{i\omega t} + e^{-i\omega t}) \tag{II,3}$$

where $\eta = 1,2$ denotes the normal vibration modes of the oscillator, $\varkappa = r, l$ for the right and for the left circularly polarized light wave.
For the right circularly polarized light wave

$$(a_{q1}^r)^2 = (\alpha^2 + \beta^2)(1 + \cos \Theta + \Phi \sin \Theta)$$
$$(a_{q2}^r)^2 = (\alpha^2 + \beta^2)(1 - \cos \Theta - \Phi \sin \Theta) \tag{II,3a}$$

for the light wave circularly polarized on the left we have

$$(a_{q1}^l)^2 = (\alpha^2 + \beta^2)(1 + \cos \Theta - \Phi \sin \Theta)$$
$$(a_{q2}^l)^2 = (\varkappa^2 + \beta^2)(1 - \cos \Theta + \Phi \sin \Theta) \tag{II,3b}$$

Under the influence of a light field the state of a system will be then commonly described through the wave-function $\psi_{\eta n}(q_\eta, t)$, which must then fulfill the Schrödinger equation (II,2)

$$i\hbar \frac{\partial \psi_{\eta n}}{\partial t} = H^{(0)} \psi_{\eta n} + H^{(1)} \psi_{\eta n}, \tag{II,4}$$

$$H^{(0)} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial q_\eta^2} + \frac{m\omega_{\eta n}^2}{2} q_\eta^2,$$

$$H^{(1)} = R_{q\eta}^{\varkappa} q_\eta$$

Considering the influence of a light wave on a system as a disturbance the equation (II,4) may be solved with the aid of the disturbance theory. In what follows let us limit ourselves on the first approximation.

Let us seek for the wave function $\psi_{\eta n}(q_\eta, t)$ in the form

$$\psi_{\eta n}(q_\eta, t) = \{\psi_{\eta n}^{(0)} + \sum_k (a_{\eta n k}\, \mathrm{e}^{i\omega t} + b_{\eta n k}\, \mathrm{e}^{-i\omega t})\, \psi_{\eta k}^{(0)}\}\, \mathrm{e}^{-i\omega_{\eta n} t}$$

$$\omega_{\eta n} = \frac{E_{\eta n}}{\hbar} - \frac{i}{2}\, \Gamma_{\eta n} \tag{II,5}$$

where $a_{\eta n k}$, $b_{\eta n k}$ represent the correction for the wave function $\psi_{\eta n}^{(0)}$. $\psi_{\eta n}^{(0)}$ must then fulfill the equation

$$H^{(0)}\psi_{\eta n}^{(0)} = E_{\eta n}\psi_{\eta n}^{(0)}$$

Substituting (II,5) in (II,4) and omitting the products $H^{(1)}a_{\eta n k}$ and $H^{(1)}b_{\eta n k}$ (which are proportional $\mathscr{E}^2$ and belonging to the second approximation) we have then

$$a_{\eta n k} = -\frac{(a_{q\eta}^{\varkappa})\, \mathrm{e}\, \mathscr{E}_0 \langle \eta k \mid q_\eta \mid \eta n \rangle}{2\hbar(\omega_{\eta n} - \omega_{\eta k} - \omega)} = -\frac{(a_{q\eta}^{\varkappa})\, \mathrm{e}\, \mathscr{E}_0 \langle \eta k \mid q_\eta \mid \eta n \rangle}{2\hbar \left[\omega_{\eta n k} - \omega - \dfrac{i}{2}\, (\Gamma_{\eta n} + \Gamma_{\eta k})\right]}, \tag{II,6}$$

$$b_{\eta n k} = -\frac{(a_{q\eta}^{\varkappa})\, \mathrm{e}\, \mathscr{E}_0 \langle \eta k \mid q_\eta \mid \eta n \rangle}{2\hbar \left[\omega_{\eta n k} + \omega - \dfrac{i}{2}\, (\Gamma_{\eta n} + \Gamma_{\eta k})\right]}, \tag{II,7}$$

$$\omega_{\eta n k} = \omega_{\eta n} - \omega_{\eta k}$$

Substituting (II,6) and (II,7) in (II,5) we have

$$\psi_{\eta n}(q_\eta, t) = \left\{ \psi_{\eta n}^{(0)}\, \mathrm{e}^{-i\omega_{\eta n} t} - \frac{(a_{q\eta}^{\varkappa})\, \mathrm{e}\, \mathscr{E}_0}{2\hbar} \sum_k \langle \eta k \mid q_\eta \mid \eta n \rangle \times \right.$$

$$\times \left. \left[\frac{\mathrm{e}^{i\omega t}}{\left[\omega_{\eta n k} - \omega - \dfrac{i}{2}\, (\Gamma_{\eta n} + \Gamma_{\eta k})\right]} + \frac{\mathrm{e}^{-i\omega t}}{\left[\omega_{\eta n k} + \omega - \dfrac{i}{2}\, (\Gamma_{\eta n} + \Gamma_{\eta k})\right]} \right] \psi_{\eta k}^{(0)} \right\} \mathrm{e}^{-i\omega_{\eta n} t} \tag{II,8}$$

Now it can be determined already the dipole moment of a system which is

$$\mathrm{d}_{q\eta}^{\varkappa} = \int \psi_{\eta n}^* \, \mathrm{e}(a_{q\eta}^{\varkappa})\, q_\eta \psi_{\eta n}\, \mathrm{d}q_\eta \tag{II,9}$$

and further we obtain

$$\mathrm{d}_{q\eta}^{\varkappa} = \int \psi_{\eta n}^{(0)*} \, \mathrm{e}(a_{q\eta}^{\varkappa})\, q_\eta \psi_{\eta n}^{(0)}\, \mathrm{d}q_\eta -$$

$$- \frac{(a_{q\eta}^{\varkappa})\, \mathrm{e}\, \mathscr{E}_0}{2\hbar} \sum_k \langle \eta n \mid q_\eta \mid \eta k \rangle \frac{\mathrm{e}^{i\omega t}}{\omega_{\eta nk} + \omega + \dfrac{i}{2}\,(\Gamma_{\eta n} + \Gamma_{\eta k})} \int \psi_{\eta k}^{(0)*}\, \mathrm{e}(a_{q\eta}^{\varkappa})\, q_\eta \psi_{\eta n}^{(0)}\, \mathrm{d}q_\eta \; -$$

$$- \frac{(a_{q\eta}^{\varkappa})\, \mathrm{e}\, \mathscr{E}_0}{2\hbar} \sum_k \langle \eta n \mid q_\eta \mid \eta k \rangle \frac{\mathrm{e}^{-i\omega t}}{\omega_{\eta nk} - \omega + \dfrac{i}{2}\,(\Gamma_{\eta n} + \Gamma_{\eta k})} \int \psi_{\eta k}^{(0)*}\, \mathrm{e}(a_{q\eta}^{\varkappa})\, q_\eta \psi_{\eta n}^{(0)}\, \mathrm{d}q_\eta \; -$$

$$- \frac{(a_{q\eta}^{\varkappa})\, \mathrm{e}\, \mathscr{E}_0}{2\hbar} \sum_k \langle \eta k \mid q_\eta \mid \eta n \rangle \frac{\mathrm{e}^{i\omega t}}{\omega_{\eta nk} - \omega - \dfrac{i}{2}\,(\Gamma_{\eta n} + \Gamma_{\eta k})} \int \psi_{\eta n}^{(0)*}\, \mathrm{e}(a q_\eta^{\varkappa})\, q_\eta \psi_{r k}^{(0)}\, \mathrm{d}q_\eta \; -$$

$$- \frac{(a_{q\eta}^{\varkappa})\, \mathrm{e}\, \mathscr{E}_0}{2\hbar} \sum_k \langle \eta k \mid q_\eta \mid \eta n \rangle \frac{\mathrm{e}^{-i\omega t}}{\omega_{\eta nk} + \omega - \dfrac{i}{2}\,(\Gamma_{\eta n} + \Gamma_{\eta k})} \int \psi_{\eta n}^{(0)*}\, \mathrm{e}(a_{q\eta}^{\varkappa})\, q_\eta \psi_{\eta k}^{(0)}\, \mathrm{d}q_\eta \; .$$

$$(\mathrm{II},10)$$

Omitting in thes expression the first membere $(a_{q\eta}^{\varkappa}) \langle \eta n \mid q_\eta \mid \eta n \rangle$ (which doesn't not take place by the dispersion) we have

$$\mathrm{d}_{q\eta}^{\varkappa} = \frac{(a_{q\eta}^{\varkappa})^2\, \mathrm{e}^2\, \mathscr{E}_0}{\hbar} \sum_k \mid \langle \eta k \mid q_\eta \mid \eta n \rangle \mid^2 \cdot \omega_{\eta kn} \times$$

$$\times \left[\frac{\mathrm{e}^{i\omega t} \left\{ \omega_{\eta nk}^2 - \left[\omega - \dfrac{i}{2}\,(\Gamma_{\eta n} + \Gamma_{\eta k}) \right]^2 \right\} + \mathrm{e}^{-i\omega t} \left\{ \omega_{\eta nk}^2 - \left[\omega + \dfrac{i}{2}\,(\Gamma_{\eta n} + \Gamma_{\eta k}) \right]^2 \right\}}{\left\{ \omega_{\eta nk}^2 - \left[\omega + \dfrac{i}{2}\,(\Gamma_{\eta n} + \Gamma_{\eta k}) \right]^2 \right\} \left\{ \omega_{\eta nk}^2 - \left[\omega - \dfrac{i}{2}\,(\Gamma_{\eta n} + \Gamma_{\eta k}) \right]^2 \right\}} \right]$$

$$(\mathrm{II},11)$$

or after some modifications

$$\mathrm{d}_{q\eta}^{\varkappa} = \frac{(a_{q\eta}^{\varkappa})^2\, \mathrm{e}^2\, \mathscr{E}_0}{\hbar} \sum_k \mid \langle \eta k \mid q_\eta \mid \eta n \rangle \mid^2\, \omega_{\eta kn} \times$$

$$\times \left\{ \frac{\left[\omega_{\eta nk}^2 - \omega^2 + \dfrac{1}{4}\,(\Gamma_{\eta n} + \Gamma_{\eta k})^2 \right] (\mathrm{e}^{i\omega t} + \mathrm{e}^{-i\omega t})}{(\omega_{\eta nk}^2 - \omega^2)^2 + \dfrac{1}{2}\,\omega^2 (\Gamma_{\eta n} + \Gamma_{\eta k})^2 + \dfrac{1}{16}\,(\Gamma_{\eta n} + \Gamma_{\eta k})^4} \right\} \qquad (\mathrm{II},12)$$

Applying in this expression the oscillator strength by means of the expression [8]

$$f_{q\eta}^{\varkappa} = \frac{m\omega_{\eta kn} \mid \langle \eta k \mid q_\eta \mid \eta n \rangle \mid^2}{\hbar} \qquad (\mathrm{II},13)$$

then it is given

$$\mathrm{d}_{q\eta}^{\varkappa} = \frac{(a_{q\eta}^{\varkappa})^2\, \mathrm{e}^2 f_{q\eta}^{\varkappa}}{m} \mathscr{E}_0 (\mathrm{e}^{i\omega t} + \mathrm{e}^{-i\omega t}) \times$$

$$\times \sum_k \left\{ \frac{\omega_{\eta nk}^2 - \omega^2 + \dfrac{1}{4}\,(\Gamma_{\eta n} + \Gamma_{\eta k})^2}{(\omega_{\eta nk}^2 - \omega^2)^2 + \dfrac{1}{2}\,(\Gamma_{\eta n} + \Gamma_{\eta k})^2\, \omega^2 + \dfrac{1}{16}\,(\Gamma_{\eta n} + \Gamma_{\eta k})^4} \right\} \qquad (\mathrm{II},14)$$

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Using the expression (II,14) we can then determine the coefficient of the polarizability of a system. Since

$$\gamma_{q\eta}^{\varkappa} = \frac{N' \, d_{q\eta}^{\varkappa}}{\mathscr{E}} = \frac{N \, d_{q\eta}^{\varkappa}}{2\mathscr{E}}, \tag{II,15}$$

where $N' = \dfrac{N}{2}$ means the number of the coupled oscillators, we can write

$$\gamma_{q\eta}^{\varkappa} = \frac{(a_{q\eta}^{\varkappa})^2 \, e^2 N}{2m} f_{q\eta}^{\varkappa} \sum_{k} \left\{ \frac{\omega_{\eta nk}^2 - \omega^2}{(\omega_{\eta nk}^2 - \omega^2)^2 + \frac{1}{2}\omega^2(\Gamma_{\eta n} + \Gamma_{\eta k})^2 + \frac{1}{16}(\Gamma_{\eta n} + \Gamma_{\eta k})^4} + \right.$$

$$\left. + \frac{\frac{1}{4}(\Gamma_{\eta n} + \Gamma_{\eta k})^2}{(\omega_{\eta nk}^2 - \omega^2)^2 + \frac{1}{2}\omega^2(\Gamma_{\eta n} + \Gamma_{\eta k})^2 + \frac{1}{16}(\Gamma_{\eta n} + \Gamma_{\eta k})^4} \right\} \tag{II,16}$$

Since the coefficient of the polarizability of a system is then given through the summation of the corresponding coefficients over all modes of vibration[10] we can then for the light wave circularly polarized on the left and on the right write as follows

$$\left. \begin{array}{l} (n_l^2 - 1)_{q\eta} = 4\pi \sum_{q_\eta} \gamma_{q\eta}^{l} \\[2mm] (n_r^2 - 1)_{q\eta} = 4\pi \sum_{q_\eta} \gamma_{q\eta}^{r} \end{array} \right\} \tag{II,17}$$

or

$$(n^2 - 1) = 4\pi \sum_{q_\eta} \sum_{\varkappa} \gamma_{q\eta}^{\varkappa} \tag{II,18}$$

Let us presume that for the both normal modes of vibration the oscillator strength doesn't depend on the polarization of the light wave. We can then write

$$\begin{array}{l} f_{q1}^{r} = f_{q1}^{l} = f_{q1} \\[2mm] f_{q2}^{r} = f_{q2}^{l} = f_{q2} \end{array} \tag{II,19}$$

From the relation (II,17) we can then easily determine the expression ($\Gamma_{\eta nk} = \Gamma_{\eta n} + \Gamma_{\eta k}$)

$$n_l^2 - n_r^2 = \frac{2\pi N \, e^2}{m} \sum_{k} \left\{ f_{q2}[(a_{q2}^{l})^2 - (a_{q2}^{r})^2] \times \right.$$

$$\times \left[\frac{\omega_{2nk}^2 - \omega^2}{(\omega_{2nk}^2 - \omega^2)^2 + \frac{1}{2}\omega^2\Gamma_{2nk}^2 + \frac{1}{16}\Gamma_{2nk}^4} + \frac{\frac{1}{4}\Gamma_{2nk}^2}{(\omega_{2nk}^2 - \omega^2)^2 + \frac{1}{2}\omega^2\Gamma_{2nk}^2 + \frac{1}{16}\Gamma_{2nk}^4} \right] +$$

$$\left. + f_{q1}[(a_{q1}^{l})^2 - (a_{q1}^{r})^2] \times \right.$$

$$\times \left[\frac{\omega_{1nk}^2 - \omega^2}{(\omega_{1nk}^2 - \omega^2)^2 + \frac{1}{2}\omega^2\Gamma_{1nk}^2 + \frac{1}{16}\Gamma_{1nk}^4} + \frac{\frac{1}{4}\Gamma_{1nk}^2}{(\omega_{1nk}^2 - \omega^2)^2 + \frac{1}{2}\omega^2\Gamma_{1nk}^2 + \frac{1}{16}\Gamma_{1nk}^4} \right]$$

$$\text{(II,20)}$$

Substituting the expressions $(a_{q_\eta}^x)^2$ with the use of the relations (II,3a) and (II,3b) we then have

$$n_l^2 - n_r^2 = \frac{4\pi N\,\mathrm{e}^2}{m}\,(\alpha^2 + \beta^2)\,\Phi\sin\Theta\sum_k \times$$

$$\times \left\{ f_{q2}\left[\frac{\omega_{2nk}^2 - \omega^2}{(\omega_{2nk}^2 - \omega^2)^2 + \frac{1}{2}\omega^2\Gamma_{2nk}^2 + \frac{1}{16}\Gamma_{2nk}^4} + \frac{\frac{1}{4}\Gamma_{2nk}^2}{(\omega_{2nk}^2 - \omega^2)^2 + \frac{1}{2}\omega^2\Gamma_{2nk}^2 + \frac{1}{16}\Gamma_{2nk}^4} \right] - \right.$$

$$\left. - f_{q1}\left[\frac{\omega_{1nk}^2 - \omega^2}{(\omega_{1nk}^2 - \omega^2)^2 + \frac{1}{2}\omega^2\Gamma_{1nk}^2 + \frac{1}{16}\Gamma_{1nk}^4} + \frac{\frac{1}{4}\Gamma_{1nk}^2}{(\omega_{1nk}^2 - \omega^2)^2 + \frac{1}{2}\omega^2\Gamma_{1nk}^2 + \frac{1}{16}\Gamma_{1nk}^4} \right] \right\}$$

$$\text{(II,21)}$$

Because of $n_l^2 - n_r^2 \doteq 2n(n_l - n_r)$, where n is the mean refraction index belonging to the phase-shift $\Phi = \dfrac{2\pi n\mathrm{d}}{\lambda}$ (where d denotes the distance between the coupled oscillators measured along the optical axis of the crystal), we will have in this condition after inducing the substitution $\lambda = \dfrac{2\pi c}{\omega}$ the modified expression (II,21) which will be substituted in the relation for polarizability

$$\varrho = \frac{\pi}{\lambda}\,(n_l - n_r) \qquad\qquad \text{(II,22)}$$

Finally we obtain

$$\varrho = \frac{\pi\,\mathrm{e}^2 N\omega^2}{mc^2}\,(\alpha^2 + \beta^2)\,\mathrm{d}\sin\Theta\sum_k \times$$

$$\times \left\{ f_{q2}\left[\frac{\omega_{2nk}^2 - \omega^2}{(\omega_{2nk}^2 - \omega^2)^2 + \frac{1}{2}\omega^2\Gamma_{2nk}^2 + \frac{1}{16}\Gamma_{2nk}^4} + \frac{\frac{1}{4}\Gamma_{2nk}^2}{(\omega_{2nk}^2 - \omega^2)^2 + \frac{1}{2}\omega^2\Gamma_{2nk}^2 + \frac{1}{16}\Gamma_{2nk}^4} \right] - \right.$$

$$\left. - f_{q1}\left[\frac{\omega_{1nk}^2 - \omega^2}{(\omega_{1nk}^2 - \omega^2)^2 + \frac{1}{2}\omega^2\Gamma_{1nk}^2 + \frac{1}{16}\Gamma_{1nk}^4} + \frac{\frac{1}{4}\Gamma_{1nk}^2}{(\omega_{1nk}^2 - \omega^2)^2 + \frac{1}{2}\omega^2\Gamma_{1nk}^2 + \frac{1}{16}\Gamma_{1nk}^4} \right] \right\}$$

$$\text{(II,23)}$$

which is the expression sought for the dispersion of the polarizability of crystals.

III. Discussion of results

The expression (II,23) is in fact more general than all the preceding ones. For rightness evidence of this expression we can consider the fact that this equation does involve as special cases the formulae (I,1), (I,2) and (I,7).

Let us presume to be in the region sufficiently distant from the absorption band, that it is valid $\omega_{1,2}^2 \gg \omega^2$ and that for the both normal modes of vibration the oscillator strengths are the same. While in the spectral region considered the damping doesn't take place, we will obtain under the above mentioned presumptions the equation (II,23) in the more simple form

$$\varrho = -\frac{\pi\,e^2 N}{mc^2}(\alpha^2 + \beta^2)\,d\,\sin\Theta\,\omega^2\left\{\frac{f_2(\omega_2^2 - \omega^2)}{(\omega_2^2 - \omega^2)^2} - \frac{f_1(\omega_1^2 - \omega^2)}{(\omega_1^2 - \omega^2)^2}\right\} =$$

$$= B\omega^2\left\{\frac{f_2}{\omega_2^2 - \omega^2} - \frac{f_1}{\omega_1^2 - \omega^2}\right\} =$$

$$= B\omega^2\left\{\frac{f_2(\omega_0^2 + 2\pi^2\varepsilon - \omega^2) - f_1(\omega_0^2 - 2\pi^2\varepsilon - \omega^2)}{(\omega_0^2 - 2\pi^2\varepsilon - \omega^2)\,(\omega_0^2 + 2\pi^2\varepsilon - \omega^2)}\right\} =$$

$$= B\,.\,f\,.\,4\pi^2\varepsilon\,.\,\frac{\omega^2}{(\omega_0^2 - \omega^2)^2} =$$

$$= B'\,\frac{\omega^2}{(\omega_0^2 - \omega^2)^2} \tag{III,1}$$

By the evaluation following presumptions, symbols and substitutions were used:

$$\omega_{1nk} = \omega_1,$$

$$\omega_{2nk} = \omega_2, \qquad \omega_{1,2}^2 \gg \omega^2,$$

$$f_{q1} = f_{q2} = f,$$

$$\left.\begin{array}{l}\omega_1^2 = \omega_0^2 + 2\pi^2\varepsilon \\ \omega_2^2 = \omega_0^2 - 2\pi^2\varepsilon\end{array}\right\} \text{[11]}$$

$$B = \frac{\pi\,e^2 N}{mc^2}(\alpha^2 + \beta^2)\,d\,\sin\Theta$$

$$B' = 4\pi^2\varepsilon\,.\,f\,.\,B$$

Introducing in the expression (III,1) the further substitution $\omega = \dfrac{2\pi c}{\lambda}$, we can write it in the form

$$\varrho = \frac{A\,.\,\lambda^2}{(\lambda^2 - \lambda_0^2)^2},$$

$$A = \frac{\pi f\,.\,\varepsilon\,e^2 N}{mc^4}(\alpha^2 + \beta^2)\,d\,\sin\Theta \tag{III,2}$$

Comparing this relation with (I,2) we can see that the (III,2) will be really Chandrasekhar's formula (I,2) in the case of the single characteristic wave length. Let us

presume now that the oscillator strengths are different for both normal modes of vibration. With respect to the relation (III,1) we will have

$$\varrho = B\omega^2 \left\{ \frac{f_2(\omega_0^2 + 2\pi^2\varepsilon - \omega^2) - f_1(\omega_0^2 - 2\pi^2\varepsilon - \omega^2)}{(\omega_0^2 - 2\pi^2\varepsilon - \omega^2)(\omega_0^2 + 2\pi^2\varepsilon - \omega^2)} \right\} =$$

$$= B\omega^2 \left\{ \frac{2\pi^2\varepsilon(f_1 + f_2)}{(\omega_0^2 - \omega^2)^2} + \frac{f_2 - f_1}{\omega_0^2 - \omega^2} \right\}, \tag{III,3}$$

$$B = \frac{\pi\, e^2 N}{mc^2} (\alpha^2 + \beta^2)\, d \sin \Theta$$

or substituting $\omega = \dfrac{2\pi c}{\lambda}$

$$\varrho = \frac{\pi N\, e^2(\alpha^2 + \beta^2)\, d \sin \Theta \varepsilon (f_2 + f_1)\, \lambda_0^4}{2mc^4} \cdot \frac{\lambda^2}{(\lambda^2 - \lambda_0^2)^2} +$$

$$+ \frac{\pi N\, e^2(\alpha^2 + \beta^2)\, d \sin \Theta (f_2 - f_1)}{mc^2} \cdot \frac{1}{\lambda^2 - \lambda_0^2} \tag{III,4}$$

which is then the relation (I,7) derived by Vyšín [7].

Let us discuss the possibility, which in all cases can take place. Namely if it is given $\omega_{1,2}^2 \gg \omega^2$. $f_1 \neq f_2$, the damping can be then omitted and the dispersion of the rotatory power will be then described by the formula (III,4). This expression involve two members which must not be always maintained equally in the case of the concrete crystal.

The second member, which is linear with respect to the characteristic wave length λ_0, will be evidently of use in this case where the difference of oscillator strengths $(f_2 - f_1)$ belonging to the two normal modes of vibration, is very considerable. In this case it is possible (provided that ε the constant of the binding is very low) to omit the first of the expression (III,4) with respect to the second member and we obtain then even the third specific case of the generalized equation (II,23) namely the Drude's equation (I,1) for the case of the single characteristic wave length of the absorption.

The evaluation made in this way shows that all the equations earlier derived for the rotatory power are really involved in the formula (II,23) as special cases.

In the conclusion we can show that from the equation (II,23) follows even the equation of the normal (frequency) dispersion, taking no account of the effects of the second order (to which belong the optical activity) setting

$$\omega_1 = \omega_2 = \omega_0, \qquad f_1 = f_2 = f.$$

The refraction index may be then determined from the equation

$$n_m^2 - 1 = \frac{1}{2} \left[(n_l^2 - 1)_{q_1} + (n_l^2 - 1)_{q_2} + (n_r^2 - 1)_{q_1} + (n_r^2 - 1)_{q_2} \right] \tag{III,5}$$

With respect to the expressions (II,16) we then obtain under the above mentioned presumptions the expression

$$n_m^2 - 1 = \frac{\pi f N\, e^2}{m} \times$$

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$$\times \left\{ \frac{(a_{q1}^r)^2 \left[(\omega_0^2 - \omega^2) + \frac{1}{4}\Gamma_1^2\right]}{(\omega_0^2 - \omega^2)^2 + \frac{1}{2}\omega^2\Gamma_1^2 + \frac{1}{16}\Gamma_1^4} + \frac{(a_{q1}^l)^2 \left[(\omega_0^2 - \omega^2) + \frac{1}{4}\Gamma_1^2\right]}{(\omega_0^2 - \omega^2)^2 + \frac{1}{2}\omega^2\Gamma_1^2 + \frac{1}{16}\Gamma_1^4} + \right.$$

$$\left. + \frac{(a_{q2}^r)^2 \left[(\omega_0^2 - \omega^2) + \frac{1}{4}\Gamma_2^2\right]}{(\omega_0^2 - \omega^2)^2 + \frac{1}{2}\omega^2\Gamma_2^2 + \frac{1}{16}\Gamma_2^4} + \frac{(a_{q2}^l)^2 \left[(\omega_0^2 - \omega^2) + \frac{1}{4}\Gamma_2^2\right]}{(\omega_0^2 - \omega^2)^2 + \frac{1}{2}\omega^2\Gamma_2^2 + \frac{1}{16}\Gamma_2^4} \right\} =$$

$$= \frac{\pi N f\, e^2}{m} \left\{ \frac{\left[(\omega_0^2 - \omega^2) + \frac{1}{4}\Gamma_1^2\right][(a_{q1}^r)^2 + (a_{q1}^l)^2]}{(\omega_0^2 - \omega^2)^2 + \frac{1}{2}\omega^2\Gamma_1^2 + \frac{1}{16}\Gamma_1^4} + \right.$$

$$\left. + \frac{\left[(\omega_0^2 - \omega^2) + \frac{1}{4}\Gamma_2^2\right][(a_{q2}^r)^2 + (a_{q2}^l)^2]}{(\omega_0^2 - \omega^2)^2 + \frac{1}{2}\omega^2\Gamma_2^2 + \frac{1}{16}\Gamma_2^4} \right\} \qquad \text{(III,6)}$$

Let us set further aven $\Gamma_1 = \Gamma_2 = \Gamma_0$. Then we can write after substitution for the expressions (II,3a) and (II,3b) obtain the forgoing equation in the form

$$n_\omega^2 - 1 = \frac{2\pi N f\, e^2}{m}(\alpha^2 + \beta^2) \times$$

$$\times \left\{ \frac{(\omega_0^2 - \omega^2) + \frac{1}{4}\Gamma_0^2}{(\omega_0^2 - \omega^2)^2 + \frac{1}{2}\omega^2\Gamma_0^2 + \frac{1}{16}\Gamma_0^2} + \frac{(\omega_0^2 - \omega^2) + \frac{1}{4}\Gamma_0^2}{(\omega_0^2 - \omega^2)^2 + \frac{1}{2}\omega^2\Gamma_0^2 + \frac{1}{16}\Gamma_0^4} \right\} =$$

$$= \frac{4\pi N f\, e^2}{m}(\alpha^2 + \beta^2) \left[\frac{(\omega_0^2 - \omega^2) + \frac{1}{4}\Gamma_0^2}{(\omega_0^2 - \omega^2)^2 + \frac{1}{2}\omega^2\Gamma_0^2 + \frac{1}{16}\Gamma_0^4} \right] \qquad \text{(III,7)}$$

which represent the general relation for the frequency dispersion of the crystal.

The merit of this relation lies in the fact that in the general form it describes the absorption band of the crystal where the damping will be expressed very expressively. In the regions are very apart from the absorption region the members of damping may be omitted and we then have the expression

$$n_\omega^2 - 1 = \frac{4\pi N f\, e^2}{m}(\alpha^2 + \beta^2) \cdot \frac{1}{\omega_0^2 - \omega^2}, \qquad \text{(III,8)}$$

which is well known.

Conclusion

As basic contribution of the present work may be considered the derivation of the equation (II,23).

The derived expression does involve 4 members, the both of which in the brackets may be considered as the quantum effects. The interpretation of these quantum members however is very difficult, since they are involving the damping. Both these quantum members will exhibit themselves very expressively as far as in the close proximity of the absorption bands, where there are, as we know, the experimental measurements practically unrealizable.

The interpretation of the quantum members will be made difficult also by the fact that we have till now no suitable analytical method by means of which we could prove to estimate, at least in an experimental way, the extent of damping.

From this point of view the equation (II,23) has, for the time being, somewhat formal character. The correctness of the equation will be no doubt verified by the evaluations made in chapter III, we have not but yet succeeded till now in the complete interpretation of the equation.

The final verification of the correctness of the equation (II,23) as so as of the complete theory of the rotatory dispersion of crystals will be then possible only on basis of the further and new measurements.

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Shrnutí

Teorie optické aktivity krystalů

VLADIMÍR JANKŮ

V předložené práci je ukázán kvantověmechanický výpočet disperse rotační polarizace krystalů. Výpočet vychází z modelu spřažených oscilátorů a je v něm také přihlédnuto k útlumu. Byla získána zobecněná rovnice disperse rotační polarizace krystalů, ze které jako speciální případy vyplývají všechny nejdůležitější dříve odvozené vzorce.

Резюме

Теория оптической активности кристаллов

ВЛАДИМИР ЯНКУ

В настоящей работе показывается квантовомеханическое определение дисперсии оптической активности кристаллов.

Используется метод связанных осцилляторов и принимается во внимание также затухание. Получено обобщенное уравнение, которое применимо для описания дисперсии оптической активности кристаллов и из которого вытекают фундаментальные предыдущие соотношения.