

Using the Kramers-Kronig Relations in the Study of the Optical Activity in Crystals

Using Kramers-Kronig relations it is shown that circular dichroism of Gaussian shape does not lead to the quadratic Chandrasekhar's formula for optical rotatory dispersion in crystals, which are optically active only in the crystalline state. On the other hand the circular dichroism curve with two extrema centered at maximum of absorption leads to Chandrasekhar's formula.

The optical rotatory power of an absorbing crystal may be considered to be a complex quantity being given by

$$\bar{\varrho} = \varrho - i\sigma. \quad (1)$$

Then by definition $\varrho = \text{Re}\bar{\varrho}$ is the rotatory power (in radians per cm) and $\sigma = \text{Im}\bar{\varrho}$ is the ellipticity of the emerging light or simply the circular dichroism. Optical rotatory dispersion (ORD) and circular dichroism (CD) curves are related by Kramers-Kronig relations [1]

$$\varrho = \frac{2\omega^2}{\pi} P \int_0^\infty \frac{\sigma(\Omega) d\Omega}{\Omega(\Omega^2 - \omega^2)}, \quad (2a)$$

$$\sigma = -\frac{2\omega}{\pi} P \int_0^\infty \frac{\varrho(\Omega) d\Omega}{\Omega^2 - \omega^2}. \quad (2b)$$

The symbol P means that only the principal value of integral is to be taken. The complete CD spectrum determines the complete ORD spectrum and vice versa.

CD is very powerful in resolving the overlapping absorption bands. The CD curve is confined to a small region, in which the optically active medium absorbs while the tail of the ORD curve extends outside the region of absorption. Because the experimental difficulties in making CD measurements have been overcome [2] we hope that the measured data of CD will be soon available.

It has been assumed that the CD curve is of Gaussian type and therefore $\sigma(\omega)$ may be expressed as

$$\sigma(\omega) = \sigma_{\max} e^{-\frac{(\omega - \omega_0)^2}{\Theta_0^2}}, \quad (3)$$

where σ_{\max} is the maximum of $\sigma(\omega)$ attained at ω_0 and Θ_0 is a width parameter. Substituting (3) into (2a) we get

$$\varrho = \frac{2\sigma_{\max}\omega^2}{\pi} \int_0^\infty \frac{e^{-\frac{(\Omega - \omega_0)^2}{\Theta_0^2}} d\Omega}{\Omega(\Omega^2 - \omega^2)}. \quad (4)$$

Before evaluating the integral in (4) we introduce an important quantity R , that is the rotatory strength given by definition [3] as

$$R = \frac{3\hbar c}{4\pi^2 N} \int_0^\infty \frac{\sigma(\omega) d\omega}{\omega}. \quad (5)$$

Using (3) we get approximately for R

$$R = \frac{3\hbar c \sigma_{\max} \Theta_0}{4\pi^{3/2} N \omega_0}. \quad (6)$$

We calculate σ_{\max} from (6) and substitute into (4) obtaining

$$\varrho = \frac{8\pi^{1/2} N R \omega_0^2 \omega^2}{3\hbar c \Theta_0} \int_0^\infty \frac{e^{-\frac{(\Omega - \omega_0)^2}{\Theta_0^2}} d\Omega}{\Omega(\Omega^2 - \omega^2)}. \quad (7)$$

Now, after evaluating the integral in (7) we get [4]

$$\varrho = \frac{4\pi N R \omega^2}{2\hbar c (\omega_0^2 - \omega^2)}. \quad (8)$$

This is the well known Drude's formula.

The experimental data concerning crystals fit the formula of Chandrasekhar, that is

$$\varrho = \frac{K \omega^2}{(\omega_0^2 - \omega^2)^2}. \quad (9)$$

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It should be pointed out that Chandrasekhar's formula holds for crystals the activity of which is due to their structure. We see that the Gaussian shape of the CD curve does not lead to the formula of Chandrasekhar.

Chandrasekhar's model is based upon the idea of coupled oscillators [5], [6]. In this model each molecule is represented by a linear harmonic oscillator. The oscillators are arrayed spirally in the crystal. Let the eigenfrequency of each oscillator be ω_0 when uncoupled. Two oscillators form one compound oscillator and all oscillators are identical. As a result of the coupling the frequency would be split into frequencies ω_1 , and ω_2 which are the frequencies of two normal modes of vibration of the compound oscillator. They are expressed as

$$\begin{aligned}\omega_1^2 &= \omega_0^2 + 2\pi^2\varepsilon, \\ \omega_2^2 &= \omega_0^2 - 2\pi^2\varepsilon,\end{aligned}\quad (10)$$

where ε is the coupling constant between the two adjacent single oscillators.

It follows from this model [5], [6] that final quadratic formula (9) is a difference of two Drude's terms involving frequencies ω_1 and ω_2 . But it should be pointed out that Chandrasekhar's formula does not contain the rotatory strength.

We assume now that the rotatory power is a sum of ϱ_{q1} and ϱ_{q2} that is each mode of vibration has the proper rotatory power. Similarly the circular dichroism σ has also two components σ_{q1} and σ_{q2} . Each of these components is of Gaussian shape. Then we have instead of (8)*

$$\varrho_{q\eta} = \frac{4\pi NR_{q\eta}\omega^2}{\hbar c(\omega_\eta^2 - \omega^2)}, \quad (11)$$

where $\eta = 1, 2$. Then

$$\varrho = \varrho_{q1} + \varrho_{q2} = \frac{4\pi N}{\hbar c} \left\{ \frac{R_{q1}\omega^2}{\omega_1^2 - \omega^2} + \frac{R_{q2}\omega^2}{\omega_2^2 - \omega^2} \right\} \quad (12)$$

and using (10) we obtain

$$\varrho = \frac{4\pi N}{\hbar c} \left\{ \frac{2\pi^2\varepsilon(R_{q2} - R_{q1})\omega^2}{(\omega_0^2 - \omega^2)^2} + \frac{(R_{q1} + R_{q2})\omega^2}{\omega_0^2 - \omega^2} \right\}. \quad (13)$$

If $R_{q2} = -R_{q1}$ then the second term is zero and (13) reduces to

$$\varrho = \frac{16\pi^3 NR_0 \varepsilon \omega^2}{\hbar c(\omega_0^2 - \omega^2)^2}, \quad (14)$$

where $2R_0 = |R_{q1}| + |R_{q2}|$. Under these conditions it follows from (12) that

$$\varrho = \frac{4\pi NR_0}{\hbar c} \left\{ \frac{\omega^2}{\omega_2^2 - \omega^2} - \frac{\omega^2}{\omega_1^2 - \omega^2} \right\}. \quad (15)$$

* We have neglected a factor 1/3 because the compound oscillators are not randomly oriented.

Formulae (14) and (15) are identical. The first one contains coupling constant ε and non-split frequency ω_0 , the second is then without ε but contains the splitted frequencies ω_1 , and ω_2 . If R_{q1} and R_{q2} are equal and positive then the first term in (13) is zero and we get Drude's formula. In the more general case when R_{q1} and R_{q2} are different we have the combined formula previously obtained by us in [7], which removes some simplifications in Chandrasekhar's theory.

Nevertheless, there exists one more matter in the use of Kramers-Kronig relations. Introducing the damped forced vibration of the linear harmonic oscillators into the model of compound oscillators we have obtained the following formula for circular dichroism of crystals [8]

$$\begin{aligned}\sigma &= \frac{A^{(1)}\gamma_0(\omega^2 - \omega_0^2)\omega^3}{[(\omega_0^2 - \omega^2)^2 + 4\gamma_0^2\omega^2]^2} + \\ &+ \frac{A^{(2)}\gamma_0\omega^3}{(\omega_0^2 - \omega^2)^2 + 4\gamma_0^2\omega^2},\end{aligned}\quad (16)$$

where γ_0 is the damping constant of single linear harmonic oscillator. $A^{(1)}$ and $A^{(2)}$ are the crystal constant described in [8]. If $A^{(2)} = 0$ and σ is nonzero only in the vicinity of ω_0 we may put in (16) $(\omega^2 - \omega_0^2) = 2\omega_0(\omega - \omega_0)$ and $\omega \sim \omega_0$. Then (16) reduces to the form

$$\sigma = \frac{2A^{(1)}(\omega - \omega_0)\gamma_0}{[(\omega_0 - \omega)^2 + \gamma_0^2]^2}. \quad (17)$$

We see that this formula is not of Gaussian shape. The quantity σ is zero for $\omega = \omega_0$ and the CD curve has two extrema at

$$\omega_{\text{ext}} = \omega_0 \pm \frac{1}{\sqrt{3}}\gamma_0. \quad (18)$$

From the condition of extremum $d\sigma/d\omega = 0$ we get for $A^{(1)}$

$$A^{(1)} = \pm \frac{8\sigma_{\text{ext}}\gamma_0^2}{3^{3/2}}. \quad (19)$$

We see that in the case $A^{(1)} > 0$ the circular dichroism is negative for $\omega < \omega_0$ and positive for $\omega > \omega_0$, and vice versa. Substituting (19) into (17) for, e.g. $A^{(1)} > 0$ we have

$$\sigma = \frac{16\sigma_{\text{ext}}\gamma_0^3(\omega - \omega_0)}{3^{3/2}[(\omega_0 - \omega)^2 + \gamma_0^2]^2}. \quad (20)$$

We return now to (2a) introducing ω_0 into this equation

$$\varrho = \frac{2\omega^2}{\pi} P \int_0^\infty \frac{\sigma(\Omega)d\Omega}{\Omega(\Omega^2 - \omega_0^2 + \omega_0^2 - \omega^2)}$$

$$= \frac{2\omega^2}{\pi} P \int_0^{\infty} \frac{\sigma(\Omega) d\Omega}{\Omega(\omega_0^2 - \omega^2) \left(1 - \frac{\omega_0^2 - \Omega^2}{\omega_0^2 - \omega^2}\right)}. \quad (21)$$

In region far from absorption band, $|\omega_0^2 - \Omega^2| \ll |\omega_0^2 - \omega^2|$ because for Ω very different from ω_0 , $\sigma(\Omega)$ is small and negligible. Therefore (21) can be approximated by

$$\varrho = \frac{2\omega^2}{\pi(\omega_0^2 - \omega^2)} \int_0^{\infty} \frac{\sigma(\Omega) d\Omega}{\Omega} + \frac{2\omega^2}{\pi(\omega_0^2 - \omega^2)^2} \int_0^{\infty} \frac{(\omega_0^2 - \Omega^2) \sigma(\Omega) d\Omega}{\Omega}. \quad (22)$$

Equation (22) has the same frequency dependence as (13). Now, we substitute (20) into (22) obtaining

$$\sigma(\omega) = \frac{32\sigma_{\text{ext}}\omega^2}{3^{3/2}\pi(\omega_0^2 - \omega^2)} \int_0^{\infty} \frac{\gamma_0^3(\Omega - \omega_0) d\Omega}{\Omega[(\omega_0 - \Omega)^2 + \gamma_0^2]} + \frac{32\sigma_{\text{ext}}\omega^2}{3^{3/2}\pi(\omega_0^2 - \omega^2)^2} \int_0^{\infty} \frac{(\omega_0^2 - \Omega^2)(\Omega - \omega_0) \gamma_0^3 d\Omega}{\Omega[(\omega_0 - \Omega)^2 + \gamma_0^2]}. \quad (23)$$

Both integrals may be solved when taking $\Omega \approx \omega_0$, $(\omega_0^2 - \Omega^2) \approx 2\omega_0(\omega_0 - \Omega)$ and substituting

$$\frac{\Omega - \omega_0}{\gamma_0} = x. \quad (24)$$

Then we have

$$\int_0^{\infty} \frac{\gamma_0^3(\Omega - \omega_0) d\Omega}{\Omega[(\omega_0 - \Omega)^2 + \gamma_0^2]} \equiv \frac{\gamma_0}{\omega_0} \int_{-\infty}^{+\infty} \frac{x dx}{(1+x^2)^2} = 0. \quad (25)$$

The lower limit is in fact, $-(\omega_0/\gamma_0)$ but ω_0 is very great in comparison to γ_0 . And the second integral

$$- \int_0^{\infty} \frac{2(\Omega - \omega_0)^2 \gamma_0^3 d\Omega}{[(\omega_0 - \Omega)^2 + \gamma_0^2]^2} \equiv - \gamma_0^2 \int_{-\infty}^{+\infty} \frac{2x^2 dx}{(1+x^2)^2} = \gamma_0^2 \int_{-\infty}^{+\infty} x \left[\frac{d}{dx} \left(\frac{1}{1+x^2} \right) \right] dx = -\pi\gamma_0^2. \quad (26)$$

Now from (26) and (23) we have

$$\varrho(\omega) = \mp \frac{32\sigma_{\text{ext}}\gamma_0^2\omega^2}{3^{3/2}(\omega_0^2 - \omega^2)^2}. \quad (27)$$

The minus sign holds for $A^{(1)} > 0$, which means that the crystal is laevorotatory. In the case of $A^{(1)} < 0$ the crystal is dextrorotatory.

Thus from these considerations we may conclude that Gaussian shape of the CD curve leads to Drude's formula. The splitting of ω_0 into two normal frequencies ω_1 and ω_2 leads to the CD curve which shows two rotatory bands of opposite sign centered at ω_0 . Using Kramers-Kronig relation it has been shown that the S-shaped CD curve leads to the quadratic formula of Chandrasekhar. The more complicated situation which appears when we cannot neglect $A^{(2)}$ in (16) will be studied in the future.

In a forthcoming paper an application of the presented consideration will be used in order to remove some discrepancies in the interpretation of ORD for α -quartz.

Application de la relation de Kramers-Kronig à l'étude de l'activité optique des cristaux

L'utilisation de la relation de Kramers-Kronig prouve que le dichroïsme circulaire à repartition de Gauss ne mène pas à la formule des carrés de Chandrasekhar pour la dispersion optique rotatoire des cristaux qui ne sont optiquement actifs qu'à l'état cristallin. De l'autre côté la courbe du dichroïsme circulaire avec deux extremums concentrés au maximum d'absorption mène à la formule de Chandrasekhar.

Применение соотношения Крамерса-Кронига для исследования оптической активности кристаллов

Применение соотношения Крамерса-Кронига показывает, что круговой дихроизм с гауссовым распределением не приводит к квадратной формуле Чандрасекара для оптической вращательной дисперсии кристаллов, которые оптически активны только в кристаллическом состоянии. С другой стороны, кривая кругового дихроизма с двумя экстремумами, сосредоточенными в максимуме абсорбции, приводит к формуле Чандрасекара.

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