OPTICAL ACTIVITY OF CRYSTALLINE MEDIA

H T VAN DAM

STELLINGEN

1. De amplitude van de gereflecteerde golf aan het grensvlak van twee optische isomeren is evenredig met de totale rotatiesterkte.

   H.B.G. Casimir, Philips Res.Repts. 21, 417 (1966)

2. Het door Terwiel aangevoerde bezwaar tegen Born's methode van het relatieve electrische dipool moment is niet juist.

   R.H. Terwiel, Proefschrift Leiden 1964

3. Het dichroïsme van tris-oxalato metallaten en $Co(en)_3^{3+}$ is ook met een dynamische doorbreking van Laporte's regel te begrijpen.

   C.J. Ballhausen, Introduction to Ligand Field Theory,
   p.192, McGraw-Hill 1962

4. Michelson's bezwaren tegen het conventionele model van poreuze anodische aluminiumoxydhuiden zijn niet steekhoudend.

   C.E. Michelson, J.Electrochem.Soc. 115, 213 (1968)

5. De conclusie van Bürgi en Schmid dat het tyrosine en tryptofaan gehalte in Zn-α_2 glycoproteine uitzonderlijk hoog is, wordt door hun experimenten tegengesproken.

   H.E. Schultze en J.F. Heremans, Molecular Biology of
   Human Proteins, p.208, Elsevier Publ.Cy. 1966

   W. Bürgi en K. Schmid, J.Biol.Chem.236, 1066 (1961)

   L. Berrens en E. Bleumink, Biochim. Biophys. Acta, 115,
   504 (1966)

6. Hed en Tannhauser hebben thermogravimetrische en electrische geleidingsmetingen aan MnO uitgevoerd. De conclusies die zij hieruit trekken over de ionizatiegraad van de vacatures en het mechanisme van de electrische geleiding zijn fout.

   A.Z. Hed en D.S. Tannhauser, J.Chem.Phys. 47, 2090 (1967)

7. "Wide range electron energy kinetics" is in wezen niets anders dan het meten van verschijningspotentialen.

   P. Brown, J.Am.Chem.Soc. 90, 4459 (1968)

8. De anomale optische absorptie van zeer dunne polybutadieen films op metalen is door complexvorming te begrijpen.

   N.M. Bashara en D.W. Peterson, J.Opt.Soc.Am. 56, 1320 (1966)

9. Bij de analyse van nitriden is de bepaling van stikstof als moleculaire stikstof te verkiezen boven die als ammoniak.

10. Het is te betreuren dat Woodward de rehabilitatie van Richard III niet vermeldt.

    E.L. Woodward, A history of England 3^{rd}_{ed} Muthuen (1965)

    Hor. Walpole, Historic doubts on the Life and Reign of King Richard III 2nd ed, London 1768

    Josephine Tey, The daughter of Time, Penguin C990

11. Het voorstel niet-dichtstgepakte bolstapelingen dichtstgepakt in bredere zin te noemen heeft geen waarde.

    Shing-Ming Ho en Bodie E. Douglas, J.Chem.Ed. 45, 474, (1968).

H.T. van Dam

Leiden, 30 oktober 1968

OPTICAL ACTIVITY OF CRYSTALLINE MEDIA

PROEFSCHRIFT

TER VERKRIJGING VAN DE GRAAD VAN DOCTOR IN DE
WISKUNDE EN NATUURWETENSCHAPPEN AAN DE RIJKSUNIVERSITEIT
TE LEIDEN, OP GEZAG VAN DE RECTOR MAGNIFICUS
DR L. KUKENHEIM Ezn, HOOGLERAAR IN DE FACULTEIT DER
LETTEREN, TEN OVERSTAAN VAN EEN COMMISSIE UIT DE
SENAAT TE VERDEDIGEN OP WOENSDAG 30 OKTOBER 1968
TE 14.15 UUR

DOOR

HENDRIK TJAPKO VAN DAM

GEBOREN TE OOSTBURG IN 1937

Promotor: Prof. Dr L. J. Oosterhoff

Introduction

The occurrence of the phenomenon of optical activity, viz. the rotation of the plane of polarization of a linearly polarized light beam by a piece of matter, can be derived from the general properties of the dielectric constant, the function that connects the dielectric displacement and the electric field in the macroscopic Maxwell theory. If this connection is assumed as here for a homogeneous medium:

$$D(\underline{x},t) = \int dt' \int dx'\, \varepsilon(\underline{x}-\underline{x}', t-t')\, E(\underline{x}',t')$$

expressing explicitly that $D(\underline{x},t)$ is related to the actual value $E(\underline{x}',t')$ at all space points $\underline{x}'$ near the point $\underline{x}$ shows the fact that such a medium shows spatial dispersion as opposed to the much more important and better known frequency dispersion, a consequence of the $(t-t')$ dependence of ε. Since it is easier to handle we shall use the Fourier transform of ε designated by the same symbol but depending on the frequency ω and the wave vector $\underline{k}$:

$$\varepsilon(\omega,\underline{k}) = \int dt \int dx\, \varepsilon(\underline{x},t) \exp[-i(\underline{k}\cdot\underline{x}-\omega t)]$$

We now assume that $\varepsilon(\underline{x},t)$ vanishes for values of x larger than a certain (characteristic) distance a, which is taken to be of atomic dimensions. For wave numbers in the visible region of the spectrum we then have $ka \approx 10{,}000 \cdot 10^{-8} = 0.0001$, small compared to unity. Expanding $\varepsilon(\omega,\underline{k})$ in terms of ka we can therefore break off after the second term:

$$\varepsilon(\omega,\underline{k}) = \varepsilon(\omega) + i\,\omega k\, g(\omega)$$

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Introduction

The existence of the phenomenon of optical activity, e.g. the rotation of the plane of polarisation of a linearly polarized light beam by a piece of matter, can be derived from the general properties of the dielectric constant, the function that connects the dielectric displacement and the electric field in the macroscopic Maxwell theory. If this connection is linear we have for a homogeneous medium:

$$\underline{D}(\underline{x},t) = \int_{-\infty}^{t} dt' \int d\underline{x}' \underline{\varepsilon}\,(t-t',x-x').\underline{E}(\underline{x}',t')$$

expressing explicitly that $\underline{D}(\underline{x}\,,\,t)$ is related to the values taken by $\underline{E}$ in all space instead of just the point $\underline{x}$ alone. One says that such a medium shows spatial dispersion in analogy to the much more important and better know frequency dispersion, a consequence of the (t-t') dependence of $\underline{\varepsilon}$. Since it is easier to handle we shall use the Fourier transform of $\underline{\varepsilon}$ designated by the same symbol but depending on the frequency ω and the wave vector $\underline{k}$:

$$\varepsilon(\omega,\underline{k}) = \int d\underline{\xi} \int d\tau\ \underline{\varepsilon}(\xi,\tau)\ \exp\{-i(\underline{k}.\underline{\xi}-\omega\tau)\}$$

We now assume that $\underline{\varepsilon}(\xi,\tau)$ vanishes for values of ξ larger than a certain characteristic distance a, which is taken to be of atomic dimensions. For wave numbers in the visible region of the spectrum we then have $k{\times}a \approx 20.000.10^{-7} = 0.002$, small compared to unity. Expanding $\varepsilon(\omega\,,\,\underline{k})$ in terms of ka we can therefore break off after the second term:

$$\underline{\varepsilon}(\omega,\underline{k}) = \underline{\varepsilon}(\omega) + i\ ka\ \underline{g}(\omega)$$

It can be shown that $\underline{g}(\omega)$ is the refinement of $\varepsilon(\omega)$ and therefore of the refractive index n that gives rise to different velocities of right- and left-handed circularly polarized light beams as well as to different absorptions of these (the circular dichroism).

The aim of a microscopic theory of optical activity now must be expressing $\underline{g}(\omega)$ in terms of molecular quantities, thus providing experimental access to these quantities. We have again taken up this subject in order to study the following main points:

1. In most theories $\underline{g}(\omega)$, or whatever equivalent expression is used, is calculated for values of ω that do not coincide with the absorption frequencies of the medium. The anomalies near these frequencies however contain the most interesting information from a chemical point of view.

2. In order to put through an expansion in ka one usually encloses the molecules by a sphere of radius a thereby confining the theory to rather small molecules. Experimentally, media composed of large molecules (e.g. polymers) hardly differ in their optical properties from those composed of small ones. The same holds for crystals in which often no isolated groups can be pointed out. We have therefore tried to find out under which general circumstances a characteristic length a can be defined. This, by the way, is the reason for slipping in the essential argument of any theory of optical acitivity (viz. $0 < ka < 1$) with the help of the dielectric constant, which is a property of an assembly of molecules not just one molecule. Usually one finds this argument, due to Born, stated with respect to one molecule saying that one has to take the finiteness of the molecular radius and wavelength ratio or equivalently the variation of the electric field over the molecule into account.

In chapter I we develop the microscopic theory of dispersion of a medium along the lines of Born's theory for ionic crystals in the infra-red region 1). Huang has extended this theory with a quantum mechanical treatment 2) and we propose to do the same for the visible region, where however the electrons are the excitable particles. The basic idea is due to Ewald 3,4) who assumed the medium to consist of charged bounded particles vibrating under the influence of an electromagnetic field. In order to be self-consistent this field must be just the field created by the vibrating charges. The demand for self-consistency leads to an eigenvalue problem from which the refractive indices are determined. In this approach there is no place for any external field that is expected to induce the vibrations in the first place, in fact, as Ewald puts it, there is no exterior to the crystal. His famous extinction theorem however shows that an external field vanishes inside the medium, from which it follows that all results derived for an infinite medium are also valid for a finite one. This theorem has recently 5) been proved to be valid also in the higher order needed for the theory of optical activity, and we therefore feel justified in using this theorem for once instead of proving it.

In chapter II we specify the medium somewhat more and compare the results with those of previous theories applied to such media, from which it appears that some assumptions can be postponed till a much later stage than is usual. We shall also derive the connection between $\underline{g}(\omega)$ and the rotatory power ϕ and the circular dichroism θ for a particular situation.

Finally in chapter III we shall estimate the rotation dispersion of a $NiSO_4 . 6H_2O$ crystal and compare the results with the experimental findings.

Litt.

1. M.Born and K.Huang, Dynamical Theory of Crystal Lattices, Oxford University Press (1962) ch. VII.
2. Kun Huang, Proc.Camb. Phil. Soc. 45, 452 (1949)
3. P.P. Ewald, Ann. Phys. Lpz. 49 (1961), 1
4. P.P. Ewald, Rev. Mod. Phys. 37 (1965)
5. W.J.A. Maaskant and L.J. Oosterhoff Mol. Phys. 8, 319.

Chapter I

Introduction

We consider a system consisting of an electromagnetic field and an assembly of charged particles in an infinitely big temperature bath. Such a system can be taken to be conservative, i.e. its hamiltonian is independent of time. Then there exists a very simple relationship between the evolution operator of the system and the resolvent $G(z) = (z-H)^{-1}$ of the hamiltonian. The latter operator is particularly suited to obtain better than first-order approximations in a perturbation theory, necessary in the neighbourhood of eigenvalues of the unperturbed hamiltonian even if the perturbation can be considered small. Furthermore it appears that these higher order corrections can be found using an algebraic method without even expanding, thus circumventing any problem of convergence.

The use of this conservative system implies however that we have to interpret the field quantities as operators, that is we have to quantize the fields. If we do this in such a way that the Lorentz condition is fulfilled we have the advantage that all field quantities can be handled on the same footing. If the Coulomb gauge is used the electrostatic part is hidden in the particle interaction and this term has to be conjured out at the end of the calculation. Both conditions give rise of course to the same final expressions since no different physics are involved. Of the several existing methods of describing quantum fields subject to a Lorentz condition we have chosen the Gupta-Bleuler formalism, because they shift the difficulties that occur to the state vectors, with the results that the appearance of the equations between the observables remains unmolested.

From the hamiltonian one can derive the equations of motion of the particles as well as the fields; these equations are coupled and eliminating e.g. the material observables the eigenvalue equations for the fields are obtained, which determine the refractive indices of the medium.

1. The coupled equations

The total time-independent hamiltonian can be taken as:

$$H = H_{\text{particles}} + H_{\text{field}} + H_{\text{interaction}}$$
$$= H_o + H' \qquad (1)$$

where $$H_{\text{particles}} = \sum_i \frac{p_i^2}{2m_i} + \sum_{i<j} V_{ij} \qquad (1^a)$$

p_i the momentum of particle i (possibly in a field other than that with circular frequency ω - in which we shall primarily be interested - e.g. a constant magnetic field), m_i its mass, V_{ij} the static Coulomb potential between particles i and j. Further

$$H_{\text{field}} = \frac{1}{8\pi}\int d\underline{x}\Big\{\frac{1}{c^2}\Big(\frac{\partial A}{\partial t}\Big)^2 + (\text{curl }\underline{A})^2 + (\text{div }\underline{A})^2 + \frac{1}{c^2}\Big(\frac{\partial\varphi}{\partial t}\Big)^2 + (\text{grad }\varphi)^2\Big\} \qquad (1^b)$$

$$H' = -\frac{1}{c}\int d\underline{x}\ \underline{j}(\underline{x}).\underline{A}(\underline{x}) + \int d\underline{x}\ \rho(\underline{x})\ \varphi(\underline{x}) \qquad (1^c)$$

Expanding the potentials in plane waves we have:

$$A_\alpha(\underline{x}) = (\tfrac{1}{2}\hbar c)^{\frac{1}{2}}\int d\underline{y}\ u_\alpha\Big[a_\alpha^-(\underline{y})\ \exp\{-2\pi i\underline{y}.\underline{x}\} + \text{c.c.}\Big] \qquad (2^a)$$

$$\varphi(\underline{x}) = (\tfrac{1}{2}\hbar c)^{\frac{1}{2}}\int d\underline{y}\ u_o\Big[a_o^-(\underline{y})\ \exp\{-2\pi i\underline{y}.\underline{x}\} + \text{c.c.}\Big] \qquad (2^b)$$

with $u_\mu = u_\alpha , u_o$ four unit vectors satisfying

$$g_{\mu\nu} = 0 \qquad \mu \neq \nu$$

$$u_\mu u_\nu = g_\mu \qquad\qquad g_{oo} = 1$$

$$g_{\alpha\alpha} = -1$$

From now on we adopt the summation convention over repeated indices of tensor components; in addition we use the first letters of the Greek alphabet to denote space variables alone (α , β ... = 1,2,3) the ones in the middle for space-time variables (μ , ν .... = 0, 1, 2,3). Interpreting the coefficients $a^-_\mu(\underline{y})$, $a^+_\mu(\underline{y})$ as annihilation and creation operators, we have them satisfy the following commutation relations:

$$\left[a^-_\mu(\underline{y}),\ a^+_\nu(\underline{y}') \right] = -g_{\mu\nu}\,\delta(\underline{y}-\underline{y}') \tag{3}$$

all others zero.

Such an interpretation is possible if we postulate that all expectation values of field operators must be computed using the indefinite Gupta scalar product 1) defined by

$$(\psi,\ \chi)_{\text{Gupta}} = (\psi\ ,\eta\,\chi)$$

where η a linear hermitian operator satisfying

$$\eta^2 = 1$$

and having the following commutation relations with the potential operators

$$\left[A_\alpha , \eta \right] = 0 \qquad\qquad \left[\varphi , \eta \right]_+ = 0$$

With this definition of the scalar product the expectation value of the hamiltonian becomes positive definite as of course it should be. It is impossible to impose the Lorentz consition on the operators themselves; instead one settles for a weaker relation in demanding that the expectation values satisfy it:

$$\langle \Psi | \eta (\mathrm{div}\ \underline{A} + \frac{1}{c}\frac{\partial\varphi}{\partial t}) | \Psi \rangle = 0 \tag{4}$$

for all t.

Together with (1) this relation makes it possible to derive the Maxwell-Lorentz equations as relations between expectation values [1]. Solutions of these equations are:

$$A_{\alpha}(\underline{x}) = \frac{1}{c}\int d\underline{x}'\; j_{\alpha}(\underline{x}')\; G(\underline{x},\underline{x}') \qquad (5^{a})$$

$$\varphi(\underline{x}) = \int d\underline{x}'\; \rho(\underline{x}')\; G(\underline{x},\underline{x}') \qquad (5^{b})$$

where, if we restrict ourselves to a field with circular frequency :

$$G(\underline{x},\underline{x}') = \frac{e^{2\pi ik\,|\underline{x}-\underline{x}'|}}{|\underline{x}-\underline{x}'|}\;,\quad 2\pi k = \frac{\omega}{c}$$

It is perhaps good to note that only in the special case of a free field do we have $y = k$. The actual relation between y and k is just what we are going to determine.

The charge and current density in (5) can also be found from an equation of motion e.g. in the Heisenberg picture:

$$\frac{d}{dt}\,\underline{j}(\underline{x}) = (i\hbar)^{-1}\Big[\,\underline{j}(\underline{x}),H\Big] \qquad (6)$$

with immediate formal solution

$$\underline{j}(\underline{x},t) = U^{+}(t)\;\underline{j}(\underline{x})\;U(t) \qquad (7)$$

where the evolution operator $U(t) = \exp -\frac{i}{\hbar}Ht$ and in the position representation:

$$\underline{j}(\underline{x}) = \sum_{i}\tfrac{1}{2}e_{i}\{\dot{\underline{x}}_{i}\,\delta(\underline{x}-\underline{x}_{i}) + c.c.\} \qquad (8)$$

assuming point charges. $\dot{\underline{x}}_i$ is the velocity operator of particle i satisfying

$$\dot{\underline{x}}_i = \frac{1}{i\hbar}\left[\underline{x}_i, H\right] \tag{9}$$

(7) gives us the total current density; in the next section we shall split off a part that is linear in the fields which we call the induced current density. The expectation value of this term will then be identified with the current density in (5). The consistency of (5) and (7) determines which $\underline{y}$ values can be admitted in the expansion of $\underline{A}$ and φ .

2. The induced current density

We have mentioned that j is to be considered as a source of radiation, so it must be a field operator. We now calculate this operator in terms of the creation and destruction operators by projecting the material subspace out. Say P_a is the projector on the eigenstate of $H_{\text{particles}}$ with eigenvalues E_a, Q_a its complement such that

$$P_a + Q_a = 1$$

We use as our basic set products of particles and field state vectors denoted by $|\Phi\rangle$ and $|\Xi\rangle$ respectively. For any state $|\Psi\rangle$ then

$$P_a\,|\Psi\rangle = P_a \Sigma\,|\Phi\rangle|\Xi\rangle = |a\rangle \Sigma\,|\Xi\rangle$$

where $|a\rangle$ an eigenstate of $H_{\text{particles}}$ with eigenvalue E_a. In the case of degeneracy this is to be replaced by the subspace spanned by such eigenstates.

At time t the current density for a state $|a\rangle$ is now given by:

$$\underline{j}(\underline{x},t) = P_a U^{+}(t)\ \underline{j}(\underline{x})\ U(t)\ P_a \tag{10}$$

We work this expression out using the algebraic method as given by Messiah[2)], using the representation for the evolution operator

$$U(t) = \frac{1}{2\pi i}\int_C dz \, \exp\left\{\frac{i}{\hbar} z t\right\} G(z) \qquad (11)$$

where $G(z) = (z - H)^{-1}$ and the contour C is taken around the real axis with all singularities of $G(z)$ on its left. Using this (10) becomes

$$\underline{j}(\underline{x},t) = (2\pi i)^{-2}\int_C dz \int_{C'} dz' \, \exp\left\{\frac{i}{\hbar}(z-z')t\right\} \underline{j}(\underline{x},z,z') \qquad (12)$$

with $\underline{j}(\underline{x},z,z') = P_a G(z)\underline{j}(\underline{x})G(z')P_a$. $\qquad (12^a)$

Now put

$$H = H_1 + H'' \qquad (13)$$

$$H_1 = P_a H P_a + Q_a H Q_a = H_o + Q_a H' Q_a$$

$$H'' = P_a H Q_a + Q_a H P_a = P_a H' Q_a + Q_a H' P_a$$

Usefull properties of these operators are

$$P_a H_1 = H_1 P_a = E_a P_a \qquad H_1, Q_a = 0 \qquad (14)$$

$$Q_a H'' = H'' P_a \qquad P_a H'' = H'' Q_a$$

Using the identity

$$(z - H)^{-1} = (z - H_1)^{-1} + (z - H_1)^{-1} H''(z - H) \qquad (15)$$

we find for $\underline{j}(\underline{x},z,z')$

$$\underline{j}(\underline{x},z,z') = P_a \frac{1}{z - H_1} \underline{j}(x) \frac{1}{z' - H_1} P_a +$$

$$+ 2 \, \mathrm{Re} \left\{ P_a \frac{1}{z - H_1} P_a \underline{j}(\underline{x}) \, Q_a \frac{1}{z' - H_1} Q_a H'' P_a \; x \right.$$

$$\left. x \; P_a \frac{1}{z' - H} P_a \right\} \qquad (16)$$

In evaluating this expression we have taken $P_a \underline{j}(\underline{x}) P_a$ to be zero as this term gives rise to higher-order contributions in H" only.

To find the diagonal part of G(z) we apply (15) once again:

$$P_a (z-H)^{-1} P_a = (z-H_1)^{-1} P_a + (z-H_1)^{-1} P_a H'' Q_a (z-H)^{-1} P_a$$

$$= (z-H_1)^{-1} P_a \left(1 + P_a H'' Q_a (z-H_1)^{-1} Q_a H'' P_a (z-H)^{-1} P_a\right)$$

Solving we have:

$$P_a (z-H)^{-1} = (z-H_1-W(z))^{-1} P_a \qquad (17)$$

where

$$W(z) = P_a H' Q_a (z-Q_a H Q_a)^{-1} Q_a H' P_a \qquad (17^a)$$

Assuming the interaction to be weak we shall retain only terms linear in H', which boils down to replacing H_1 by H_o. Recognising the fact that $\underline{j}(\underline{x})$ also contains terms with h', as follows from (9):

$$\begin{aligned} \dot{\underline{x}}_i &= (i\hbar)^{-1} \left[\underline{x}_i, H_o\right] + (i\hbar)^{-1} \left[\underline{x}_i, H'\right] \\ &= \dot{\underline{x}}_i^o + \dot{\underline{x}}_i' \end{aligned}$$

we obtain for the induced part of $\underline{j}(\underline{x}, z, z')$:

$$\underline{j}_{ind}(\underline{x}, z, z') = P_a \frac{1}{z-H_o} \underline{j}'(\underline{x}) \frac{1}{z-H_o} P_a +$$

$$+ 2 \operatorname{Re} \frac{1}{z-H_o} P_a \underline{j}^o(\underline{x}) Q_a \frac{1}{z'-H_o} Q_a H' P_a \frac{1}{z'-H_o-W(z')} P_a \qquad (18)$$

In order to keep the equations from overflowing the pages we write:

$$H' = (\tfrac{1}{2}\hbar c)^{\frac{1}{2}} \int d\underline{y} \left(a_\mu^-(\underline{y}) H_\mu^-(\underline{y}) + a_\mu^+(\underline{y}) H_\mu^+(\underline{y}) \right) \qquad (19)$$

where

$$H^{+}_{\mu}(\underline{y}) = -\frac{1}{c}\int d\underline{x}\ \tfrac{1}{2}\left[j^{o}_{\nu}(\underline{x}), u_{\nu}\, e^{\mp 2\pi i \underline{y}\cdot\underline{x}}\right]_{+}\delta_{\mu\nu} \qquad (19^{a})$$

owing to the fact that H' must be a hermitian operator. Replacing $\underline{j}(\underline{x})$ by $\underline{j}^{o}(\underline{x})$ here is consistent with the fact that we only take terms linear in H' into account.

Further the energy of a photon is $\hbar\omega$, since we assumed a monochromatic field; we then have the following property

$$(z-H_{o})^{-1}a^{-}_{\mu}(\underline{y}) = a^{-}_{\mu}(\underline{y})\ (z-H_{o}+\hbar\omega)^{-1} \qquad (20)$$

that we use to shift the creation and annihilation operators around in (18). Substituting (19) in (18) the term between brackets with H^{-} e.g. becomes

$$(\tfrac{1}{2}\hbar c)^{\frac{1}{2}}\int d\underline{y}\ a^{-}_{\mu}(\underline{y})\frac{1}{z-H_{o}+\hbar\omega}P_{a}\underline{j}^{o}(\underline{x})Q_{a}\frac{1}{z'-H_{o}+\hbar\omega}Q_{a}\ \mathrm{x} \qquad (21)$$

$$\mathrm{x}\ Q_{a}H^{-}_{\mu}(\underline{y})P_{a}\ \frac{1}{z'-H_{o}-W(z')}$$

When these are put into (12) we can evaluate the integrals by the method of residues. The induced current density is then found to be:

$$\underline{j}_{ind}(\underline{x},t) = \frac{1}{c}(\tfrac{1}{2}\hbar c)^{\frac{1}{2}}\frac{2}{\hbar}\mathrm{Re}\left\{\int d\underline{y}\ a^{-}_{\mu}(\underline{y})\sum_{b=a}P_{a}\underline{j}^{o}(\underline{x})P_{b}H^{-}_{\mu}(\underline{y})P_{a}\right.$$

$$\left.\mathrm{x}\ \left(\frac{\sigma^{-}}{1}-\frac{e^{-\varsigma^{-}t}}{\varsigma^{-}}\right)\exp\left\{-i\omega t-\frac{i}{\hbar}W^{+}(E_{a})t\right\}+(\text{ibid}\ +\text{signs})\right\}$$

$$-\frac{1}{c}(\tfrac{1}{2}\hbar c)^{\frac{1}{2}}\int d\underline{y}\left\{a^{-}_{\mu}(\underline{y})\ P_{a}\ \mathrm{x}\right.$$

$$\left.\mathrm{x}\ \sum_{i}\frac{e_{i}}{2i\hbar}\left[\underline{x}_{i}\ (\underline{x}-\underline{x}_{i})+\text{c.c}, H^{-}_{\mu}(\underline{y})\right]P_{a}\exp\{-i\omega t\}-\text{c.c.}\right\} \qquad (22)$$

with $\sigma^{\pm} = \omega_{ba} \pm \omega - \frac{1}{\hbar}W^{+}(E_{a})$,

$\varsigma^{\pm} = \omega_{ba} \pm \omega - \frac{1}{\hbar}W^{+}(E_{b} \pm \hbar\omega)$ and

where $Q_a = \sum_{b=a} P_b$ has been used and $\omega_{ba} = \frac{1}{\hbar}(E_b - E_a)$.
$W^+(x)$ stands for $\lim W(x + i\eta)$ as a reminder that we approach the real axis from the positive side. Taking this limit we have :

$$\begin{aligned}
\lim_{\eta\downarrow 0} W(x + i\eta) &= P_a H'Q_a \frac{\mathcal{P}}{x-H_o} Q_a H'P_a + \\
&\quad - i\pi P_a H'Q_a \,\delta(x-H_o) Q_a H'P_a \qquad (23) \\
&= \hbar\Delta(x) - \tfrac{1}{2} i\hbar\Gamma(x)
\end{aligned}$$

$\mathcal{P}$ stands for principal value.
$\Delta(x)$ corresponds to a frequency shift and can therefore be taken in the eigenvalue of H_o ; we will neglect it from now on. $\Gamma(x)$ describes the decay of the eigenstates of H_o. These are no longer stationary due to the presence of the electromagnetic field.
It is seen that due to the presence of the factor

$$\exp -\frac{i}{\hbar}Wt = \exp\left\{-i\Delta t - \tfrac{1}{2}\Gamma t\right\}$$

the medium provides a sink for fotons. In order to obtain steady state conditions we therefore need an outside source to compensate for this loss. We assume such a source to be present from now on, by neglecting this factor.
Simplification of the ugly looking expression (22) involves a lot of tedious arithmetic, which we therefore omit, mentioning pointwise a few of the arguments used :

1. For large t the frequency dependent terms between brackets of the form

$$\varsigma^{-1} \exp -i\varsigma t$$

will make negligible contributions only. This follows from the fact that in actual experiments a monochromatic lightwave will have a certain linewidth implying that we have to evaluate expressions such as

$$\int d\varsigma \; g(\varsigma)\, \varsigma^{-1} \exp -i\varsigma t$$

Owing to the rapid variation of the exponential this integral vanishes. Since compared to line widths of absorption in dense media $g(\quad\varsigma\quad)$ peaks sharply around some definite frequency we approximate it by a δ-distribution for the other terms.

2. Let us define a point $\underline{x}'$ such that the expectation value of $P_a\,\underline{y}.(\underline{x}_i - \underline{x}')P_b$ is small compared to unity. Whether such points can be found depends on the medium and we shall not concern ourselves with it here. Let us just note that this is obviously the case when the wave functions, with respect to which the expectation values are taken, happen to be different from zero in a small region around $\underline{x}'$ only. Using the formal property of the δ-function

$$\delta(x) = \exp ikx\ \delta(x)$$

We rewrite terms such as $P_a j^o_\alpha(\underline{x})P_b H^-_\mu(\underline{y})P_a$ as follows:

$$P_a j^o_\alpha(\underline{x})P_b H^-_\mu(\underline{y})P_a =$$

$$P_a\Big[\sum_i \tfrac{1}{2}e_i\big\{\dot{x}_{i\alpha}\,\delta(\underline{x}-\underline{x}_i) + \text{c.c}\big\}P_b \times$$

$$\times P_b \sum_i \tfrac{1}{2}e_i\big\{\dot{x}_{i\nu}\ u_\nu \exp\big(-2\pi i\underline{y}.\underline{x}_i\big) + \exp\big(-2\pi i\underline{y}.\underline{x}_i\big)\dot{x}_{i\nu}\big\}\delta_{\mu\nu}\Big]P_a$$

$$= \exp\big(-2\pi i\underline{y}.\underline{x}\big)P_a\Big[\sum_i \tfrac{1}{2}e_i\big\{\dot{x}_{i\alpha}\exp 2\pi i\underline{y}.(\underline{x}_i-\underline{x}')\ \delta(\underline{x}-\underline{x}') + \text{c.c.}\big\} \times \tag{24}$$

$$\times P_b \sum_i \tfrac{1}{2}e_i\big\{\dot{x}_{i\nu}\,u_\nu \exp -2\pi i\underline{y}.(\underline{x}_i-\underline{x}') +$$

$$\exp -2\pi i\underline{y}.(\underline{x}_i-\underline{x}')\ \dot{x}_{i\nu}\,u_\nu\big\}\ \delta_{\mu\nu}\Big]P_a$$

$$= \exp\big(-\ 2\pi i\underline{y}.\underline{x}\ \big)J^-_{\alpha\mu}(\underline{x},\underline{x}',\underline{y})$$

Expanding the exponentials we have

$$J_{\alpha\mu}(\underline{x},\underline{x}',\underline{y}) = J_{\alpha\mu}(\underline{x}) - 2\pi i y_{\varepsilon} R_{\alpha\mu\varepsilon}(\underline{x},\underline{x}') + - 4\pi^2 y_{\varepsilon} y_{\eta} S_{\alpha\mu\varepsilon\eta}(\underline{x},\underline{x}') \qquad (25)$$

3. Before expanding similarly

$$P_a \sum_i \frac{e_i}{2i\hbar} \left[x_{i\alpha} \delta(\underline{x} - \underline{x}_i) + \text{c.c}, H^-_{\mu}(\underline{y}) \right] P_a$$

we simplify this expression with the help of the commutation relations for $\dot{\underline{x}}$ and $\underline{x}$

$$\left[x_{i\alpha}, x_{i\beta} \right] = \frac{i\hbar}{m_j} \delta_{ij} \delta_{\alpha\beta}$$

We find

$$P_a \sum_i \frac{e_i}{2i\hbar} \left[x_{i\alpha} \delta(\underline{x} - \underline{x}_i) + \text{c.c}, H^-_{\mu}(\underline{y}) \right] P_a =$$

$$P_a \sum_i \frac{e_i^2}{m_i} \delta(\underline{x} - \underline{x}_i) \exp\left(- 2\pi i \underline{y}.\underline{x}\right) u_{\alpha} P_a =$$

$$u_{\alpha} \exp\left(- 2\pi i \underline{y}.\underline{x}\right) P_a \sum_i \frac{e_i^2}{m_i} \delta(\underline{x} - \underline{x}_i) P_a$$

From $J_{\alpha\mu}(\underline{x})$ we can separate just such a term with opposite sign because, applying (9) once we have amongst others

$$\frac{1}{i\hbar} \left\{ P_a \sum_i e_i x_{i\alpha} \delta(\underline{x} - \underline{x}_i) Q_a \sum_i e_i \dot{x}_{i\beta} P_a + - P_a \sum_i e_i \dot{x}_{i\beta} Q_a \sum_i e_i x_{i\alpha} \delta(\underline{x} - \underline{x}_i) P_a \right\} =$$

$$\sum_i \frac{e_i}{m_i} P_a \delta(\underline{x} - \underline{x}_i) P_a$$

Replacing Q_a by unity is permitted because $P_a \dot{x}_{i\alpha} P_a = 0$

4. $R_{\alpha\mu\varepsilon}(\underline{x},\underline{x}')$ reads explicitly, as follows from its definition

$$R_{\alpha\mu\varepsilon}(\underline{x},\underline{x}') = P_a \sum_i \tfrac{1}{2} e_i \left[\dot{x}_{i\alpha} \delta(\underline{x} - \underline{x}_i), (x'_{\varepsilon} - x_{i\varepsilon}) \right]_+ P_b \times$$

$$\times P_b \sum_i e_i \dot{x}_{i\mu} P_a - P_a \sum_i \tfrac{1}{2} e_i \dot{x}_{i\alpha} \delta(\underline{x} - \underline{x}_i) P_{b\ i} \times$$

$$\times P_b \sum_i \tfrac{1}{2} e_i \left[\dot{x}_{i\mu}, (x'_{\varepsilon} - x_{i\varepsilon}) \right]_+ P_a$$

It is convenient to split the anti-commutator into its symmetric and anti-symmetric parts

$$\text{a.c.} = (i\hbar)^{-1}\left[x_{i\alpha}x_{i\beta}\,\delta(\underline{x}-\underline{x}_i),H_o\right] + \chi_{\alpha\beta\gamma}\chi_{\gamma\vartheta\eta}x_{i\eta}\dot{x}_{i\vartheta}(\underline{x}-\underline{x}_i) \tag{26}$$

where $\chi_{\alpha\beta\gamma}$ the completely anti-summetric tensor satisfying

$$\chi_{\alpha\beta\gamma}\begin{cases} = 0 & \text{two indices equal} \\ = +1 & \text{even permutations of (123)} \\ = -1 & \text{odd permutations of (123)} \end{cases}$$

For the case of $\mu = 0$ corresponding to terms involving the scalar potential φ we have to include the second order term $S_{\alpha o\beta\gamma}$ since the second spatial derivative of this potential is connected with the first derivative of the electric field. When we work this term out we can cast it into the same form as comes out of $R_{\alpha\beta\gamma}$ using the fact that the curl of the gradient of any function vanishes:

$$\text{Curl}_\gamma\ \text{grad}\,\varphi(\underline{x}) = \chi_{\alpha\beta\gamma}\frac{\partial^2}{\partial x_\alpha \partial x_\beta}\varphi(\underline{x}) = 0$$

Because of this we can add terms such as

$$\chi_{\alpha\beta\gamma}\chi_{\gamma\vartheta\eta}x_{i\eta}\dot{x}_{i\vartheta}\frac{\partial^2}{\partial x_\alpha \partial x_\beta}\varphi(\underline{x})$$

wherever necessary. Further $J_{\alpha o}$ vanishes since it contains:

$$Q_a \sum_i e_i \dot{x}_{io} P_a = ic \sum_i e_i Q_a P_a = 0$$

Note that we do not need the electric neutrality of the system.

Doing the Fourier integration over $\underline{y}$ and taking expectation values we obtain finally

$$j^-_\alpha(\underline{x},t) = \frac{\omega}{c}\left\{p^o_{\alpha\beta}(\underline{x}) + p^1_{\alpha\beta\gamma}(\underline{x})\frac{\partial}{\partial x_\gamma}\right\}A_\beta(\underline{x})\exp{-i\omega t} +$$

$$+ i\omega\left\{p^o_{\alpha\beta}(\underline{x})\frac{\partial}{\partial x_\beta} + p^1_{\alpha\beta\gamma}(\underline{x})\frac{\partial^2}{\partial x_\beta \partial x_\gamma}\right\}\varphi(\underline{x})\exp{-i\omega t} \tag{27}$$

where, if we assume $\frac{\Gamma}{\omega_{ba}}$ to be small and realise that Γ is finite only in the neighbourhood of a resonance frequency i.e. $\omega_{ba} \approx \omega$ the p's take the following simple form.

$$p^{0}_{\alpha}(\underline{x}) = \frac{2}{\hbar} \sum_{b} \frac{\omega_{ba}}{\omega_{ba}^{2} - \omega^{2} + i\omega\Gamma} \left\{ \mathrm{Re}\; p_{\alpha}(\underline{x}) p_{\beta} + i \frac{\omega_{ba}}{\omega} \mathrm{Im}\; p_{\alpha}(\underline{x}) p_{\beta} \right\}$$

$$\text{where} \quad p_{\alpha}(\underline{x}) = \langle a | \sum_{i} e_{i}\, x_{i\alpha}\, \delta(\underline{x} - \underline{x}_{i}) | b \rangle \qquad (28)$$

$$p_{\alpha}(\underline{x}) = \langle a | \sum_{i} e_{i}\, x_{i\alpha} | b \rangle$$

$$p^{1}_{\alpha\beta\gamma}(\underline{x}) = \frac{2}{\hbar} \sum_{b} \frac{\omega_{ba}}{\omega_{ba}^{2} - \omega^{2} + i\omega\Gamma} \left\{ \mathrm{Re}\left(p_{\alpha}(\underline{x}) q_{\beta\gamma} - q_{\alpha\gamma}(\underline{x}) p_{\beta} \right) + \right.$$

$$\left. + i \frac{\omega_{ba}}{\omega} \mathrm{Im}\left(p_{\alpha}(\underline{x}) q_{\beta\gamma} - q_{\mu\gamma}(\underline{x}) p_{\beta} \right) \right\} +$$

$$+ \frac{1}{\omega_{ba}^{2} - \omega^{2} + i\omega\Gamma} \left\{ \mathrm{Im}\left(p_{\alpha}(\underline{x}) m_{\varepsilon}\, \chi_{\varepsilon\beta\gamma} + m_{\varepsilon}(\underline{x})\, \chi_{\varepsilon\alpha\gamma} p_{\beta} \right) + \right.$$

$$\left. + i \frac{\omega_{ba}{}^{-}}{\omega} \mathrm{Re}\left(p_{\alpha}(\underline{x}) m_{\varepsilon}\, \chi_{\varepsilon\beta\gamma} + m_{\varepsilon}(\underline{x})\, \chi_{\varepsilon\alpha\gamma} p_{\beta} \right) \right\}$$

$$\text{where} \quad q_{\alpha\gamma}(\underline{x}) = \langle a | \sum_{i} e_{i}\, x_{i\alpha}\, x_{i\gamma}\, \delta(\underline{x} - \underline{x}_{i}) | b \rangle \qquad (29)$$

$$m_{\varepsilon}(\underline{x}) = \langle a | \sum_{i} \tfrac{1}{2} e_{i}\, x_{i\eta}\, \dot{x}_{i\vartheta}\, \chi_{\varepsilon\vartheta\eta}\, \delta(\underline{x} - \underline{x}_{i}) | b \rangle$$

The definition of $q_{\alpha\gamma}$ and m_{ε} is similar to that of p_{α} in (28). This notation is only correct if we take note of the order of the quantities in the equations. Each symbol would however be hidden in its indices were we to include a and b explicitly. Thus

$$p_{\alpha}(\underline{x}) p_{\beta} \neq p_{\beta} p_{\alpha}(\underline{x})$$

in fact we have instead

$$p_{\alpha}(\underline{x}) p_{\beta} = \left(p_{\beta} p_{\alpha}(\underline{x}) \right)^{*}$$

Putting $p^{1}_{\alpha\beta\gamma}(\underline{x}) = \frac{2}{\hbar} \sum_b \frac{1}{\omega^2_{ba} - \omega^2 + i\omega\Gamma} R^{ab}_{\alpha\beta\gamma}$.

we can readily show the important property

$$\sum_b R^{ab}_{\alpha\beta\gamma} = 0 \qquad (30)$$

Since using (26) we have

$$\sum_b \omega_{ba} \operatorname{Re}\left\{p_\alpha(\underline{x})q_{\beta\gamma} - q_{\alpha\gamma}(\underline{x})p_\beta\right\} + \operatorname{Im}\left\{p_\alpha(\underline{x})m_\varepsilon \chi_{\varepsilon\beta\gamma} + m_\varepsilon(\underline{x})\chi_{\varepsilon\alpha\gamma}p_\beta\right\}$$

$$= \sum_b \operatorname{Im}\langle a| \sum_i \tfrac{1}{2}e_i x_{i\alpha}\,\delta(\underline{x}-\underline{x}_i)|b\rangle\langle b| \sum_i \tfrac{1}{2}e_i\left[\dot{x}_{i\beta}, x_{i\gamma}\right]_+|a\rangle +$$

$$+ \operatorname{Im}\langle a| \sum_i \tfrac{1}{2}e_i\left[\dot{x}_{i\alpha}, x_{i\gamma}\right]_+ \delta(\underline{x}-\underline{x}_i)|b\rangle\langle b|\sum_i \tfrac{1}{2}e_i x_{i\beta}|a\rangle$$

$$= \operatorname{Im}\langle a|\,\Omega\,|a\rangle = 0$$

because Ω is a hermitian operator. A similar argument applies to the remaining term, proving (30). From the second line of this derivation we also obtain immediately that

$$R^{ab}_{\alpha\beta\gamma} = -R^{ab}_{\beta\alpha\gamma}$$

i.e. we can always write

$$p^{1}_{\alpha\beta\gamma}(\underline{x}) = \chi_{\alpha\beta\varepsilon}\, g_{\varepsilon\gamma}(\underline{x})$$

Introducing the electric field strength given by

$$\underline{E} = -\frac{1}{c}\frac{\partial A}{\partial t} - \operatorname{grad}\varphi$$

we can combine and obtain finally:

$$j_\alpha(\underline{x},t) = -i\omega\left\{p^{o}_{\alpha\beta}(\underline{x}) + p^{1}_{\alpha\beta\gamma}(\underline{x})\frac{\partial}{\partial x_\gamma}\right\}E_\beta(\underline{x})\exp{-i\omega t} \qquad (31)$$

We note that the differentiation $\frac{\partial}{\partial x_\gamma}$ operates on $\underline{E}(\underline{x})$ only. This is not problematic in the equation given here.

We shall however in the next section multiply $\underline{j}(\underline{x})$ by another function of $\underline{x}$ and this notation might then be confusing.

3. The electric field

The electric field strength can now very easily be computed from the current and charge density with the help of (5). The latter density is known because $\underline{j}$ and are connected by a continuity equation, a fact that is conveniently expressed by a polarization density $\underline{p}$ satisfying

$$\dot{\underline{p}} = \underline{j} \qquad \text{and} \qquad = -\text{div}\,\underline{p}$$

Substituting in (5) we have, omitting the time factor

$$A_\alpha(\underline{x}) = \frac{i\omega}{c}\int d\underline{x}'\ p_\alpha(\underline{x}')G(\underline{x},\underline{x}')$$

$$\varphi(\underline{x}) = -\int d\underline{x}'\ \frac{\partial}{\partial x'_\alpha}\,p_\alpha(\underline{x}')G(\underline{x},\underline{x}')$$

$$= \int d\underline{x}'\ p_\alpha(\underline{x}')\,\frac{\partial}{\partial x'_\alpha}\,G(\underline{x},\underline{x}')$$

$$= -\int d\underline{x}'\ p_\alpha(\underline{x}')\,\frac{\partial}{\partial x_\alpha}\,G(\underline{x},\underline{x}')$$

Combining we have for $\underline{E}$:

$$E_\alpha(\underline{x}) = \int d\underline{x}'\left\{\frac{\omega^2}{c^2}\delta_{\alpha\beta} + \frac{\partial^2}{\partial x_\alpha \partial x_\beta}\,p_\beta\right\}(\underline{x}')G(\underline{x},\underline{x}') \qquad (32)$$

In view of the extinction theorem we do not have to take solutions of the homogeneous equations into account. This theorem also implies that the integration may be taken over all space. The integral in (32) is improper if for $\underline{x}' = \underline{x}$ $\quad p_\alpha(\underline{x}')$ is different from zero because of the singularity of $G(\underline{x}, \underline{x}')$ at that point. This singularity can be removed if we realise that the field acting on a charge does not include the field of the charge itself. This exciting field that occurs in (31) and which we denote by $\underline{E}^e$ can be obtained by substracting from (32) the field at $\underline{x}$ due to the currents and charges at $\underline{x}$, written as $\underline{E}^s$ i.e.:

$$E^e_\alpha(\underline{x}) = \lim_{\underline{x}'\to\underline{x}} \left\{E_\alpha(\underline{x}') - E^s_\alpha(\underline{x}')\right\}$$

Similarly we have for the derivative of the exciting field:

$$E^e_{\alpha\varepsilon}(\underline{x}) = \lim_{\underline{x}'\to\underline{x}} \left\{\frac{\partial}{\partial x'_\varepsilon} E_\alpha(\underline{x}') - \frac{\partial}{\partial x'_\varepsilon} E^s_\alpha(\underline{x}')\right\}$$

We use the notation $E^e_\alpha(\underline{x})$ in favour of the misleading $\frac{\partial}{\partial x_\varepsilon} E^e_\alpha$, which we reserve for the expression

$$\frac{\partial}{\partial x_\varepsilon} E^e_\alpha(\underline{x}) = \frac{\partial}{\partial x_\varepsilon} \lim_{\underline{x}'\to\underline{x}} \left\{E_\alpha(\underline{x}') - E^s_\alpha(\underline{x}')\right\}$$

which, because of the singularity of $\underline{E}(x)$ at $\underline{x}$ is not necessarily equal to $E^e_{\alpha\varepsilon}$.

These definitions imply that $\underline{E}^e$ is given by (32) if we exclude a volume v around $\underline{x}$ from the integration and take the limit of vanishing $v(\underline{x})$. In general the charge and current distribution at $\underline{x}$ need not be symmetric and we therefore have to choose v such that $\underline{E}^s$ has the same value everywhere on its surface $s(\underline{x})$.

Substituting $\underline{p}(\underline{x})$ from (31) we have:

$$E^e_\alpha(\underline{x}) = \int_v d\underline{x}'\, T_{\alpha\beta}(\underline{x})\, p^0_{\beta\gamma}(\underline{x}') E^e_\gamma(\underline{x}') + \\ + p^1_{\beta\gamma\varepsilon}(\underline{x}') E^e_{\gamma\varepsilon}(\underline{x}')\, G(\underline{x},\underline{x}')$$

where

$$T_\alpha(\underline{x}) = \frac{\omega^2}{c^2}\delta_{\alpha\beta} + \frac{\partial^2}{\partial x_\alpha \partial x_\beta}$$

and also

$$E^e_{\alpha\varepsilon}(\underline{x}) = \int_v d\underline{x}'\, T_{\alpha\beta}(\underline{x}) p^0_{\beta\gamma}(\underline{x}') E^e_\gamma(\underline{x}') \frac{\partial}{\partial x_\varepsilon} G(\underline{x},\underline{x}')$$

This result is obtained because it is sufficient to go only to zeroth order since $E^e_{\alpha\varepsilon}$ will appear only in first order terms. Furthermore we have used that for $\underline{E}$ the order of integration and differentiation is immaterial.

To find the connection between $\underline{E}$ and $\underline{E}^e$ we use the fact that

$$\frac{\partial}{\partial x_\alpha}\int_v d\underline{x}'\, p(\underline{x}')\, G(\underline{x},\underline{x}') = \int_v d\underline{x}'\, p(\underline{x}')\, \frac{\partial}{\partial x_\alpha} G(\underline{x},\underline{x}') + - \int_s d\underline{x}'\, p(\underline{x}')\, G(\underline{x},x')\, n_\alpha$$

where n_α the normal to the surface $s(\underline{x})$, taken positive in the outward direction. Applying this relation a number of times, substituting higher derivatives of $G(\underline{x},\underline{x}')$ one can derive:

$$E^e_\alpha(\underline{x}) = T_{\alpha\beta}(\underline{x})\int_v d\underline{x}' \left\{ p^o_{\beta\gamma}(\underline{x}')\, E^e_\gamma(\underline{x}') + p^1_{\beta\gamma\varepsilon}(\underline{x}')E^e_\varepsilon(\underline{x}')\right\} \times G(\underline{x},\underline{x}') + \int_s d\underline{x}' \left\{ p^o_{\beta\gamma}(\underline{x}')E^e_\gamma(\underline{x}') + p^1_{\beta\gamma\varepsilon}(\underline{x}')E^e_{\gamma\varepsilon}(\underline{x}')\right\} \frac{\partial}{\partial x_\beta} G(\underline{x},\underline{x}')\, n_\alpha \qquad (33^a)$$

and

$$E^e_{\alpha\varepsilon}(\underline{x}) = \frac{\partial}{\partial x_\varepsilon} T_{\alpha\beta}(\underline{x})\int_v d\underline{x}'\, p^o_{\beta\gamma}(\underline{x}')E^e_\gamma(\underline{x}')\, G(\underline{x},\underline{x}') + \frac{\partial}{\partial x_\varepsilon}\int_s d\underline{x}'\, p^0_{\beta\gamma}(\underline{x}')E^e_\gamma(\underline{x}')\, \frac{\partial}{\partial x_\beta} G(\underline{x},\underline{x}')\, n_\alpha + \int_s d\underline{x}'\, p^o_{\beta\gamma}(\underline{x}')E^e_\gamma(\underline{x}')\, \frac{\partial^2}{\partial x_\alpha \partial x_\beta} G(\underline{x},\underline{x}')\, n_\varepsilon \qquad (33^b)$$

The first integral that appears in both expressions is identical to the one that occurs in (32) except for the exclusion of the valume $v(\underline{x})$. If we calculate the macroscopic value of $\underline{E}$ the singularities vanish on averiging and we then have therefore that the average values of these integrals are equal. Let us transform this integral with the help of a representation of $G(\underline{x},\underline{x}')$, due to Ewald$^{3)}$:

$$G(\underline{x},\underline{x}') = 2\pi^{-\frac{1}{2}}\int_0^\infty d\rho\, \exp\left\{- |\underline{x}-\underline{x}'|^2 \rho^2 + \pi^2 k^2 \rho^{-2}\right\}$$

Substituting at the same time the Fourier transform of $\underline{p}$, we get: $I = \int d\underline{x}' \int d\underline{y} \int_0^\infty d\rho \; 2\pi^{-\frac{1}{2}} \; \underline{p}(\underline{y}) \; x$

$$\exp\left(-2\pi i \underline{y}.\underline{x}' - |\underline{x}-\underline{x}'|^2 \rho^2 + \pi^2 k^2 \rho^{-2}\right)$$

$$= \int d\underline{y} \; \underline{p}(\underline{y}) \exp -2\pi i \underline{y}.\underline{x} \int_0^\infty d\rho \int d\underline{x}' \; 2\pi^{-\frac{1}{2}} \; x$$

$$\exp\left(2\pi i \underline{y}.\left(\underline{x} - .\underline{x}'\right) - |\underline{x}-\underline{x}'|^2 \rho^2 + \pi^2 k^2 \rho^{-2}\right)$$

$$= 2\pi \int d\underline{y} \int_0^\infty d\rho \; \rho^{-3} \; \underline{p}(\underline{y}) \exp\left(-2\pi i \underline{y}.\underline{x} - (\pi^2 y^2 - \pi^2 k^2)\rho^{-2}\right)$$

$$= \int d\underline{y} \; \underline{p}(\underline{y}) \frac{\pi}{\pi^2 y^2 - \pi^2 k^2} \exp -2\pi i \underline{y}.\underline{x}$$

Suppose now that the macroscopic behaviour of $\underline{p}(\underline{x})$ can be represented by a single plane wave. Operating with $\underline{T}(\underline{x})$ on $I(\underline{x})$ we find in that case:

$$T_{\alpha\beta}(\underline{x}) I(\underline{x}) = \left(\frac{\omega^2}{c^2}\delta_{\alpha\beta} + \frac{\partial^2}{\partial x_\alpha \partial x_\beta}\right) \frac{\pi}{\pi^2 y^2 - \pi^2 k^2} \, p_\beta \; \exp -2\pi i \underline{y}.\underline{x}$$

$$= \frac{4\pi}{n^2 - 1}\left(\delta_{\alpha\beta} - n^2 \frac{y_\alpha y_\beta}{y^2}\right) p_\beta(\underline{x}) \qquad (34)$$

where $n = \frac{y}{k}$. This is the expression for a plane electromagnetic wave propagating through a medium with refractive index n.

The remaining integrals in $(33^{a,b})$ are obviously determined by local conditions only: the inner fields. Their evaluation hinges on the knowledge of $s(\underline{x})$; sin since for general $s(\underline{x})$ the equations become quite ugly we shall shorten the arithmetic by choosing $v(\underline{x})$ to be a sphere i.e. the medium is isotrpic. In the next chapter we shall treat the only a little more complicated case of a uniaxial crystal and derive its rotatory power. For an isotropic medium we have

$$\overset{o}{p}_{\alpha\beta} = \overset{o}{p}\,\delta_{\alpha\beta}$$

$$\overset{1}{p}_{\alpha\beta\gamma} = \overset{1}{p}\,\chi_{\alpha\beta\gamma}$$

Expanding around $\underline{x}$ one finds for the inner fields 5):

$$\int_s d\underline{x}'\ p_\beta(\underline{x}')\ \frac{\partial}{\partial x_\beta} G(\underline{x},\underline{x}')\ n_\alpha = \frac{4\pi}{3}\delta_{\alpha\beta}\, p_\beta(\underline{x})\ .$$

$$\int_s d\underline{x}'\ p_\beta(\underline{x}')\ \frac{\partial^2}{\partial x_\alpha \partial x_\beta} G(\underline{x},\underline{x}')\ n = -\frac{4\pi}{3}\delta_{\alpha\varepsilon}\frac{\partial}{\partial x_\varepsilon} p_\alpha(\underline{x}) + $$

$$+ \frac{4\pi}{15}(\delta_{\alpha\beta}\delta_{\delta\varepsilon} + \text{cycl.})\ \frac{\partial}{\partial x_\delta} p_\delta(\underline{x})$$

Substituting into (33) we obtain:

$$E^e_\alpha(\underline{x}) = E_\alpha(\underline{x}) + \frac{4\pi}{3} p^o E^e_\alpha(\underline{x}) + \frac{4\pi}{3} p^1 \chi_{\alpha\beta\varepsilon}\, E^e_{\beta\varepsilon}(\underline{x}) \qquad (35^a)$$

$$E^e_{\alpha\varepsilon}(\underline{x}) = \frac{\partial}{\partial x_\varepsilon} E_\alpha(\underline{x}) + \frac{4\pi}{15}(\delta_{\alpha\beta}\delta_{\delta\varepsilon} + \text{cycl.})\ \frac{\partial}{\partial x_\delta} p^o E^e_\beta(\underline{x}) \qquad (35^b)$$

Introducing the divergence free dielectric displacement $\underline{D}$ defined by:

$$\underline{D} = \underline{E} + 4\pi\underline{p}$$

we have

$$D_\alpha = E_\alpha + 4\pi p^o E^e_\alpha + 4\ p^1 \chi_{\alpha\beta\varepsilon}\, E^e_{\beta\varepsilon}$$

which becomes with the help of (35):

$$D_\alpha = \varepsilon\, E_\alpha + 4\pi p^1 \frac{\varepsilon+2}{3} \chi_{\alpha\beta\gamma} \frac{\partial}{\partial x_\gamma} E_\beta$$

where $\varepsilon \equiv 1 + 4\pi p^o (1 - \frac{4\pi}{3} p^o)^{-1}$

Together with (34) this well-known expression describes the optical behaviour of an isotropic system.

Litt:

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Chapter II

Introduction

In this chapter we discuss some more specialised systems. First we take a medium composed of small identical molecules, neglect their interaction at first but use the same line of reasoning in calculating the exciting field. This model has been used by Terwiel and Maaskant [1)] who have shown that the main overall behaviour can be described by a simple plane wave. Next we take the case of an ideal crystal, the results of which we propose to apply to a specific compound. Finally we give the explicit formulae for wave propagation in a crystal with tetragonal symmetry.

1. System of small identical molecules

Say we have a medium composed of N small identical molecules and let us divide the particle hamiltonian into sums of molecular hamiltonians and interaction potentials between these molecules.

$$H_{\text{particles}} = \sum_{\sigma} H_{\sigma} + \sum_{\sigma > \rho} V_{\rho\sigma} \tag{1}$$

where
$$H_{\sigma} = \sum_{k} \frac{p_{k\sigma}^{2}}{2\,m_{k}} + \sum_{k>\ell} V_{\ell\sigma,k\sigma}$$
$$V_{\rho\sigma} = \sum_{k\sigma,\ell\rho} V_{k\sigma,\ell\rho}$$

A similar procedure is adopted for the other operators

$$\sum_{i} e_{i}\, t_{i} = \sum_{k\sigma} e_{k}\, t_{k\sigma} \tag{2}$$

where t_k a one particle operator.

We now approximate the wave function for the whole system by a product of the eigenfunctions of H_{σ}

$$(H_{\sigma} - E_{b})\,\psi_{b\sigma} = 0$$

For the ground state we have

$$\Psi_a = \prod_\sigma \psi_{a\sigma}$$

for the excited, using only singly excited products :

$$\Psi_b = \psi_{b\sigma} \prod_{\rho\neq\sigma} \psi_{a\rho}$$

This restriction is not really necessary because of the occurrence of the δ-distribution in $\underline{j}(\underline{x})$ from which it follows that if the molecules do not penetrate one another only one of them can contribute to $\underline{j}(\underline{x})$. That molecules do not penetrate is expressed by the orthonormality condition we impose on the wave functions :

$$\int d\tau \; \psi^*_{a\sigma} \psi_{b\rho} = \delta_{ab} \, \delta_{\rho\sigma}$$

Substituting in an expression such as $p_\alpha(\underline{x})p_\beta$ we have :

$$p_\alpha(\underline{x})p_\beta = \int d\tau \; \psi^*_{a\sigma} \sum_k e_k x_{k\sigma\alpha} \delta(\underline{x}-\underline{x}_{k\sigma}) \psi_{b\sigma} \quad \times$$

$$\times \int d\tau \; \psi^*_{b\sigma} \sum_k e_{k\sigma\beta} \psi_{a\sigma}$$

$$= p'_\alpha(\underline{x})p'_\beta$$

where σ denotes the molecule occupying that region of space that contains $\underline{x}$. Since we are dealing with small molecules this region is but a few angstroms in any direction and choosing $\underline{x}'$, assumed to exist in the first chapter, to be the position of the centre of the molecule we can surely expand obtaining :

$$\omega_{ba} p'_\alpha(\underline{x})p'_\beta = \omega_{ba} p'_\alpha p'_\beta \delta(\underline{x}-\underline{x}') + \omega_{ba} q'_{\alpha\gamma} p'_\beta \frac{\partial}{\partial x'_\gamma} \delta(\underline{x}-\underline{x}') +$$

$$+ i m'_\varepsilon \chi_{\varepsilon\alpha\gamma} p'_\beta \frac{\partial}{\partial x'_\gamma} \delta(\underline{x}-\underline{x}')$$

Similar expansions are derived for the other terms; for those we need only the first one to obtain the same order of magnitude. Substituting in (32) we meet expressions such as:

$$\Big\{ p'_\alpha p'_\beta \delta(\underline{x}-\underline{x}') - q'_{\alpha\gamma} p'_\beta \frac{\partial}{\partial x_\gamma} \delta(\underline{x}-\underline{x}') + p'_\alpha q'_{\beta\gamma} \; \delta(\underline{x}-x') \frac{\partial}{\partial x_\gamma} \; +$$

$$- \; q'_{\alpha\gamma} p'_\beta \; \delta(\underline{x}-\underline{x}') \frac{\partial}{\partial x_\gamma} \Big\} E_\beta(\underline{x}) \; G(\underline{x},\underline{x}")$$

where we have changed the differentiation of the δ-function from $\underline{x}$'to $\underline{x}$,

$$= p'_\alpha p'_\beta \delta(\underline{x}-\underline{x}') E_\beta(\underline{x}) G(\underline{x},\underline{x}") + p'_\alpha q'_{\beta\gamma} \; \delta(\underline{x}-\underline{x}') \frac{\partial}{\partial x_\gamma} E_\beta(\underline{x}) \quad \times$$

$$\times \; G(\underline{x},\underline{x}") + q'_{\alpha\gamma} p'_\beta \delta(\underline{x}-\underline{x}') E_\beta(\underline{x}) \frac{\partial}{\partial x_\gamma} G(\underline{x},\underline{x}")$$

The integration over all space in (32) can be written as:

$$\int_V d\underline{x} \longrightarrow \sum_\sigma{}' \int_{\mathrm{mol}\,\sigma} d\underline{x}$$

where the prime signifies that the molecule at $\underline{x}"$ has to be excluded. We than find:

$$E^e_\alpha(\underline{x}) = \sum{}' T_{\alpha\beta}(\underline{x}) \Big\{ \alpha_{\beta\gamma} E^e_\gamma\big(\underline{x}(\sigma)\big) G\big(\underline{x},\underline{x}(\sigma)\big) \; +$$

$$+ \; \beta_{\beta\gamma\delta} E^e_\gamma\big(\underline{x}(\sigma)\big) \frac{\partial}{\partial x_\gamma(\sigma)} \big(G \; \underline{x},\underline{x}(\sigma)\big) \; +$$

$$+ \; \beta'_{\beta\gamma\delta} \frac{\partial}{\partial x_\delta(\sigma)} \; E^e\big(\underline{x}(\sigma)\big) G\big(\underline{x},\underline{x}(\sigma)\big) \qquad (3)$$

The polarizability tensors in equation (3) are similar in appearence to those of (ch.I,28) and can be obtained from them by replacing all the expectation values of the moments by primed ones, independent of position. Further $\underline{\beta}$ corresponds to that part of $\underline{p}^1$, that contains terms with $\underline{p}$ $\underline{q}$ and $\underline{p}$ $\underline{m}$, $\underline{\beta}'$ to the one with $\underline{q}$ $\underline{p}$ and $\underline{m}$ $\underline{p}$. Except for the occurrence of Γ in the tensors this is just the equation found by Terwiel and his starting point for the derivation of the integral equations for the statistical averages. The influence of $V_{k\sigma,\ell\rho}$, so far neglected is then accounted for in the configuration distribution functions used to derive the macroscopic quantities. These macroscopic fields turn out to consist of three contributions : the average of the field and the inner field themselves, fluctuation terms describing deviations of these average values and an inner field reflecting the granular structure of the medium. He shows that such a macroscopic field satisfies indeed an equation of the type we have derived in chapter I. He also includes in his derivation an external field, proving on the way that such a field vanishes inside the medium (extinction theorem), thus making the theory valid for a finite piece of matter.

We would like to make some comment at this point on Γ . From its defining equation (ch. I, 23) we see that the total unperturbed hamiltonian H_o is involved, which means that Γ is a property of the whole system. If the $V_{k\sigma,\ell\rho}$ are not neglected in its calculation it describes the thermal line broadening encountered in dense media, a result that is difficult to obtain if the response of the system is built up from those of the individual molecules.

2. Crystalline medium

Say the crystal consists of N unit cells and define the position of any particle by

$$\underline{x}_i \longrightarrow \underline{x}\binom{1}{k} = \underline{x}(1) + \underline{x}(k)$$

where $\underline{x}(1)$ the position vector of the 1^{th} unit cell, $\underline{x}(k)$ that of the k^{th} particle in the cell. Choosing $\underline{x}'$ of chapter I to be the $\underline{x}(1)$ we expand in terms of $y.\langle \underline{x}(k) \rangle$, where the brackets stand for expectation value. This implies that we have to check to what extent particle k, when excited can be located. Using the fact that the crystal wave functions transform under translations T over a lattice vector $\underline{x}(1)$ according to :

$$T\,\underline{x}(1)\Psi_a = \exp -i\underline{q}_a.\underline{x}(1)\;\;\Psi_a$$

we find that matrix elements such as p_α can only be different from zero if

$$\underline{q}_a - \underline{q}_b = 2\pi\underline{y}(h)$$

where $\underline{y}(h)$ a vector in the reciprocal lattice :

$$\underline{y}(h).\underline{x}(1) = (h.1)$$

$$h = \{h_1 h_2 h_3\} \qquad , \qquad h_i \text{ an integer.}$$

For an expression as $p_\alpha(\underline{x})p_\beta$ we have, since $\sum_{1k} e_k x_\alpha\binom{1}{k}$ is invariant under $T(\underline{x}(1))$ for large 1:

$$p_\alpha(\underline{x})p_\beta = V^{-1}\sum_{b,h} \langle a| \sum_{1k} e_k x_\alpha\binom{1}{k} \exp\{2\pi i\underline{y}(h).(\underline{x}-\underline{x}\binom{1}{k})\}\,|b\rangle \tag{4}$$

$$\times \langle b| \sum_{1k} e_k x_\beta\binom{1}{k}\,|a\rangle$$

$$= V^{-1}\sum_h p_\alpha(h)p_\beta \exp\left(2\pi i\underline{y}(h).\underline{x}\right)$$

Here we have substituted the Fourier transform of $\delta(\underline{x}-\underline{x}\binom{1}{k})$ and V stands for the volume of the crystal. Similar expressions are obtained for the other terms, so that we can write $\underline{j}(\underline{x})$ as :

$$j_\alpha(\underline{x}) = i\omega V^{-1}\sum_h \exp\left\{2\pi i\underline{y}(h).\underline{x}\right\}\Big[p^o_{\alpha\beta}(h)\,E^e_\beta(\underline{x}) + p^1_{\alpha\beta\gamma}(h)\,E^e_{\beta\gamma}(\underline{x})\Big]$$

If we neglect short range correlations we have for the macroscopic value of $\underline{j}$, defined as the average over a physically infinitesimal volume:

$$\overline{j_\alpha(\underline{x})} = i\omega V^{-1}\sum_h p^o_{\alpha\beta}(h)\overline{\exp\left\{2\pi i\underline{y}(h).\underline{x}\right\}}\;\overline{E^e_\beta(\underline{x})} + \sum_h p^1_{\alpha\beta\gamma}(h)\overline{\exp\left\{2\pi i\underline{y}(h).\underline{x}\right\}}\;\overline{E^e_{\beta\gamma}(\underline{x})}$$

$$= i\omega V^{-1}\left(p^o_{\alpha\beta}(0)\,\overline{E^e(\underline{x})} + p^1_{\alpha\beta\gamma}(0)\,\overline{E^e_{\beta\gamma}(\underline{x})}\right) \qquad (6)$$

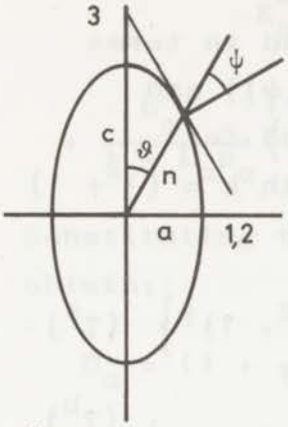
since only the term with h=0 survives averaging. In the same approximation we have e.g:

$$\overline{\int_V d\underline{x}'\,\underline{p}(\underline{x}')G(\underline{x},\underline{x}')} = \int_V d\underline{x}'\,\overline{\underline{p}(\underline{x}')}\;\overline{G(\underline{x},\underline{x}')}$$

which enables us to evaluate the innerfields. As the actual calculation of p^o and p^1 is rather uncertain, we did not think it worthwhile to go to the trouble of including short range correlations.

3. Wave propagation in a tetragonal crystal

Let us now derive the dispersion equation for the case of a uniaxial crystal. The surface $s(\underline{x})$ occurring in the expressions for the inner fields is then the surface of a rotation ellipsoid with axes a and c. Taking the limit of vanishing $v(\underline{x})$ the ratio $\frac{a}{c} = \lambda$ has to be kept constant in order that $\underline{E}^s$ has the same value on $s(\underline{x})$ everywhere. The normal to such a surface is given by



$$n_\alpha = \frac{x'_\alpha - x_\alpha}{|\underline{x}-\underline{x}'|} \cos\psi$$

where

$$\tan\psi = \frac{\cot\vartheta - \lambda^2\cot\vartheta}{1 + \lambda^2\cot\vartheta}$$

from which

$$\cos\psi = \frac{1 - u^2\cos^2\vartheta}{\left\{u^2(\lambda^2 + 1)\cos^2\vartheta + 1\right\}^{\frac{1}{2}}}$$

where

$$u^2 = 1 - \lambda^2$$

Further the distance $r = |\underline{x}-\underline{x}'|$ from a point on the surface to the centre is given by

$$r = a(1 - u^2\cos^2\vartheta)^{-\frac{1}{2}}$$

and $\lim\limits_{\underline{x}' \to \underline{x}} G(\underline{x},\underline{x}') = \frac{1}{r}$

With the aid of this we find expanding around $\underline{x}$ for the surface integrals in polar coordinates

$$\int_s d\underline{x}'\ p_\beta(\underline{x}')\ \frac{\partial}{\partial x_\beta} G(\underline{x},\underline{x}') n_\alpha = p_\beta(\underline{x})\ x$$

$$\int_{-1}^{+1} d\cos\vartheta \int_0^{2\pi} d\phi\ \frac{(x'_\alpha - x_\alpha)(x'_\beta - x_\beta)}{r^2} \left\{\frac{1 - u^2\cos^2\vartheta}{1 + u^2(1 + \lambda^2)\cos^2\vartheta}\right\}^{\frac{1}{2}} =$$

$$= L_\alpha\ p_\alpha(\underline{x})$$

The last equality follows immediately from the Ø dependence. Similarly we find that the indices have to be pair-wise equal in :

$$\int_s d\underline{x}'\, p_\beta(\underline{x}')\, \frac{\partial^2}{\partial x_\alpha \partial x_\beta} G(\underline{x},\underline{x}')\, n_\varepsilon =$$

$$\int_s d\underline{x}'\, p_\beta(\underline{x}') \left\{ -\frac{\delta_{\alpha\beta}}{r^3} + \frac{3(x'_\alpha - x_\alpha)(x'_\beta - x_\beta)}{r^5} \right\} n_\varepsilon$$

$$= - L_\varepsilon \frac{\partial}{\partial x_\varepsilon} p_\alpha(\underline{x}) + (K_{\alpha\delta}\, \delta_{\alpha\beta}\, \delta_{\delta\varepsilon} + \text{cycl.}) \frac{\partial}{\partial x_\delta} p_\beta(\underline{x})$$

The integrals L_α and K_α can be expressed in terms of elliptic integrals of the first $(F(k,\psi))$ and second kind $(E(k,\psi))$. These are tabulated for different values of their arguments. With $k = (\lambda^2 + 1)$ and $\psi = \arcsin \mu(\lambda^2 + 1)$ we find:

$$L_3 = \frac{4\pi}{3} \mu^{-3} (\lambda^2 + 1)^{-\frac{3}{2}} \left\{ \lambda^2 E + \mu^2 E - \mu \lambda^3 (\lambda^2 + 1)^{\frac{1}{2}} \right\} \qquad (7^a)$$

$$L_1 = L_2 = 2\pi\mu^{-1} (\lambda^2 + 1)^{-\frac{1}{2}} E - \tfrac{1}{2} L_3 \qquad (7^b)$$

It turns out that the $K_{\alpha\beta}$ drop out from the equations so that their evaluation will not be given here. This is a consequence of the tetragonal symmetry from which

$$p^o_{\alpha\beta} = p^o_\alpha \delta_{\alpha\beta}$$

and for the class D_4[2] in which we will be interested in the next chapter:

$$p^1_{\alpha\beta\varepsilon} = \chi_{\alpha\beta\mu}\, g_\mu\, \delta_{\mu\varepsilon}$$

Substituting these results into (I,33) we obtain:

$$E^e_\alpha(\underline{x}) = E_\alpha(\underline{x}) + L_\alpha\, p^o_\alpha E^e_\alpha(\underline{x}) + L_\alpha\, \chi_{\alpha\beta\mu} g_\mu \delta_{\mu\varepsilon} E^e_{\beta\varepsilon}(\underline{x}) \qquad (8^a)$$

$$E^e_{\alpha\varepsilon}(\underline{x}) = \frac{\partial}{\partial x} E_\alpha(\underline{x}) + (L_\alpha - L_\varepsilon) \frac{\partial}{\partial x_\varepsilon} p^o_\alpha E^e_\alpha(\underline{x}) + (K_{\alpha\delta} \delta_{\alpha\beta} \delta_{\delta\varepsilon} + \text{cycl.}) \frac{\partial}{\partial x_\delta} p^o_\beta E^e_\beta(\underline{x}) \qquad (8^b)$$

With sufficient accuracy we have

$$\frac{\partial}{\partial x_\varepsilon} E^e_\alpha = (1 - L_\alpha\, p^o_\alpha)^{-1} \frac{\partial}{\partial x_\varepsilon} E_\alpha \quad .$$

from which together with (8):

$$E^e_\alpha(\underline{x}) = (1 - L_\alpha\, p^o_\alpha)^{-1} E_\alpha(\underline{x}) +$$

$$+ \frac{L_\alpha}{1 - L_\alpha p_\alpha}\left(1 + \frac{(L_\alpha - L_\varepsilon)p_\beta}{1 - L_\beta\, p_\beta}\right) \chi_{\alpha\beta\mu} g_\mu \delta_{\mu\varepsilon} \frac{\partial}{\partial x_\varepsilon} E_\beta$$

Substituting this expression into $\underline{D} = \underline{E} + 4\pi\underline{p}$ we obtain:

$$D_\alpha = (1 + \frac{4\pi p_\alpha}{1 - L_\alpha\, p_\alpha})E_\alpha + 4\pi \chi_{\alpha\beta\mu} g_\mu\, \delta_{\mu\varepsilon} \; x$$

$$x \;(1 + \frac{(L_\alpha - L_\varepsilon)p_\beta}{1 - L_\beta\, p_\beta})(\frac{L_\alpha\, p_\alpha}{1 - L_\alpha\, p_\alpha} + 1) \frac{\partial}{\partial x_\varepsilon} E_\beta$$

$$= \varepsilon_\alpha E_\alpha + 4\pi \chi_{\alpha\beta\mu}\, g_\mu \delta_{\mu\varepsilon} f(\varepsilon) \frac{\partial}{\partial x_\varepsilon} E_\beta$$

where $\varepsilon_\alpha = 1 + 4\pi p_\alpha(1 - L_\alpha\, p_\alpha)^{-1}$ (9)

From the wave propagating equation (I,34) and the definition of $\underline{D}$ we can eleminate $\underline{p}$ obtaining the more familiar:

$$D_\alpha = n^2\left\{\delta_{\alpha\beta} - \frac{y_\alpha y_\beta}{y^2}\right\} E_\beta$$

For light travelling along the optical axis of the crystal the normal to the wave front is in the 3-direction and we have:

$$D_1 = n^2 E_1 \qquad D_2 = n^2 E_2 \qquad D_3 = 0 \qquad (10)$$

Rewriting the dispersion equation such that $\underline{E}$ is given as a function of D, substituting the possible values of the indices and eliminating E we obtain:

$$(n^{-2} - \varepsilon_1^{-1}) D_1 = -i \; D_2 \, \varepsilon_1^{-1} \, \varepsilon_2^{-1} \; f(\varepsilon) g_3$$

$$(n^{-2} - \varepsilon_2^{-1}) D_2 = i \; D_1 \, \varepsilon_1^{-1} \, \varepsilon_2^{-1} \; f(\varepsilon) g_3$$

from which, since for tetragonal crystals $\varepsilon_1 = \varepsilon_2 \neq \varepsilon_3$

$$D_1 \pm iD_2 = 0$$

This corresponds to a right and lefthanded circularly polarized wave each travelling with a different speed, which we determine by eliminating $\frac{D_1}{D_2}$:

$$(n^{-2} - \varepsilon^{-1}) = \pm \frac{f(\varepsilon)}{\varepsilon^2} g_3,$$

showing that the difference between n^2 and is of the order of g so that we can write:

$$n = \varepsilon^{\frac{1}{2}} \left\{ 1 \pm \frac{1}{2\,\varepsilon} f(\varepsilon) g_3 \right\} \qquad (11)$$

Now the rotatory power is defined by

$$\varnothing = \frac{\pi}{\lambda} (n_+ - n_-) \qquad (12)$$

where $\varnothing$ the rotation angle in radians per cm, λ the wavelength in vacuo, n_+ and n_- the refractive indices for right and lefthanded circularly polarized light in the medium. If n is complex, as it is in an absorption region, then so is $\varnothing$; its imaginary part then describes the phenomenon of circular dichroism θ. According to (11) and (12) we have:

$$\varnothing = \frac{\pi}{n\,\lambda} f(\varepsilon) g_3 = \frac{\pi}{n\,\lambda} f(n^2) g_3$$

Litt.

1. R.H. Terwiel Thesis Leiden (1964)
R.H. Terwiel and P. Mazur, Physica 30, 625 (1964)
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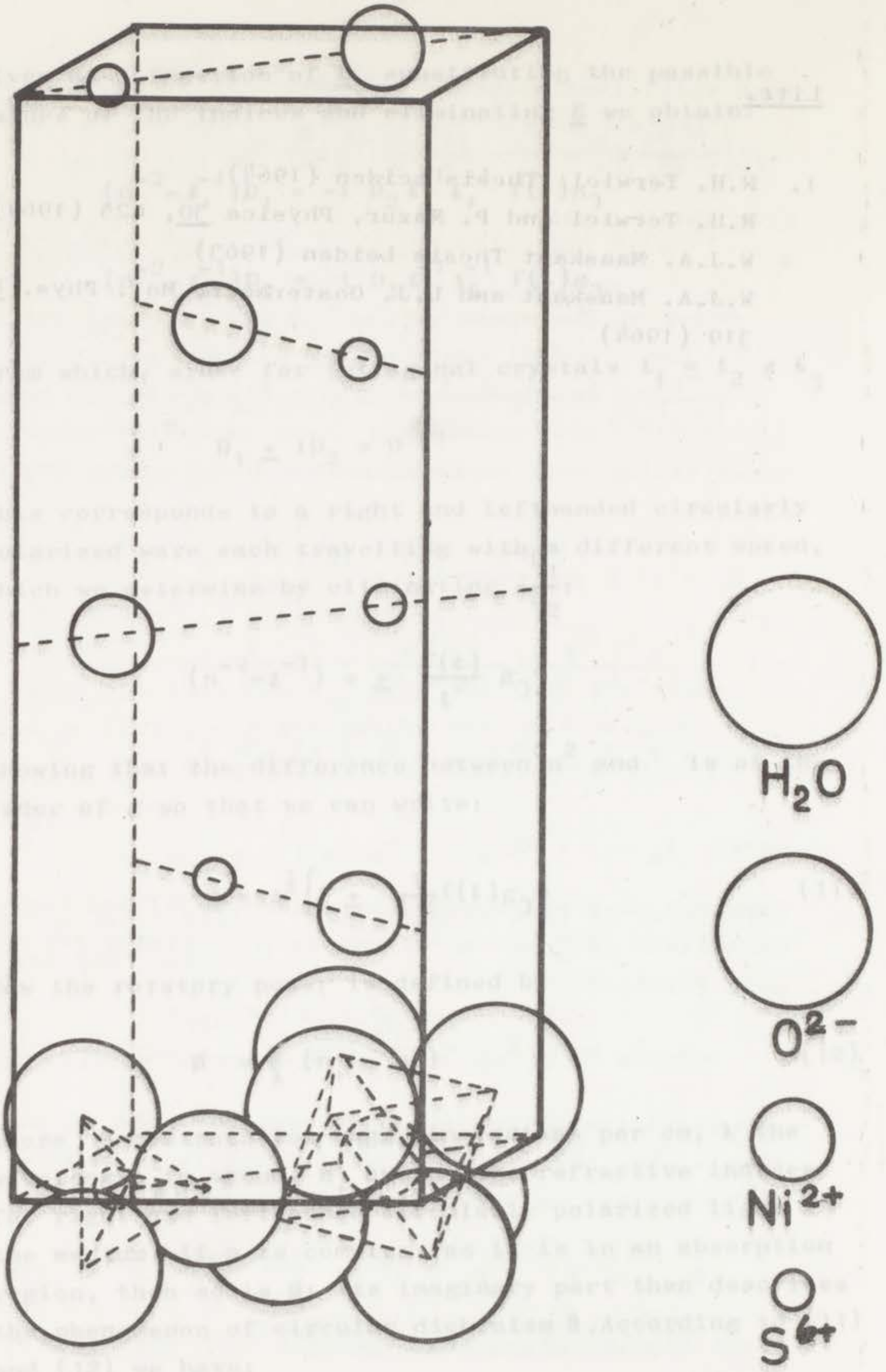


fig. 1. The crystal structure of -$NiSO_4.6H_2O$

Chapter III

In this chapter we shall try to calculate the rotatory power for a definite substance for which we have chosen the tetragonal modification of $NiSO_4.6H_2O$. The structure of this compound has been determined by Beevers and Lipson $^{1)}$. It can be considered as built up from $Ni(H_2O)_6$ octahedrons and SO_4 tetrahedrons, these groups lying on a helix along the crystal C-axis. All together there are 4 octahedrons and consequently 4 tetrahedrons per unit cell (using a modified unit cell with c = 18.3 Å and a = 6.8 Å) with their centers on the special points of the space group D_4^4 or D_4^8, these being each others mirror image. The oxygen ions and water molecules are situated on the general positions. The necessary parameters are :

				x	y	z
Ni	x = 0.71	H_2O	(1)	.67	.45	.054
S	x = 0.21		(2)	.97	.75	.054
			(3)	.56	.86	.077
		O	(1)	.12	.12	.068
			(2)	.43	.86	.000

Part of the structure is illustrated in fig. 1. Now the absorption spectrum of the crystal in the visible region does not differ markedly from that of the equeous solution, which can be interpreted satisfactorily in terms of excitations of an octahedrally coordinated Ni^{2+} ion. Therefore we take as our wave functions products of wave functions pertaining to the individual octahedrons thereby neglecting the sulphate groups. For the ground state :

$$\Psi_a = (nN!)^{\frac{1}{2}} A \prod_{1} \ldots \psi^a\left(\frac{1}{\sigma}\right) \ldots \qquad (1)$$

with n = the number of particles in a unit cell,

N = the number of unit cell in the crystal,

A = the antisymmetriser :

$$A = (nN!)^{-1} \sum_P \delta_P U_P \qquad (2)$$

U_p is the unitary operator that induces the transformed state under the permutation p of the variables, δ_p the parity pf that permutation. $\psi^a\binom{l}{\sigma}$ represents the wave function of the ground state of the octahedron at the σ^{th} position in the l^{th} cell. Similarly for excited states :

$$\Psi'_b = (nN!)^{\frac{1}{2}} A \, \psi^f\binom{l}{\sigma} \prod_{k\rho \neq l\sigma} \cdots \psi^a\binom{k}{\rho} \qquad (3)$$

Lifting the positional degeneracy by choosing a linear combination of such functions and using the translational symmetry of the crystal we obtain :

$$\Psi''_b = (nN!)^{-\frac{1}{2}} \sum_{l\sigma} B_\sigma \exp\{i\underline{k}.\underline{x}(l)\} \Psi'_b \qquad (4)$$

The coefficients B_σ are determined from the set of equations one finds in diagonalising the hamiltonian. For non-trival solutions we have the usual secular equation of the n^{th} degree in the energy leading to n different values labelled μ. In all one obtains n^2 coefficients B^μ_σ whose values can also be found from the following considerations [2)] : according to (4) the probability of finding an excited octahedron at $\binom{l}{\sigma}$ is given by $(nN)^{-1} |B^\mu_\sigma|^2$ and as all positions are equivalent we must have

$$|B^\mu_\sigma|^2 = \text{constant}$$

Moreover we demand the functions

$$\Psi_b = (nN)^{-\frac{1}{2}} \sum_{l\sigma} B^\mu_\sigma \exp\{i\underline{k}.\underline{x}(l)\} \Psi'_b$$

to form an orthonormal set from which for B^μ :

μ\σ	1	2	3	4
1	a	a	a	a
2	b	-b	b	-b
3	c	-c	-c	c
4	d	d	-d	-d

(6)

where $|a|^2 = |b|^2 = |c|^2 = |d|^2 = 1$.
We want to find the expectation values of the sums of one-particle operators such as $\sum_k e_k \underline{x}(k) = \sum_\sigma \underline{p}(\sigma)$ where $\underline{p}(\sigma)$ is the dipole moment operator of an octahedral group. Similar expressions represent the quadrupole and magnetic dipole operators. Substituting we find e.g. for an expression as $p_\alpha q_{\beta\varepsilon}$ of equation (4) ch. II :

$$p_\alpha q_{\beta\varepsilon} = \frac{N}{V}(nN!)^2(nN)^{-1}\sum_{\substack{1'1'' \\ \sigma'\sigma''}} \left\langle ..\binom{1}{\sigma}_a . \middle| A\sum_\sigma p_\alpha(\sigma)A \middle| ..\binom{1'}{\sigma'}_b . \right\rangle \text{ x}$$

$$\text{x} \left\langle ..\binom{1''}{\sigma''}_b .. \middle| A\sum_\sigma q_{\beta\varepsilon}(\sigma)A \middle| ..\binom{1'''}{\sigma'''}_a . \right\rangle B^\mu_{\sigma'} B^\mu_{\sigma''} \text{ x}$$

$$\text{x } \exp\left\{ i\underline{\varkappa}.(\underline{x}(1)-\underline{x}(1'''))\right\} \qquad (7)$$

$$= \frac{N}{V} n^{-1} \sum_{\sigma\sigma'} \langle \psi^a_\sigma | p_\alpha(\sigma) | \psi^\sigma_b \rangle \langle \psi^{\sigma'}_b | q_{\beta\varepsilon}(\sigma) | \psi^a_{\sigma'} \rangle B^\mu_\sigma B^\mu_{\sigma'}$$

The socalled Davydov splitting (states differing only in μ) is small $^{2)}$ so that we can take ${}_{ba}$ to be independent of μ and sum over these neighbouring states from now on i.e. :

$$\sum_b \longrightarrow \sum_{\mu f \underline{\varkappa}} = \sum_{f\underline{\varkappa}} \left(\sum_\mu \right) \qquad (8)$$

Using (6) we have :

$$p_\alpha q_{\beta\varepsilon} = \frac{N}{V} \sum_\sigma \langle \psi^o_\sigma | p_\alpha(\sigma) | \psi^f_\sigma \rangle \langle \psi^f_\sigma | q_{\beta\varepsilon}(\sigma') | \psi^o_\sigma \rangle \qquad (9)$$

The operators $\underline{p}$, $\underline{q}$ and $\underline{m}$ are defined with respect to a fixed point in the unit cell ($\underline{x}(1)$). To obtain an expression in terms of the octahedral quantities themselves we put :

$$\underline{x}\binom{1}{i} = \underline{x}'\binom{1}{i} + \underline{r}^i \qquad (10)$$

where $\underline{x}'$ measures the distance from the positions of the Ni^{2+} ions, $\underline{r}$ the distance of these ions to the fixed point (9) then becomes :

$$p_\alpha q_{\beta\varepsilon} = \sum_i \langle\psi_i^o|p_\alpha(i)|\psi_i^f\rangle\langle\psi_i^f|p_\beta(i)|\psi_i^o\rangle\, r_\varepsilon^i +$$

$$+ \langle\psi_i^o\, p_\alpha(i)\, \psi_i^f\rangle\langle\psi_i^f\, p_\varepsilon(i)\, \psi_i^o\rangle\, r_\beta^i + \qquad (11)$$

$$+ \langle\psi_i^o\, p_\alpha(i)\, \psi_i^f\rangle\langle\psi_i^f\, q'_{\beta\varepsilon}(i)\, \psi_i^o\rangle$$

$$= \sum_i p_\alpha^i p_\beta^i r_\varepsilon^i + p_\alpha^i p_\varepsilon^i r_\beta^i + p_\alpha^i q_{\beta\varepsilon}^i$$

in an obvious abbreviated notation. The total quadrupole contribution becomes, since real wave functions will be used :

$$\mathrm{Re}(p_\alpha q_{\beta\varepsilon} - q_{\alpha\varepsilon} p_\beta) = \sum_i p_\alpha^i p_\varepsilon^i r_\beta^i - p_\varepsilon^i p_\beta^i r_\alpha^i + p_\alpha^i q_{\beta\varepsilon}^i - p_\beta^i q_{\alpha\varepsilon}^i$$

Similarly for the magnetic contribution, using $\dot{\underline{x}} = (i\hbar)^{-1}\left[\underline{x}, H_\sigma\right]$:

$$\mathrm{Im}(p_\alpha m_\nu \chi_{\nu\beta\varepsilon} + m_\nu \chi_{\nu\alpha\varepsilon} p_\beta) = \omega_{ba} \sum_i p_\alpha^i p_\varepsilon^i r_\beta^i - p_\varepsilon^i p_\beta^i r_\alpha^i +$$
$$+ \mathrm{Im}(p_\alpha^i m_\nu^i \chi_{\nu\beta\varepsilon} + m_\nu^i \chi_{\nu\alpha\varepsilon} p_\beta^i)$$

Owing to the symmetry of the crystal it is easy to express the different $\underline{p}^i$ etc. in terms of one another; so the 3-component is not changed at all by the symmetry operations i.e. $p_3^i = p_3$ for all and for the 1- and 2-components we find using the fourfold rotation axis :

	p_1	p_2	m_1	m_2	q_{23}	q_{13}
1	p_1	p_2	m_1	m_2	q_{23}	q_{13}
2	$-p_2$	p_1	$-m_2$	m_1	q_{13}	$-q_{23}$
3	$-p_1$	$-p_2$	$-m_1$	$-m_2$	$-q_{23}$	$-q_{13}$
4	p_2	$-p_1$	$-m_1$	$-m_1$	$-q_{13}$	q_{23}

(14)

We have seen that for light travelling along the optical axis we only have to know g_3 and since .

$$p^{1}_{\alpha\beta\gamma} = \chi_{\alpha\beta\mu}\, g_\mu\, \delta_{\mu\varepsilon}$$

only $p^{(1)}_{123}$ for this case. Substituting and using (14) we have for the rotation strength R^{ab}_{123} in :

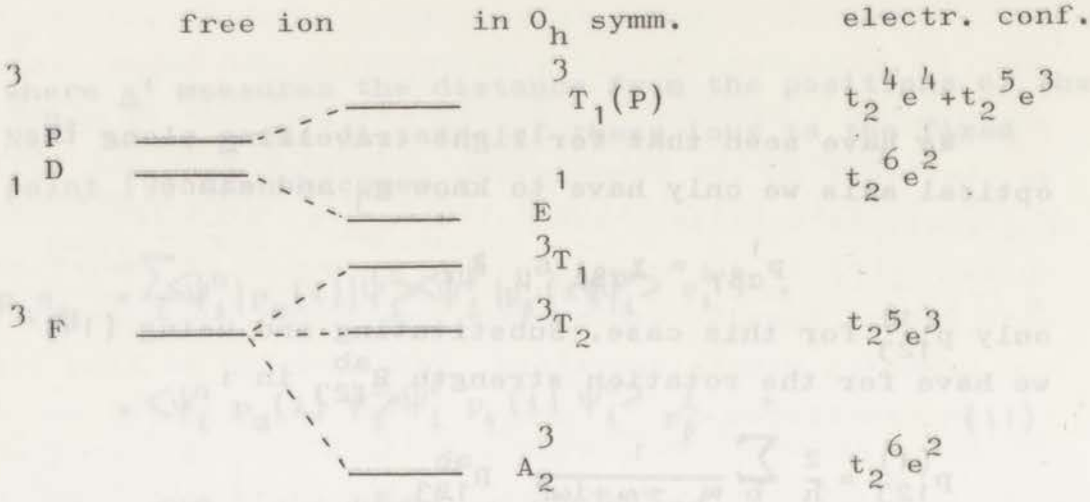
$$p^{(1)}_{123} = \frac{2}{\hbar} \sum_b \frac{1}{\omega_{ba} - \omega + i\omega\Gamma}\, R^{ab}_{123}$$

$$R^{ab}_{123} = 2\,\omega_{ba} p_1 p_3 (r_2^{\,1} - r_2^{\,3} - r_1^{\,2} - r_1^{\,4}) - 2\,\omega_{ba} p_1 p_3 (r_2^{\,2} - r_2^{\,4} + r_1^{\,1} - r_1^{\,3}) + 4 (p_1 q_{23} - p_2 q_{13}) + 4\, \mathrm{Im} (p_1 m_1 + p_2 m_2)$$

which becomes with the values of r^{i}_{α} as found from the position parameters :

$$R^{ab}_{123} = 0.32\,\omega_{ba}\, a(p_1 - p_2) p_3 + 4\,\omega_{ba}\,(p_1 q_{23} - p_2 q_{13}) + 4\,\mathrm{Im}(p_1 m_1 + p_2 m_2) \qquad (16)$$

where a the base length of the unit cell. (16) consists of three contributions which we shall call the relative dipole moment (R_r), quadrupole moment (R_q) and magnetic dipole moment (R_m) rotation strength respectively. To estimate these we make use of ligand field theory, which is able to explain the observed absorption spectrum of octahedrally coordinated nickel as transitions between the possible electron configuration of 8 equivalent d-like electrons or since 10 such electrons constitute a filled shell 2 d-like holes. In reducing the symmetry of the free Ni^{2+}-ion to octahedral symmetry the degeneracy of the ^3F ground state is lifted and three new energy levels result. The relevant termscheme together with the electron configuration is depicted in fig. 2.



According to this scheme the energy of the transition $^3A_2 \longrightarrow {}^3T_2$ is equal to the ligand field splitting Δ. Assigning the absorption at 8400 cm^{-1} to this transition the mixing of the two states with T_1 symmetry can be calculated as well as their respective energies. One finds

	energy	electron conf.
$T_1(p)$	25.000 cm^{-1}	$0.67\ t^2_2 + 0.74\ t_2e$
$T_1(F)$	13.350 cm^{-1}	$0.74\ t^2_2 - 0.67\ t_2e$

in reasonable agreement with experiment. We have also drawn the $^1E(D)$ state, about which some controversy exists. According to Ballhausen and Liehr 3), who calculated the complete term scheme of Ni^{2+} in O_h symmetry including spin-orbit coupling, the energy of this state is nowhere near that of the $^3T_1$ as proposed by Jörgensen 4). Moreover their calculation gives much too small a value for the transition probability. However in addition to extensive new experimental evidence 5) in favor of Jörgensen's assignment we think that the optical activity of $NiSO_4.6H_2O$ can be explained better by assuming the given term scheme.

Dipole moments calculated for these electron configurations vanish and one has to take the vibrational motion of the water molecules into account to obtain finite values for the p_α. For an estimate of these integrals we shall follow Englman 6) in assuming that the charge transfer states in the ultraviolet are by far the most important electronic states to which the excited states of interest are connected by a vibrational hamiltonian H_v. For this hamiltonian we take the odd part of the total vibrational hamiltonian in cartesian coordinates given by (Koide and Pryce [7]) :

$$H_v = \tfrac{1}{2}(X_1 + X_4 - 2X_o)\frac{\partial}{\partial x}(V_1 + V_4) + \tfrac{1}{4}(X_2 + X_3 + X_5 - 4X_o)$$

$$\times \frac{\partial}{\partial x}(V_2 + V_3 + V_5 + V_6) + \tfrac{1}{4}(X_1 - X_3 + X_5 - X_6) \times$$

$$\times \frac{\partial}{\partial x}(V_2 - V_3 + V_5 - V_6) + \ldots$$

where X_i $(i = 0, \ldots, 6)$ the displacement in the x-direction of the molecules, V_i the potential due to the i^{th} molecule in its equilibrium position acting on an electron. With the help of perturbation theory the p_α become :

$$p_\alpha = \sum_C (E_{A_2} - E_C)^{-1} \langle A_2;n'|\, H_v\, |C;n\rangle\langle C;n|\, p_\alpha\, |T;n\rangle +$$

$$+ \sum_C (E_T - E_C)^{-1} \langle A_2;n'|\, p_\alpha\, |C;n\rangle\langle C;n'|\, H_v\, |T;n\rangle$$

where C stands for the charge transfer states, thus rejecting all others and n, n' for vibrational states. The electronic d-like wave functions are given in the following table. The correct symmetry bahaviour was found in the tables of Griffith's book [8]. Brackets denote antisymmetrisation e.g.

$$(\theta\,\varepsilon) = 2^{-\frac{1}{2}}\ \left(\ |\theta(1)\ \varepsilon(2)\rangle - |\varepsilon(1)\,\theta(2)\rangle\ \right)$$

further $\quad \varepsilon \sim x^2 - y^2$

$$\theta \sim 3^{-\frac{1}{2}}\ (2z^2 - x^2 - y^2)$$

$$\xi \sim yz\ ,\ \eta \sim xz\ ,\ \zeta \sim xy.$$

Table I

octahedral state	wave function
$3\ A_2$	$\theta\ \varepsilon$
$3\ T_1 x$ (F)	$0.74(\zeta\ \eta)+0.34(\xi\ \varepsilon)+0.59\ (\xi\ \theta)$
y	$0.74(\xi\ \zeta)+0.34(\eta\ \varepsilon)-0.59(\eta\ \theta)$
z	$0.74(\eta\ \xi)-0.67(\zeta\ \varepsilon)$
$^3T_2\ \xi$	$-\frac{1}{2}V_3(\xi\ \varepsilon)+\frac{1}{2}\ (\xi\ \theta)$
η	$\frac{1}{2}V_3(\eta\ \varepsilon)+\frac{1}{2}\ (\eta\ \theta)$
ζ	$-(\zeta\ \theta)$
$^3T_1 x$	$0.67(\zeta\ \eta)-0.37\ (\xi\ \varepsilon)-0.64(\xi\ \theta)$
y	$0.67(\xi\ \zeta)-0.37\ (\eta\ \varepsilon)+0.64(\eta\ \theta)$
z	$0.67(\eta\ \xi)+0.74\ (\zeta\ \varepsilon)$

Englman now further argues that, disregarding for the moment the vibrational matrix element of the cores, the dominant term for say the ζ-component of T_2 is

$$(E_{T_2}-E_C)^{-1}\langle\zeta|p_y|\alpha_x\rangle\langle\alpha_x|\frac{\partial}{\partial x}(V_1+V_4)|\theta\rangle$$

and a similar expression for p_y; p_z giving zero. Here α_x represents a charge transfer wave function extending along the x-axis. The second and third term of H_v give rise to integrals in which the integrand contains three factors, each large in a different region and will therefore be neglected. A similar argument holds for terms such as :

$$(E_{A_2}-E_C)^{-1}\langle\zeta|\frac{\partial}{\partial x}(V_1+V_4)|\alpha_y\rangle\langle\alpha_y|p_y|\theta\rangle$$

and these will accordingly be neglected.

Putting $\langle\zeta|p_y|\alpha_x\rangle = eQ$

$$\langle\varepsilon|\frac{\partial}{\partial x}(V_1+V_4)|\alpha_x\rangle = 3^{\frac{1}{2}}\ I$$

we find for the remaining one-electron integrals :

$$\langle\zeta\,|p_x|\alpha_y\rangle=\langle\eta|p_z|\alpha_x\rangle=\langle\eta|p_x|\alpha_z\rangle=\langle\xi\,|p_y|\alpha_z\rangle=$$
$$=\langle\xi|p_z|\alpha_y\rangle = eQ\ ;\quad \langle\varepsilon|\frac{\partial}{\delta\ y}(V_2+V_5)|\alpha_y\rangle= -3^{\frac{1}{2}}\ I$$

$$\langle\theta|\frac{\partial}{\delta\ z}(V_3+V_6)|\alpha_z\rangle = 2\ I\ ,\ \langle\varepsilon|\frac{\partial}{\delta\ z}(V_3+V_6)|\alpha_z\rangle = 0$$

$$\langle\theta|\frac{\partial}{\delta\ x}(V_1+V_4)|\alpha_x\rangle= \langle\theta|\frac{\partial}{\delta\ y}(V_2+V_5)|\alpha_y\rangle= -I$$

The expectation values of the components of the dipole moments are collected in the following table

transition		p_x	p_y	p_z
$^3A_2 \rightarrow {}^3T_1$	x (F)	0	0.68	0.68
	y m	0.68	0	0.68
	z	0.68	0.68	0
$^3T_2$	ξ	0	$-\sqrt{3}$	$\sqrt{3}$
	η	$\sqrt{3}$	0	$-\sqrt{3}$
	ζ	$-\sqrt{3}$	$\sqrt{3}$	0
$^3T_1$	x (P)	0	-0.74	-0.74
	y	-0.74	0	-074
	z	-0.74	-0.74	0

all to be multiplied with $\frac{e}{\Delta\ E}\ QI\langle n|H_v|n'\rangle$

As follows for the expressions for the wave functions these quantities refer to an orientation of the octahedrons such that the water molecules lie on the coordinate axes. In (16) however they are expressed in the coordinate system of the unit cell. We therefore rotate the first system over the following Euler angles, as calculated from the X-ray diffraction data, using Goldstein's [9)] definition of these angles :

$$\varphi = \frac{7\pi}{4}$$

$$\vartheta = 312^\circ\ 6'$$

$$\psi = \frac{\pi}{4}$$

The rotation matrix is found to be :

$$\begin{pmatrix} -0.16 & 0.84 & -0.52 \\ -0.84 & 0.16 & 0.52 \\ 0.52 & 0.52 & 0.67 \end{pmatrix}$$

with the help of which the dipole moments in the new coordinate system become :

transition	p_1	p_2	p_3
$^3A_2$ ^3T_1x (F)	0.22	0.46	0.81
y	0.46	-0.22	0.81
z	0.46	-0.46	0.71
$^3T_2\xi$	-2.36	0.62	0.26
η	0.62	0.55	-0.26
ζ	1.73	1.73	1.00
^3T_1x (P)	-0.24	-0.50	-0.88
y	0.50	0.24	-0.88
z	-0.50	0.50	-0.77

again times $\frac{e}{\Delta E}\,QI\langle n|H_v|n'\rangle$

The observed p^2 are given by

$$p_1^{\,2} + p_2^{\,2} = k\left(\frac{e}{\Delta E}\,QI\langle n'|H_v|n\rangle\right)^2$$

where k a numerical factor derived from the table. For simplicity we use these experimental values in our further calculation of R_r. Englman calculated these integrals and obtained reasonable agreement with the experimental values of their products. With his value of Q we might expect to be able to predict the rotation strength of the charge transfer band. However it turns out that the R_r term vanishes when only this kind of integral is taken into account. One also has to know the value of integrals of the type $\langle\alpha_x|p_y|\theta\rangle$ which we discarded in the foregoing as relatively unimportant. From the experimental rotation strength we can make an estimate of such integrals giving $|\langle\alpha_x|p_y|\theta\rangle|^2 = 0.7 \times 10^{-36}$ as compared to $e^2Q^2 = 2.1 \times 10^{-36}$.

The p_α derived in the above way give no contribution to R_q and R_m since positive and negative values are equally likely to occur while $\underline{q}$ and $\underline{m}$ do not change sign. Realizing that the octahedron is embedded in the crystal the vibrational motions of the water molecules are much more restricted and deviations from the equilibrium positions need no longer be equal in opposite directions. Because an evaluation of the resulting p_α is discouraged by the complexity of the problem we have settled for taking the magnitude of the p_α to be proportional to those for an isolated octahedron. It might be thought that a static distortion of the octahedral field is responsible for the non-vanishing p_α in these terms. The potential acting on an electron at $\underline{x}$ to be added to the octahedral hamiltonian is given by

$$V(\underline{x}) = \int d\underline{x}' \, \frac{e\rho(x')}{|\underline{x} - \underline{x}'|}$$

where $\rho(\underline{x})$ the static charge distribution of the crystal. Taking the origin at the center of an octahedron we can expand $\frac{1}{|\underline{x} - \underline{x}'|}$ in Legendre polynominals giving

$$V(\underline{x}) = -\int d\underline{x}' \sum_1 |\underline{x}'|^{-1-1} |\underline{x}|^1 \, e\rho(\underline{x}') \, P_1(\cos\alpha)$$

where $\cos\alpha = \frac{\underline{x}\cdot\underline{x}'}{|\underline{x}||\underline{x}'|}$

which with the help of the spherical addition theorem becomes in polar coordinates :

$$\begin{aligned} V(\underline{x}) &= \int d\underline{x}' \sum_{1m} \frac{21+1}{4\pi} \, \rho(\underline{x}') \, |\underline{x}|^1 \, |\underline{x}'|^{-1-1} \, \bar{Y}_1^m(\vartheta,\varphi) Y_1^m(\theta,\phi) \\ &= \sum_{1m} |\underline{x}|^1 \, \gamma_{1m} \, Y_1^m(\theta,\phi) \end{aligned}$$

with

$$\gamma_{lm} = \frac{2l+1}{4}\int d\underline{x}' \; e\rho(\underline{x}')\,|\underline{x}'|^{-l-1}\; Y_l^m(\vartheta,\varphi)$$

The static charge distribution $\rho(\underline{x})$ is invariant under the symmetry operations of the space group D_4^4 or D_4^8. Now the general equivalent points of these groups can be taken in pairs such that their distances to the x=y plane as well as the z=0 plane, on the intersection of which the Ni^{2+} ions are situated, are equal, which amplies that for every θ its complement$(\pi - \theta)$ occurs. Since the parity of the Y_l^o is $(-)^l$ we have that for odd l all the γ_{lo} vanish; but in these coefficients lies the difference between the two enantiomorphous space groups as the projecting on the z=0 plane is the same for both. We can therefore expect no contribution to optical activity from the static deformation of the octahedral field.

The situation is less complicated for the magnetic dipole and quadrupole moment. Since d-electrons are so called for having an angular momentum of 2 atomic units the states connected by magnetic dipole transitions will have the absolute value for this quantity

$$|m| = \frac{e}{2mc}\,2\hbar = 2\,\mu_B.$$

The only state that can thus be reached from the A_2 ground state is the T_2 one because $\underline{m}\,|A_2\rangle$ transforms as the direct product $T_1 \times A_2 = T_2$. Due however to spin-orbit coupling the other states can also obtain some T_2 character; using perturbation theory the states $|T_i\rangle$ corrected for spin-orbit coupling are given by :

$$|T_i\rangle' = |T_i\rangle + \sum_j |T_j\rangle \frac{\langle T_j|\,\underline{L}.\underline{S}\,|T_i\rangle}{E(T_i)-E(T_j)}$$

where $T_i = A_2$, E , T_i or T_2.

Instead of diving into extensive arithmetic it is worth while to consult tables of the values of the spin-orbit coupling matrix elements such as have been compiled by Griffith $^{8)}$. To use these we first have to find the function corresponding to the different

$\underline{J} = \underline{L} + \underline{S}$ and $M_J = M_L + M_S$ values or their analogues in the reduced O_h symmetry. The necessary Clebsch-Gordon coupling coefficients can also be found in Griffith's book. For a $^3T_2$ state the addition of $\underline{L}$ and $\underline{S}$ leads to $\underline{J}$ values corresponding to the irreducible representations contained in the direct product $T_1 \times T_2$ since for $S = 1$ $|S\rangle$ transforms as T_1. Taking e.g. the E component we have from the tables:

$$|E\,;{}^3T_2\rangle = 2^{-\frac{1}{2}}\,|S1T_21\rangle + 2^{-\frac{1}{2}}\,|S{-1}T_2{-1}\rangle$$

The value of $\langle E;\,{}^3T_1|\,\underline{L}\,.\,\underline{S}\,|\,E;\,{}^3T_2\rangle$ is found to be $-\frac{1}{4}\,\zeta$, where ζ the integral over the radial part of the above expressions and therefore a constant within this d^8 configuration. Combining we have that one term of the corrected $^3T_1$ is given by

$$-\tfrac{3}{4}\,\frac{\zeta}{E(T_1)-E(T_2)}\quad 2^{-\frac{1}{2}}\,|S1T_21\rangle + 2^{-\frac{1}{2}}\,|S{-1}T_2{-1}\rangle$$

Proceeding similarly for all other terms and neglecting the spin-orbit splitting within a term we find the following absolute values of the magnetic dipole moments

electron configuration	m
e^2	$\frac{\sqrt{6}\,\zeta}{\Delta E}\;\mu_B$
t_2e	$\frac{1.08\,\zeta}{\Delta E}\;\mu_B$
t_2^2	$\frac{2.16\,\zeta}{\Delta E}\;\mu_B$

Due to the same mechanism of spin-orbit coupling mixing between the ^1E and $^3T_1$ states occurs. From perturbation theory we derive as the approximate configurations, normalised to second order

state	configuration
^1E	$0.39\ t_2e + 0.92\ e^2$
$^3T_1$ (F)	$0.74\ t_2^2 - 0.59\ t_2e + 0.38\ e^2$

from which incidentally it can be seen that the expectation value of the dipole moment of the spin-forbidden transition is 0.66 times that of the one to the $^3T_1(F)$ state, in good agreement with the experimental estimate.

Finally the quadrupole moment gives non-zero results only for the T_1 states, because the operator behaves as $x_\alpha\ x_\beta$ and these products transform as either T_2 or E. The transition $^3A_2 \longrightarrow {}^1E$ being spin-forbidden we have only

$$\underline{q} \quad |^3A_2\rangle \sim T_2 \times A_2 = T_1$$

Writing the operator in polar coordinates the evaluation of its expectation value is a straighforward matter. We find :

$$\langle ^3T_1\,|q_{\alpha\beta}|\,^3A_2\rangle = \frac{2\ e}{7\sqrt{3}}\ \overline{r^2}$$

Since the order of magnitude of the quadrupole moment times the frequency is much smaller than the Bohr magnetron it is pointless to take a spin-orbit coupling refinement into account.

In order to obtain values that can be compared with experimental results we assume the values of the dipole moments in R_q and R_m to be about 6% of the ones derived from the spectrum. From the absorption spectrum we derive the following values for the dipole moment per octahedron :

state	energy (cm^{-1})	p ($\times 10^{-19}$)
$^3T_1$ (P)	26000	0.56
^1E	15400	0.31
$^3T_1$ (F)	14100	0.45
$^3T_2$	8400	0.63

Taking the spin-orbit coupling parameter ζ from experiment $^{)}$ to have the value $\zeta = 540\ cm^{-1}$ and $\overline{r^2}$ to be about $0.48 \times 10^{-16}\ cm^2$ (ionic radius of Ni^{2+} = = 0.69 Å) we obtain the following estimate for R :

	$R_r \times 10^{-40}$	$4R_m \times 10^{-40}$	$4R_q \times 10^{-40}$	$R_{tot} \times 10^{-40}$
$^3T_1(P)$	0.03	0.08	0.05	0.16
^1E	-	0.14	0.02	0.16
$^3T_1(F)$	0.01	0.18	0.02	0.21
$^3T_2$	0.003	2.80	-	2.80

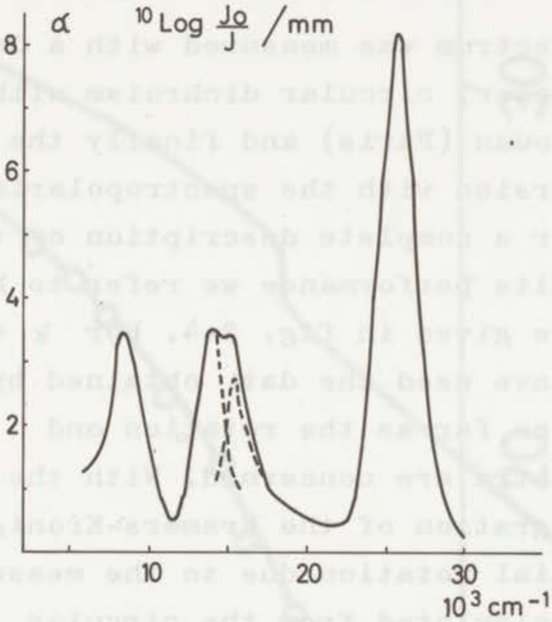


fig. 2. The absorption spectrum of $-NiSO_4.6H_2O$

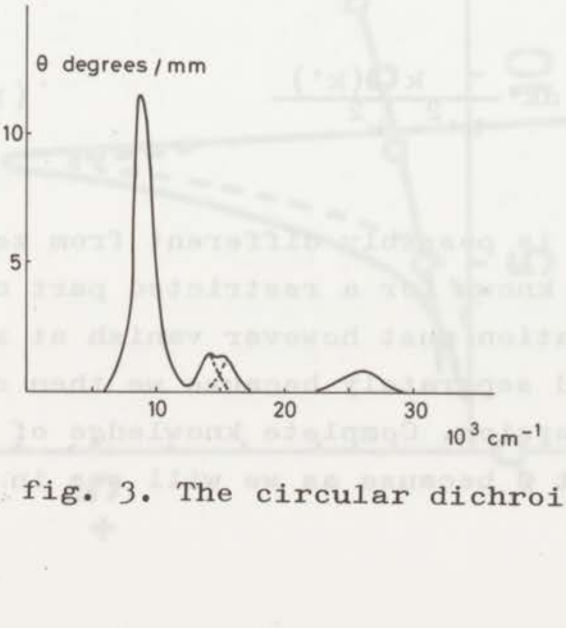


fig. 3. The circular dichroism spectrum.

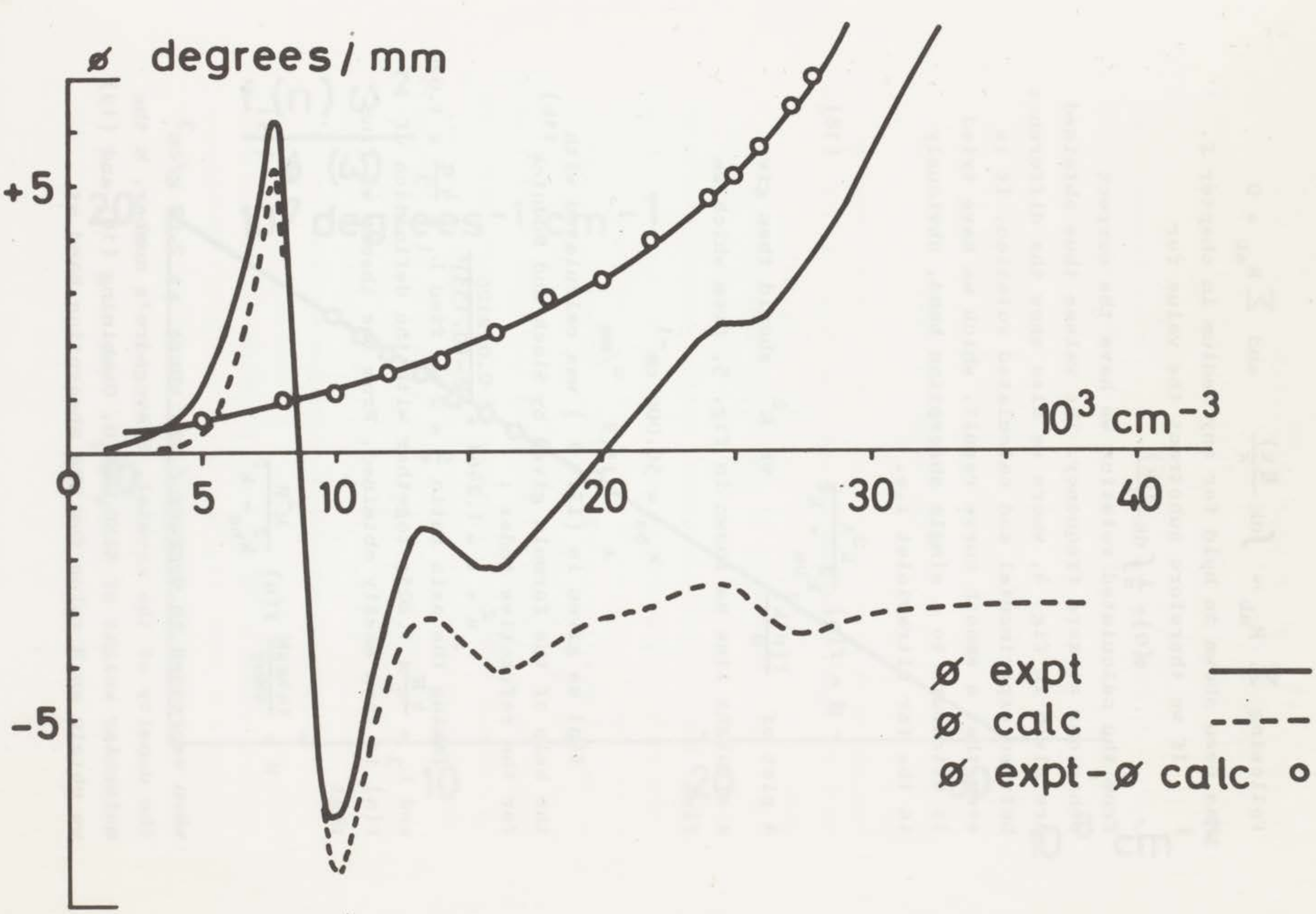
Experimental

Tetragonal crystals of the hexahydrate of nickelsulfate were grown from slightly acidified solutions at room temperature by evaporation or by controlled cooling down in a thermostat from 35°C. Large faultless crystals were easily obtained, that could be cleaved into thin plates, with smooth surfaces perpendicular to the optical axis. The direction of this axis was checked by inspection of the interference figures under the conoscope.

The absorption spectrum was measured with a Gary, model 14 spectrophotometer, circular dichroism with a Dichrographe Roussel-Jouan (Paris) and finally the optical rotation dispersion with the spectropolarimeter built by Emeis [10]. For a complete description of this instrument as well as its performance we refer to his thesis. The results are given in fig. 2-4. For k values below 12.500 cm^{-1} we have used the data obtained by Ingersoll et al. [11a] as far as the rotation and circular dichroism spectra are concerned. With the help of numerical integration of the Kramers-Kronig relations [12] the partial rotation due to the measured absorption bands was calculated from the circular dichroism data, the results of which are also given in fig. 4. The connection between ϕ and used in this calculations is:

$$\phi(k) = \frac{2}{\pi}\, \mathcal{P}\int_0^\infty dk' \frac{k'\theta(k')}{k'^2 - k^2} \qquad (17)$$

It is seen that ϕ (0) is possibly different from zero since θ(k) is only known for a restricted part of the spectrum. The rotation must however vanish at zero frequency for any band separately because we then cannot have any spatial dispersion. Complete knowledge of θ(k) would give the correct ϕ because as we will see in the


ø degrees/mm
+5
-5
10^3 cm^{-3}
0
5
10
20
30
40
ø expt
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following $\sum R_{ab} \sim \int dk \frac{\theta(k)}{k}$ and $\sum R_{ab} = 0$ has been shown to hold for any medium in chapter I.

If we therefore substract the value for

$$\phi(0) = \frac{2}{\pi}\int dk \frac{\theta(k)}{k}$$

from the calculated rotation we have the correct behaviour at zero frequency. The values thus obtained are given in fig. 4, where we also show the difference between experimental and calculated rotation. It is seen that a smooth curve result, which we have tried to attribute to a single absorption band, obviously in the far ultraviolet i.e.

$$\varnothing = f(n) \frac{k^2 A}{k_{ba}^2 - k^2} \qquad (18)$$

A plot of $\frac{f(n)k^2}{\varnothing}$ vs k^2 should then give a straight line as shown in fig. 5, from which we find

$$k_{ba} = 56.000 \text{ cm}^{-1}$$

$$A = 15{,}8 \ {}^{\circ}/\text{mm}$$

f(n) as given in (II, 9) was calculated with the help of the formula given by Slack and Rudnick[11b)] for the refractive index :

$$n^2 - 1 = 1.2461 + \frac{0.012126}{\lambda^2 - (0.135)^2}$$

Taking the axis ratio $\frac{c}{a} = 2$ we find $L_1 = \frac{4\pi}{3} \times 1.020$ and $L_3 = \frac{4\pi}{3} \times 1.205$; together with the definition of f(n) is then easily obtained. From the theory we find that

$$\varnothing = \frac{144\pi\rho N}{4Mhc} f(n) \frac{k^2 R}{k_{ba}^2 - k^2} \qquad (19)$$

when expressed in degrees / mm, where $\rho = 2.07$ g/cm^3 the density of the crystal, N Avogadro's number, M the molecular weight of $NiSO_4.6H_2O$. Combining (18) and (19) we obtain an R value for the absorption band at

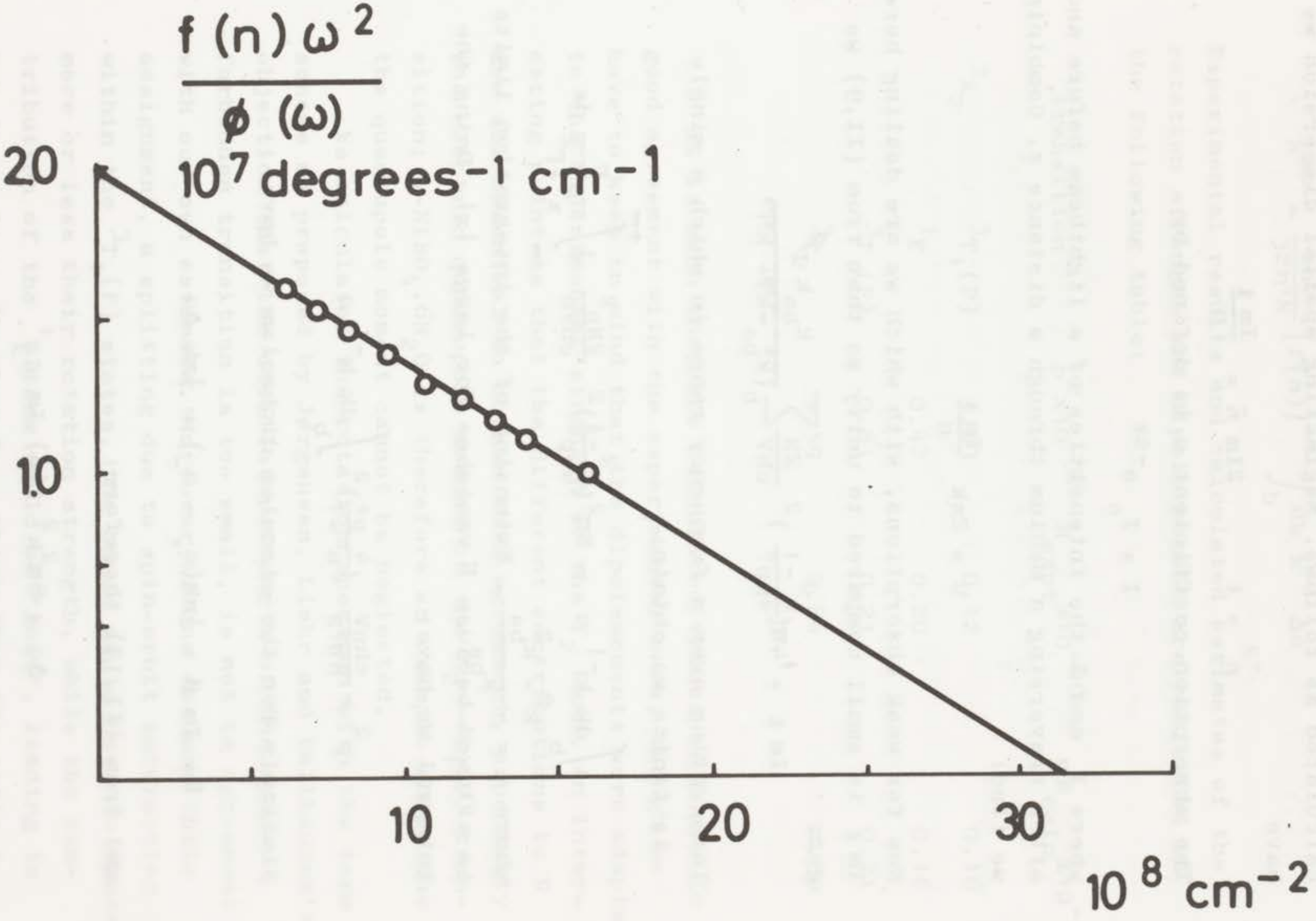

Fig 5

56,000 cm^{-1} : $R = 0.59 \times 10^{-38}$

The experimental values for the dipole moments are calculated as follows. Neglecting spatial dispersion we have

$$\tilde{n}^2 = \varepsilon \qquad 2\mathrm{Im}\ \tilde{n} = \frac{\mathrm{Im}\ \varepsilon}{n}$$

The absorption coefficient α is defined by

$$I = I_o\ e^{-\alpha z}$$

where I_o and I the intensities of a lightbeam before and after traversing a medium through a distance z. Combining we find:

$$\alpha = 2\pi k\ \frac{\mathrm{Im}\ \varepsilon}{n}$$

Now for weak absorptions, with which we are dealing here $\mathrm{Im}\ \varepsilon$ is small compared to unity so that from (II,9) we get:

$$\mathrm{Im}\ \varepsilon = 4\pi\left(\frac{n^2-1}{4\pi p^\circ}\right)^2 \frac{2N}{chV} \sum_b \frac{k_{ba} k\ p^2}{(k_{ba}^2-k^2)^2 + k^2\Gamma^2}$$

Integrating over a frequency range in which a single is finite we obtain:

$$\int_b dk\ k^{-1}\ \alpha = 8\pi^2\left(\frac{n^2-1}{4\pi p^\circ}\right)^2 \frac{2Np^2}{chVn}\ \frac{1}{2}\int_{-\infty}^{+\infty} \frac{\Gamma}{x^2+\Gamma^2}\,dx$$

where $x = \dfrac{k^2 - k_{ba}^2}{k_{ba}}$. Extension of the integration limits is allowed because Γ vanishes for large $|x|$. Doing the integral we have:

$$p^2 = \frac{chnV}{8\pi^3 N}\ \left(\frac{4\ p^\circ}{n^2-1}\right)^2 \int_b dk\ k^{-1}\ \alpha$$

Similarly for the circular dichroism we have:

$$\theta = \mathrm{Im}\ \phi = \tfrac{1}{2}\pi k(\alpha_+ - \alpha_-) = \tfrac{1}{2}\pi k\ \Delta\alpha$$

and from (II,13) therefore:

$$\Delta\alpha = 8\pi^2 k^2\ f(n)\ \mathrm{Im}\ g_3$$

Ex

so that for the rotation strength:

$$R^{ab} = \frac{chV}{32\pi' N} \left\{ f(n) \right\}^{-1} \int_b dk\, k^{-1}\, \Delta\alpha$$

Experimental results and calculated estimates of the rotation strength and dipole moment are collected in the following table:

transition		$p^2 x10^{-38}$	$R_{expt} x10^{-40}$	$R_{calc} x10^{-40}$
$^3A_2$	$^3T_1(P)$	1.23	0.12	0.16
	^1E	0.42	0.20	0.16
	$^3T_1(F)$	0.81	0.21	0.21
	$^3T_2$	1.59	2.84	2.80

It is seen that the calculated values of R are in good agreement with the experimental ones, though we have to keep in mind that the dipolemoments were adapted to the experimental strength of the T_2 band. An interesting point is that the different contributions to R are all essential to obtain this agreement, especially the electric quadrupole moment of the $A_2 \longrightarrow T_1(P)$ transition; α-$NiSO_4.6H_2O$ is therefore an example where the the quadrupole moment cannot be neglected.

We calculated the rotation spectrum with the term scheme as proposed by Jørgensen. Liehr and Ballhausen's objection that the oscillatorstrength of the spin-forbidden transition is too small, is not in agreement with our own estimate. Moreover if one assumes their assignment, a splitting due to spin-orbit interaction within the $^3T_1(F)$ states, the bands would have to share more or less their rotation strength, while the contribution of the ^1E term would be "lost", leading to too low values. We therefore think that the optical measurements of this crystal support Jørgensen's proposal. This by the way shows that optical activity might be an important tool in solving questions of band assignment and that, when at least the crystalline form is gyrotropic, the compound itself doesn't have to be asymmetric. It is seen that the calculations are relatively easy for transition metal compounds and that, since for the forbidden d-d transitions the R_r are small, the crystal structure need not be known.

Finally the rotation dispersion, being easier accessible than that of the refractive index, affords a means of obtaining information of absorption bands in the far-ultraviolet, as we have seen. One could even hope for more, because according to the sumrule for the R^{ab} still another strongly active band with opposite sign must be present. The only thing that can be said on the basis of our experimental data is that this band should be situated at 96,000 cm^{-1} or even higher.

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Samenvatting

Metingen van de natuurlijke optische activiteit vormen een waardevolle uitbreiding van de gebruikelijke absorptie metingen, daar hieruit informatie over het magnetisch dipool en het electrisch quadrupool moment te verkrijgen is. In de anorganische chemie echter komen slechts een gering aantal verbindingen voor, die de voor de eigenschap van optische activiteit noodzaklijke asymmetrie bezitten. Deze asymmetrie is echter door inbouw in een geschikt kristal aan te brengen; een voorbeeld hiervan is het octaëdrisch omringde Ni^{2+}-ion, dat als zodanig te symmetrisch is, maar in het α-$NiSO_4.6H_2O$ optische activiteit vertoont.

In het eerste hoofdstuk wordt met de oorzaak van het verschijnsel van optische activiteit, de op atomaire schaal merkbare variatie van het electromagnetische veld, in een niet nader omschreven medium rekening gehouden. Om ook de in de scheikunde juist zo interessante anomale rotatie dispersie en het circulair dichroïsme te beschrijven wordt uitgegaan van een modelsysteem bestaande uit een oneindig uitgebreid medium waarin zich licht bevindt. Tengevolge van de wisselwerking van dit licht met de geladen deeltjes die het medium vormen kan dan op eenvoudige wijze worden aangetoond dat er licht verdwijnt en er dus absorptie optreedt. Hiertoe is het echter noodzakelijk ook het electromagnetische veld te kwantizeren, hetgeen met behulp van het Gupta-Bleuler formalisme gedaan wordt. Nadat de reactie van het materiële systeem op het electromagnetisch berekend is worden verwachtingswaarden genomen en kan verder de klassieke theorie worden toegepast. Met behulp van Ewald's uitdovingsstelling wordt een connectie met de physische realiteit van een eindig medium verkregen. Tevens wordt een criterium aangegeven dat bepaalt wanneer de toepasbaar-

heid van een eerste orde ontwikkeling van de ruimtelijke dispersie gerechtvaardigd is, zodat de theorie ook voor grote moleculen van toepassing kan zijn.

In hoofdstuk II wordt aangetoond dat de verkregen uitdrukkingen leiden tot de resultaten voor kleine moleculen en wordt een voor experimentele doeleinden bruikbare macroscopische vergelijking van de lichtvoortplanting in kristallen afgeleid.

Deze wordt tenslotte in hoofdstuk III op het α-$NiSO_4.6H_2O$ toegepast. Hierbij blijkt dat het electrisch quadrupool moment een niet te verwaarlozen bijdrage levert en dat de door Jørgensen op experimentele gronden voorgestelde interpretatie van het spectrum van Ni^{2+} in een liganden veld kan worden onderschreven.

Met behulp van de Kramers-Kronig relaties wordt de rotatie van een in het verre ultraviolet gelegen absorptie band van die in het zichtbare gebied gescheiden en de ligging van de eerst genoemde bepaald.

Op verzoek van de Faculteit der Wiskunde en Natuurwetenschappen volgt hier een overzicht van mijn academische studie.

Na het behalen van het diploma gymnasium-B aan het Maerlant Lyceum te Den Haag in 1956, begon ik dat jaar met de scheikunde studie aan de Rijksuniversiteit te Leiden. Het kandidaatsexamen, letter F, werd in 1959 afgelegd, waarna ik mij onder leiding van de hoogleraren Dr. A.E. van Arkel, Dr. L.J. Oosterhoff en Dr. C. Visser op het doctoraal examen voorbereidde, dat in 1962 werd afgelegd, met als hoofdvak anorganische scheikunde.

In 1960 werd ik als assistent aan het Laboratorium voor Anorganische en Fysische Chemie aangesteld, in 1962 als hoofdassistent, later dat jaar tot wetenschappelijk ambtenaar benoemd.

Sedert 1967 ben ik als wetenschappelijk medewerker werkzaam op het Natuurkundig Laboratorium van de N.V. Philips' Gloeilampenfabrieken.

Na mijn doctoraal examen werd onder leiding van Prof.Dr. A.E. van Arkel, naderhand onder Prof.Dr. E.W. Gorter een onderzoek uitgevoerd aan gemengde verbindingen van zuurstof en stikstof. In 1964 werd met het in dit proefschrift beschreven onderzoek een begin gemaakt.

Bij het tot stand komen van dit proefschrift wil ik graag van mijn dankbaarheid blijk geven jegens Dr. C.A. Emeis die de metingen van de optische rotatie dispersie deed en Mevr. G. de Vries, die de computer berekening van de Kramers-Kronig relaties uitvoerde.

De directie van het Natuurkundig Laboratorium ben ik zeer erkentelijk voor de gelegenheid die zij mij gegeven heeft het manuscript te voltooien.

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