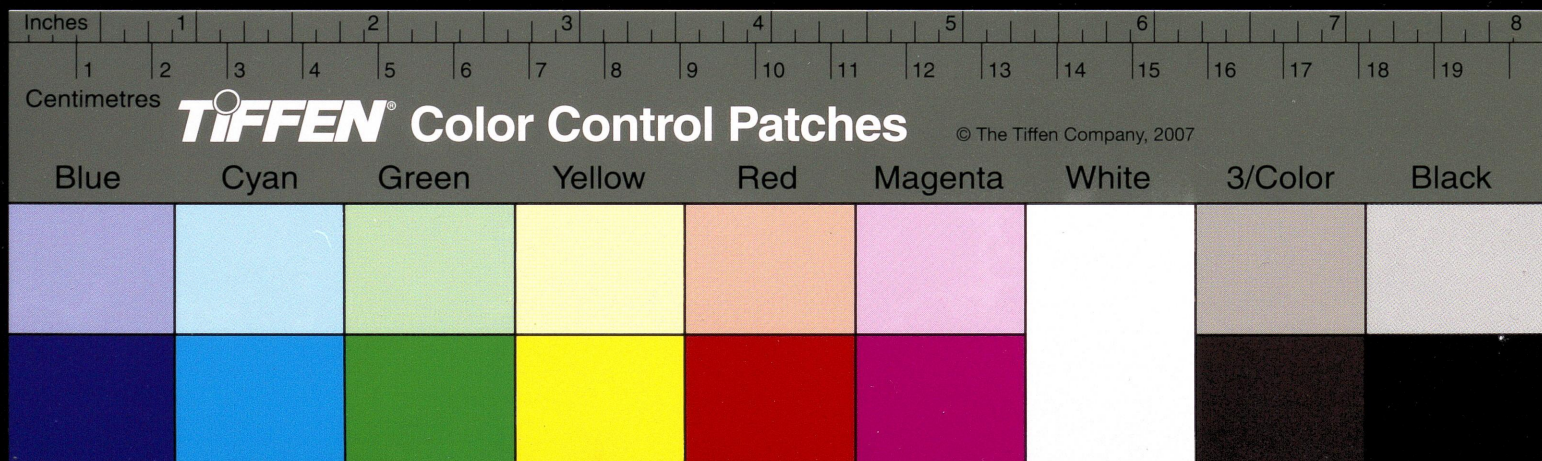


On the optical anisotropy of molecular crystals.

Introduction: Studies in the birefringence of liquids and the depolarisation of light scattered by liquids have shown that the effect of increasing the density is to cause an apparent diminution in the optical anisotropy of the molecule and this has been ascribed to the mutual influence of the molecules. In a recent paper by S. B. Hendricks and W. E. Demming it has been shown ~~the~~ by examining a number of oxalate crystals that, as a class, molecular crystals show extraordinarily high birefringence as compared with simple ionic compounds and ^{this is} ascribed ~~this~~ to molecular interaction. It is proposed here to apply the general theory of the propagation of a plane wave in a point lattice, due to Ewald ^{and Born,} to derive and separate out the effect of this mutual coupling action of the molecules. The complete theory required is developed in ^{Pr.} Born's articles in the *Enzy. & Handbuch*.

(§1) Before applying this general method of the electromagnetic lattice potential, it might be pointed out that the above mentioned diminution in anisotropy when the mutual influence is taken into consideration, can also be shown ~~is~~ to be true when we consider a molecular crystal and treat it as a lattice of dipoles and consider the potential due to a static doublet.

Let the lattice be assumed rhombic with the lattice constants a, b, c and taking for origin that molecule ^{on} for which we wish to ascertain the influence of the remaining ones we can take the coordinates x, y, z of any other molecules as $(n_1 a, n_2 b, n_3 c)$



where n_1, n_2, n_3 are integers. The potential due to a doublet at r is given by $(p, \text{grad } \frac{1}{r}) = \frac{xp_x + yp_y + zp_z}{r^3}$ where p is the moment of the dipole. Hence the components of the force due to this potential are given by

$$F_x = -\frac{\partial \phi}{\partial x} = \frac{1}{r^5} \{ p_x(3x^2 - r^2) + 3xy p_y + 3xz p_z \}$$

$$\begin{aligned} \text{Hence the total force } E_x' &= \sum F_x = \sum \frac{1}{(\alpha^2 n_1^2 + \dots)^{5/2}} \left[p_x(2n_1^2 a^2 - n_2^2 b^2 - n_3^2 c^2) \right. \\ &\quad \left. + 3n_1 n_2 p_y + 3n_1 n_3 p_z \right] \\ &= S_{11} p_x + S_{12} p_y + S_{13} p_z \end{aligned}$$

From considerations of symmetry $S_{12} = S_{13} = 0$. We can take the principal polarisabilities $\alpha_1, \alpha_2, \alpha_3$ ($\alpha_1 > \alpha_2 > \alpha_3$) in the directions of the x, y, z axes + if $\alpha_1', \alpha_2', \alpha_3'$ represent these quantities when we take the above mutual field into consideration, the relation between α_i + α_i' can be put formally as

$$\begin{aligned} \alpha_1 E_x &= \alpha_1' E_x' = \alpha_1' (E_x + E_x') \\ &= \alpha_1' (E_x + S_{11} p_x) \\ &= \alpha_1' (E_x + \frac{\alpha_1'}{\alpha_1} E_x) \text{ using an approximation} \end{aligned}$$

$$\text{i.e. } \alpha_1 = \alpha_1' + S_{11} \alpha_1'^2$$

$$\text{Similarly } \alpha_2 = \alpha_2' + S_{22} \alpha_2'^2$$

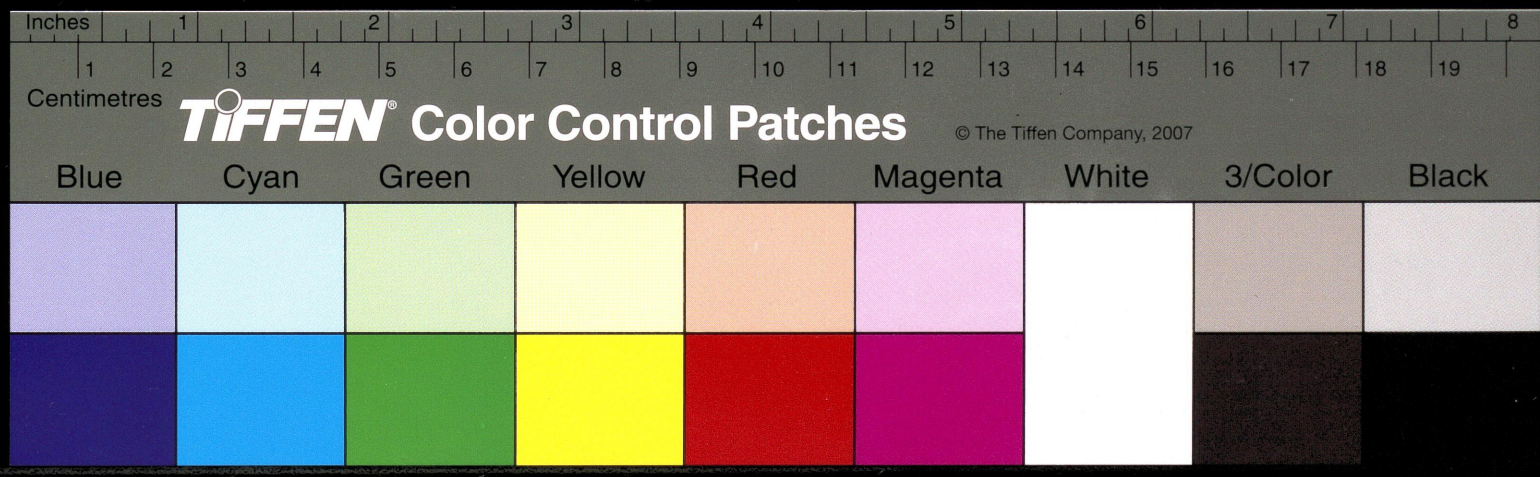
$$\alpha_3 = \alpha_3' + S_{33} \alpha_3'^2$$

$$\therefore \alpha_1 - \alpha_2 = (\alpha_1' - \alpha_2') + (S_{11} \alpha_1'^2 - S_{22} \alpha_2'^2)$$

Thus $\alpha_1' - \alpha_2' < \alpha_1 - \alpha_2$ or there is diminution of isotropy if $S_{11} > S_{22}$ (since $\alpha_1' > \alpha_2'$).

$$\text{We can write } S_{11} - S_{22} = 3 \sum_{n_1, n_2, n_3} \frac{n_1^2 a^2 - n_2^2 b^2}{(n_1^2 a^2 + n_2^2 b^2 + n_3^2 c^2)^{5/2}}$$

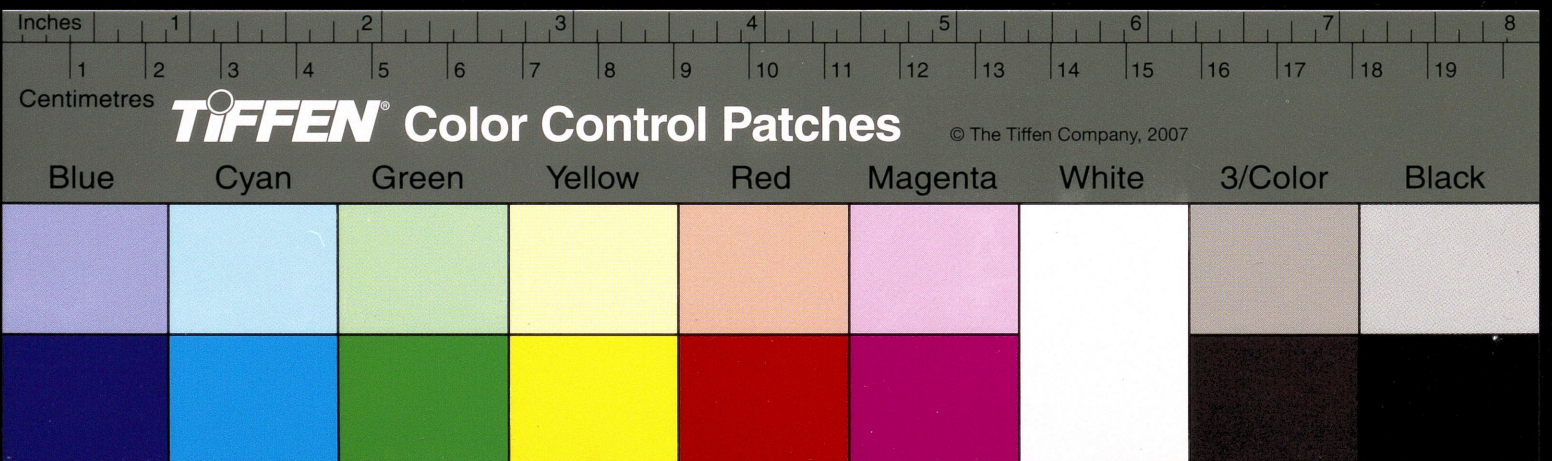
of $a \geq b$, it appears highly probable that $S_{11} > S_{22}$. A can be shown that



the proof of this would involve the transformation ^{an integral involving} ~~to~~ ~~series by use~~
of elliptic modular functions ~~and the proof is not yet complete~~
~~but there appears a definite probability that it is true.~~ It can
similarly be shown that $\alpha_2 - \alpha_3$ and $\alpha_1 - \alpha_3$ also diminish provided
 $a < b < c$
~~or vice versa~~. An interesting result may also be noted that if we take
 $a = b = c$ i.e. a cubic crystal it follows that $S_{11} = S_{22} = S_{33}$ so that
the anisotropy is unchanged a result already obtained by
Lorentz and also pointed out by Darwin. The assumption of
a rhombic lattice appears therefore material to the
investigation and is in accord with the remark of Ewald that
optical anisotropy in crystals does not merely depend upon
the arrangement of isotropic particles but that structural

effect plays a great part. A defect in the above investigation is
that the sums S are taken throughout space without paying any
attention to the boundaries of the crystal but it cannot be said
to be absolutely of no value that if it be observed that the
sums in question are ~~for convergent~~ represented by convergent
series.

§2. In the general investigation of the propagation of a plane light
wave in a general crystal, the particles are taken as excited by
the incident optical wave and behave as oscillating Hertzian
doublets. Let the electromagnetic plane wave in the lattice
be due to the displacements of the lattice points according to
the formula



$$u_k^l = \mathcal{U}_k e^{-i\omega t} e^{i\tau(s+r_k^l)} \quad \left[\tau = \frac{2\pi}{\lambda} \right] \quad (1)$$

accompanied by an electromagnetic field described by the usual Hertzian vector

$$\mathcal{Z} = \mathcal{Y} e^{-i\omega t} e^{i\tau(s+r)} \quad (2)$$

satisfying the wave equation

$$\nabla^2 \mathcal{Z} - \frac{1}{c^2} \frac{\partial^2 \mathcal{Z}}{\partial t^2} = 0 \quad (3)$$

and the field being given by

$$\left. \begin{aligned} \mathcal{E} &= \text{grad div } \mathcal{Z} - \frac{1}{c^2} \frac{\partial^2 \mathcal{Z}}{\partial t^2} \\ \mathcal{H} &= \frac{1}{c} \text{rot } \frac{\partial \mathcal{Z}}{\partial t} \end{aligned} \right\} \quad (4)$$

The ^{space} vector \mathcal{Y} must be analytic everywhere except at r_k^l where it should have a simple pole of residue $e_k \mathcal{U}_k = p_k$, should be periodic in the lattice and should satisfy the differential equation obtained by

substituting (2) in (3). These conditions are satisfied if we take

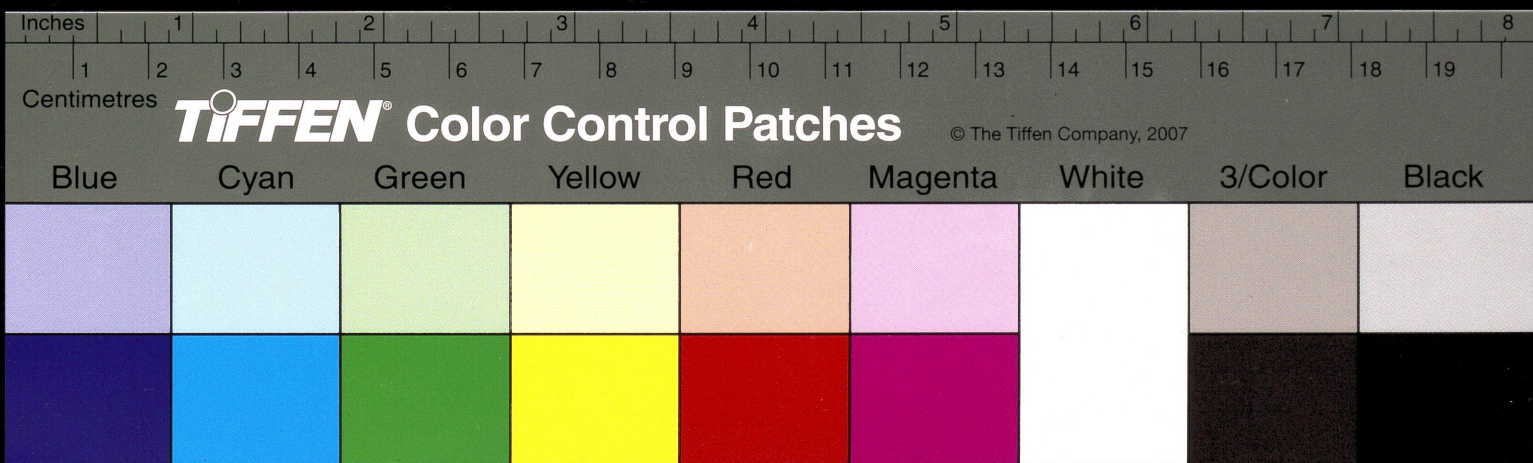
$$\mathcal{Y} = \sum_k p_k S(r - r_k)$$

where again S is periodic, satisfies a similar differential equation to \mathcal{Y} and is of the form $\frac{1}{r} + \text{Analytic function}$. The classical method of the electromagnetic potential now consists in assuming for S the triple Fourier Series

$$S = \sum_l \sigma_l e^{i(q^l r)}$$

where $q^l = 2\pi(l_1 b_1 + l_2 b_2 + l_3 b_3)$ and b_1, b_2, b_3 are the fundamental vectors of the reciprocal lattice i.e. $b_1 = \frac{1}{\Delta} [a_2 a_3]$, etc and determine it so as to satisfy the above conditions. Such a solution is possible and gives for S

$$S = \frac{4\pi}{\Delta} \sum_l \frac{e^{i(q^l r)}}{(q^l + \tau s)^2 - \frac{\tau^2}{n^2}} \quad (5) \quad \left[n = \frac{c\tau}{\omega} \right]$$



This series is non-uniformly convergent and cannot be differentiated term by term and is not suitable to determine ϵ from equation (4). By the application of Ewald's theta-transformation formula it can however be brought reduced to a form satisfying all the conditions above postulated for S and which is moreover rapidly convergent. This form is

$$S = \sum_L \frac{e^{i\tau(r_k^L - r, s) + \frac{i\tau}{n}|r_k^L - r|}}{|r_k^L - r|}$$

and gives for Z the expression

$$Z = e^{-i\omega t} \sum_K \sum_L p_K e^{i\tau(r_k^L, s)} \frac{e^{\frac{i\tau}{n}|r_k^L - r|}}{|r_k^L - r|} \quad (6)$$

The electromagnetic field which acts on a particular point particle is naturally that due to the remaining particles and the Hertzian vector of this "exciting field" is obtained from the above by omitting the term $k'=k, l'=l$ in

$$Z_K^L = e^{-i\omega t} \sum_{K'} \sum_{L'} \frac{e^{i\tau[(r_{K'}^{L'}, s) + \frac{1}{n}|r_{K'}^{L'} - r|]}}{|r_{K'}^{L'} - r|} \quad (7)$$

Taking into consideration the periodicity of Ψ and S we can put $l=0$ &

obtain

$$Z_K^L = e^{-i\omega t} e^{i\tau(r_k^L, s)} \sum_{K'} \Psi_{KK'} p_{K'} \quad (8)$$

If F_K^L be the electromagnetic force acting on the particle r_k^L we can

write $F_K^L = [e_K \epsilon]_{r_k^L}$ (neglecting the magnetic part)

$$= e_K \left[\text{grad div } Z_K^L + \frac{\tau^2}{n^2} Z_K^L \right]_{r_k^L}$$

and the x -component of F_K^L is given by

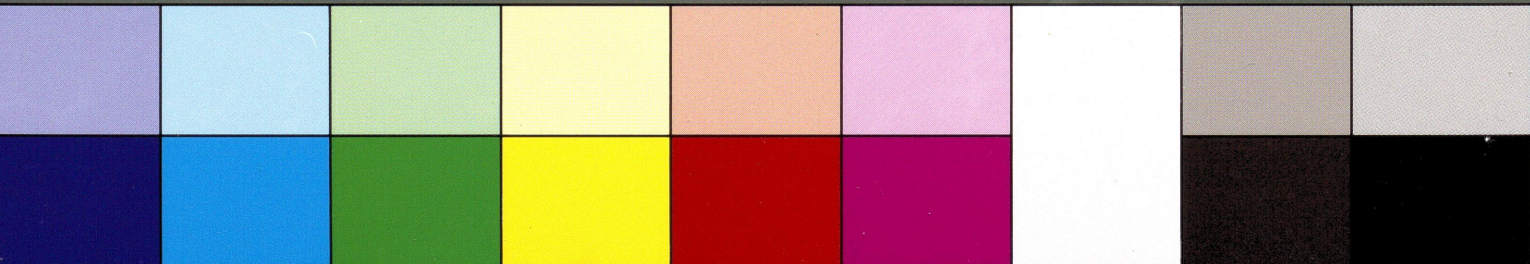
$$F_{Kx}^L = e_K e^{-i\omega t} e^{i\tau(r_k^L, s)} \sum_{K'} \sum_y \left(\frac{\partial^2 \Psi_{KK'}}{\partial x \partial y} + \delta_{xy} \frac{\tau^2}{n^2} \Psi_{KK'} \right)_{r_k^L} p_{K'y} \quad (9)$$

Inches 1 2 3 4 5 6 7 8

Centimetres 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19

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We now proceed to the limiting case of visible light i.e. large λ compared with the cell dimensions and put $\tau = 0$. The Ψ reduces to Ewald's electrostatic lattice potential ϕ satisfying the equation

$$\Delta \phi = 4 \nabla^2 \phi = \frac{4\pi}{\Delta} \text{ and not } \nabla^2 \phi = 0 \text{ and eqn (9) becomes (neglecting time part)}$$

$$F_{Kx}^l = e_k \bar{E}_x + \sum_{K'} \sum_y \left[\begin{matrix} K & K' \\ x & y \end{matrix} \right]^{(e)} \sigma_{K'y} \quad (10)$$

the first term on the right arises from the constant term $l=0$ in the Fourier expansion for S and denotes the product of e_k with the mean electric field which is what would be observed if the interaction given by the second term were absent. In the notation of Electrostatic lattice potential theory

$$\left[\begin{matrix} K & K' \\ x & y \end{matrix} \right]^{(e)} = e_k e_{k'} \left[\frac{\partial^2 \phi}{\partial x \partial y} \right]_{r_{KK'}} \quad (11)$$

Specialising now to the case of a crystal lattice which is regular and in which a lattice point is so symmetrically situated that the resulting field of the remaining particles in its immediate neighbourhood is spherically symmetric,

and using $\nabla^2 \phi = 4\pi/\Delta$ we can write

$$\left[\begin{matrix} K & K' \\ x & x \end{matrix} \right]^{(e)} = \left[\begin{matrix} K & K' \\ y & y \end{matrix} \right]^{(e)} = \left[\begin{matrix} K & K' \\ z & z \end{matrix} \right]^{(e)} = \frac{4\pi}{3} \frac{e_k e_{k'}}{\Delta}$$

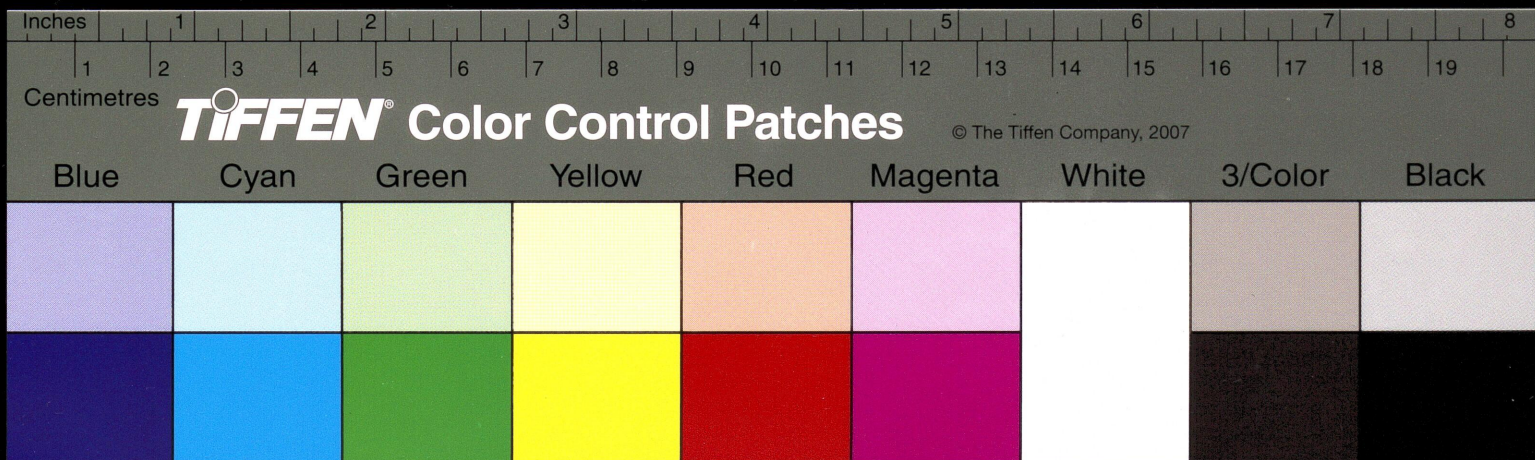
$$\left[\begin{matrix} K & K' \\ x & y \end{matrix} \right]^{(e)} = 0 \quad (x \neq y)$$

Eqn (10) becomes in this case

$$F_{Kx}^l = e_k \bar{E}_x + \sum_{K'} \frac{4\pi}{3} \frac{e_k e_{k'}}{\Delta} \sigma_{K'y} \quad (12)$$

A final simpler form can be obtained by assuming a simple lattice i.e. where there is only one basis index. (12) in this case

$$\text{becomes } F_{Kx}^l = e_k \bar{E}_x + \frac{4\pi}{3} e_k \sigma_{Kx} \quad (13)$$



• Formula (13) can be made to yield the results about anisotropy.

Writing $F_{Kx}^l = e_K \bar{E}_x^l$ and taking the bar from \bar{E} we can write

$$E_x^l = E_x + \frac{4\pi}{3\Delta} p_x$$

Assuming, as in §1, $\alpha_1, \alpha_2, \alpha_3$ in the x, y, z directions we get

$$\alpha_1 = \alpha_1' + \frac{4\pi}{3\Delta} \alpha_1' \alpha_1$$

$$\text{Similarly } \alpha_2 = \alpha_2' + \frac{4\pi}{3\Delta} \alpha_2' \alpha_2$$

$$\therefore (\alpha_1 - \alpha_2) = (\alpha_1' - \alpha_2') + \frac{4\pi}{3\Delta} (\alpha_1' \alpha_1 - \alpha_2' \alpha_2) \quad (14)$$

which shows that anisotropy is diminished. Measuring anisotropy by the ratios $\alpha_1 : \alpha_2 : \alpha_3$ we can show

$$\left(\frac{\alpha_1'}{\alpha_2'}\right) \div \left(\frac{\alpha_1}{\alpha_2}\right) = \frac{1 + \frac{4\pi}{3\Delta} \alpha_2}{1 + \frac{4\pi}{3\Delta} \alpha_1} \text{ which is } < 1. \quad (14')$$

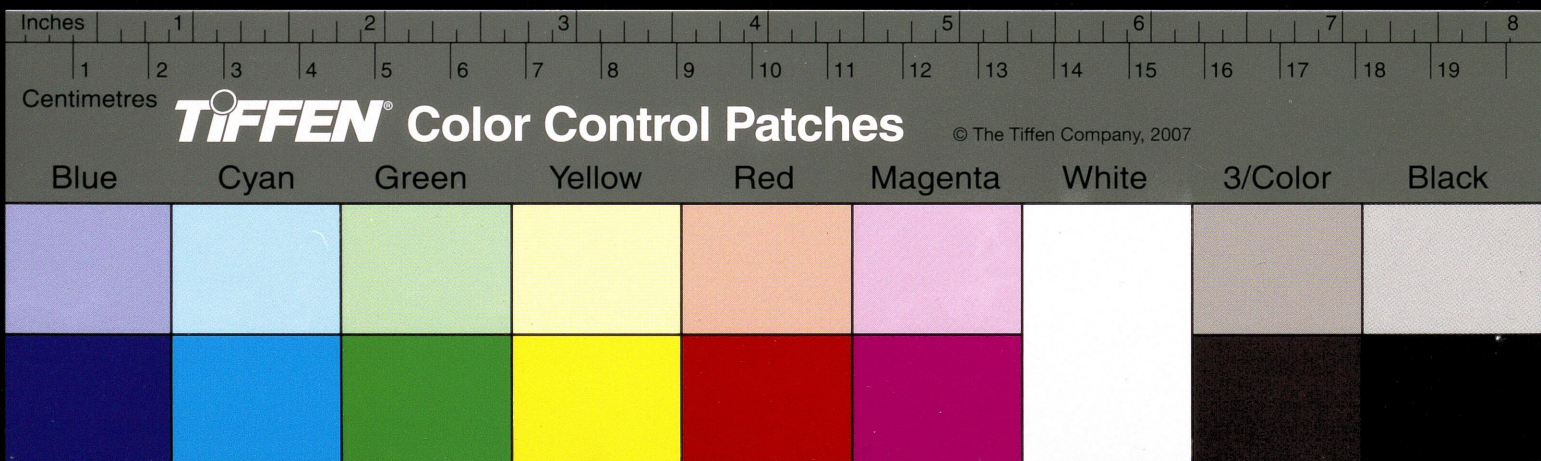
For any one of the principal polarisabilities

$$\alpha' = \frac{\alpha}{1 + \frac{4\pi}{3\Delta} \alpha} \quad (14'')$$

and $\frac{\alpha'}{\alpha}$ may be taken as a measure of the field arising out of the interaction of molecules and this is least when $\alpha = \alpha_1$ or in other words

the direction in the molecule corresponding to maximum polarisability is that along which the field due to its neighbours has a minimum value, a result obtained by Raman & Krishnan.

As regards the result of Hendricks and Deming that molecular crystals show extraordinary high frequencies birefringence as compared with ionic compounds, this is perhaps a result of the variation of Δ . In (14') the R.H.S is an increasing fn of Δ . If Δ be larger in molecular crystals there is less change of anisotropy i.e. higher birefringence.



Co₂

Coming now finally to the actual application of (14) to special substances we have for crystal sufficient data for Δ but not for $\alpha_1, \alpha_2, \alpha_3$ whereas for liquids (if we could apply (14) at all) we have, thanks to molecular refraction, Kerr effect & depolarisation of scattered light good data regarding $\alpha_1, \alpha_2, \alpha_3$ but it is difficult to see what Δ should be taken as. Perhaps it can be properly taken as the intramolecular distance. Such data is available by x-ray diffraction in liquids

