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The Theory of Forced Double Refraction

K. F. Herzfeld and R. H. Lee, *Johns Hopkins University, Baltimore*

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An attempt is made to better understand the nature of the double refraction in crystals by calculating the forced double refraction induced in rocksalt and KCl crystals through elastic stress (photoelasticity). In a previous paper only the change in the Lorentz-Lorenz force had been taken into account. In this paper is also considered the "potential dip" which is due to the forced anisotropic arrangement of the ionic charges. The formulas are developed according to classical theory and to wave mechanics but they contain too many unknown constants to be checked against experiment.

Introduction

The question how the anisotropy of noncubic crystals results in double refraction is not yet solved. Ewald[1] who investigated the question first assumed that the anisotropy of the Lorentz-Lorenz force was alone responsible. This anisotropy results from the fact that in different directions from a particle the surroundings are different. He could give only rough estimates as insufficient data were known at the time. Bragg[2] and Hylleraas[3] calculated double refraction for carbonates, nitrates, alum, quartz, Hg_2Cl_2, Hg_2Br_2 and succeeded in getting approximately correct values. They took into account not only the anisotropy of the Lorentz-Lorenz force but also that of the charges of the surrounding atoms. They could adapt the values which they ascribed to the polarizability of the constituent ions to fit their results.

If an isotropic, transparent medium is subjected to pressure perpendicular to two parallel surfaces it becomes double refractive. If one chooses as such a medium sodium or potassium chloride one has a cubic crystal made artificially double refracting by changing the structure by a known amount and has to deal only with ions, the refractivity of which is known from the investigation of the undisturbed state. For this reason Herzfeld[4] calculated the double refraction resulting from the anisotropy of the Lorentz-Lorenz force (as had been done before in an unpublished thesis by Heine[5]) and compared it with experimental results of Pockels[6] and Maris.[7] No agreement was, however, reached. In a discussion with Professor Ewald and Dr. Hermann of Stuttgart it was pointed out that the success of Bragg and Hylleraas depended on the fact that these two investigators took into account what Ewald called the potential dip. In the case of an ionic lattice the field from the electrical (excess) charges of the surrounding ions forms a potential dip at the place of the ion which we have just considered, a dip which changes the restoring force on an electron subjected to the influence of an outside electric wave. Hence the anisotropy of arrangement due to the pressure might result in an anisotropy of the potential dip and, therefore, in an anisotropy of the restoring force and of the refractive index itself. These effects are calculated here for a sodium chloride type lattice under the action of pressure. It turned out that in the undisturbed lattice the potential dip is zero to the order considered here.

General Theory of Forced Double Refraction

Following the notation of Herzfeld we consider a lattice of the rocksalt type compressed in the

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[1] P. P. Ewald, *Thesis*, Munich, 1912; Ann. d. Physik **49**, 1 (1916).

[2] W. L. Bragg, Proc. Roy. Soc. **A105**, 370 (1924); **A106**, 346 (1924).

[3] E. Hylleraas, Zeits. f. Physik **36**, 859 (1926); **44**, 871 (1927).

[4] K. F. Herzfeld, J.O.S.A. **17**, 1 (1928).

[5] W. Heine, *Thesis*, Munich, 1922.

[6] F. Pockels, Ann. d. Physik **39**, 440 (1890).

[7] H. B. Maris, J.O.S.A. **15**, 194 (1927).

z direction. The outside electrical field might have either the z or the y direction. We call the electrical moment induced in a positive ion $p_{\|+}$ and $p_{\perp+}$ respectively in the two cases. For the negative ions we have similarly $p_{\|-}$ and $p_{\perp-}$. If we have N ions of each kind per cubic centimeter the total polarization is

$$P_{\|} = Np_{\|+} + Np_{\|-}. \tag{1}$$

The connection with the refractive index is

$$(n_{\|}^2 - 1)/n_{\|}^2 = 4\pi P_{\|}/D, \tag{2}$$

where D is the electric displacement. Furthermore the moment p of an ion is given by

$$p = (3r/4\pi)(D + E'), \tag{3}$$

where E' is the field at the place of the ion due to all the other ions and is, in the undisturbed lattice, given by

$$E' = -4\pi P + (4/3)\pi P, \tag{4}$$

where the second term on the right side of the equation is the Lorentz-Lorenz force. $3r/4\pi$ is the polarizibility of the ion and is given by

$$r = \sum_i f_i e^2/3\pi m(\nu_i^2 - \nu^2). \tag{5}$$

When pressure is applied, the lattice is compressed in the z direction so that the lattice distance becomes $a_0(1+\delta_{\|})$ in the z direction and $a_0(1+\delta_\perp)$ in the x and y directions. That modifies the factor $(4/3)\pi$ in (4) as well as r in (3).

Assume that in the parallel case the Lorentz-Lorenz force on a positive ion gives

$$E'_{\|+} = -\tfrac{2}{3}4\pi N(p_{\|+} + p_{\|-}) + 4\pi N(\alpha_{\|} p_{\|+} + \beta_{\|} p_{\|-})\delta, \tag{6}$$

where

$$\delta = \delta_{\|} - \delta_\perp.$$

The coefficients of $p_{\|+}$ and $p_{\|-}$ are different because the positive ion considered is not arranged geometrically in the same way in respect to other positive ions as in respect to negative ions; but for $E'_{\|-}$, the force on negative ions, p_+ and p_- are exchanged.

CALCULATION OF LORENTZ-LORENZ FORCE

E' is due to the action of all other ions, each polarized in the z direction by a homogeneous field, on the ion considered, which we locate at the origin. The potential of a dipole is $-p(\partial/\partial z)(1/r)$. Accordingly the resultant potential at the origin is

$$V_1 = -p_+(\partial/\partial z) \sum_+ (1/r) - p_-(\partial/\partial z) \sum_- (1/r), \tag{7}$$

where the summations have to be extended, respectively, over all positive and negative ions, excluding the one at the origin. It follows that

$$E' = -(\partial V_1/\partial z) = +(\partial^2/\partial z^2)\left[p_+ \sum_+ (1/r) + p_- \sum_- (1/r)\right]. \tag{8}$$

From this, Herzfeld has calculated

$$\alpha_{\|} = -0.585, \quad \alpha_\perp = -0.081,$$
$$\beta_{\|} = 1.248, \quad \beta_\perp = -2.255. \tag{9}$$

CALCULATION OF THE POTENTIAL DIP

The potential due to the excess charges is

$$V_2 = e \sum_+ (1/r) - e \sum_- (1/r). \tag{10}$$

The electric field E' is $-e\partial V_2/\partial z$ and is zero at the origin, because of the symmetry of the arrangement. The restoring force on an electron k in the z direction is defined by

$$(-e)E_z = -kz = (-e)[E(z=0) + z\partial E/\partial z], \tag{11}$$

where z is the small deviation of the electron from the origin. Therefore

$$\frac{k}{e} = -\frac{\partial^2 V_2}{\partial z^2} = -\left[e\frac{\partial^2}{\partial z^2}\sum_+ \frac{1}{r} - e\frac{\partial^2}{\partial z^2}\sum_- \frac{1}{r}\right]. \tag{12}$$

Comparing with (8), one sees that no new coefficients are needed but that

$$k_+/e = -4\pi Ne[\alpha - \beta]\delta. \tag{12'}$$

There, k and $\alpha - \beta$ take simultaneously either the index $\|$ or the index $\perp$. That applies to positive ions. For negative ions the ions of like sign (i.e., contributing the coefficient α) have the opposite charge, k_- has the opposite sign.

For an undistorted rocksalt lattice the charges contribute nothing to the restoring force.

The task of calculating the influence of the additional restoring force on r is different according to the classical and the quantum theory.

Classical Theory

The restoring force on one electron without the potential dip, is

$$k^0=4\pi^2 m\nu_j^{02}. \tag{13}$$

The restoring force in the distorted lattice is then

$$k^0+k=4\pi^2 m(\nu_j^{02}+\Delta\nu_j^2). \tag{13$'$}$$

The corresponding addition to each term of (5) is

$$-\frac{f_j e^2}{3\pi m(\nu_j^2-\nu^2)}\frac{\Delta\nu_j^2}{\nu_j^2-\nu^2}=\pm\frac{f_j e^2}{3\pi m(\nu_j^2-\nu^2)}\frac{e^2}{4\pi^2 m}4\pi\frac{N\delta(\alpha-\beta)}{\nu_j^2-\nu^2}=\pm\frac{f_j e^2}{3\pi m(\nu_j-\nu^2)}\frac{e^2 N\delta(\alpha-\beta)}{\pi m(\nu_j^2-\nu^2)}, \tag{14}$$

where the sign is the sign of the charge of the ion.

According to Herzfeld and Wolf, it is possible to represent the mol refraction of rocksalt and sylvin by three terms

$$[(n^2-1)/(n^2+2)]=(e^2N/3\pi m)([f_1/(\nu_1^2-\nu^2)]+[f_2/(\nu_2^2-\nu^2)]+[f_3/(\nu_3^2-\nu^2)]). \tag{5$'$}$$

Of these, the third was attributed to the positive ion, the first two to the negative. If we change the numbering of the terms and call them (including the common factor outside the bracket) P_1, P_2, P_+ designate the second term in (5′) by P_1 (which is by far the largest and is due to the negative ion), the first term P_2 and the last P_+ we can, upon introducing the values α and β from (9), write for $n_{||}'-n_\perp'$, the difference due to the potential dip,

$$\frac{(n_{||}'-n_\perp')2n}{(n^2+2)^2}=-\frac{4.007}{f_1}P_1^2\left[1+\frac{P_2}{P_1}\frac{\nu_1^2-\nu^2}{\nu_2^2-\nu_2}-\frac{P_+}{P_1}\frac{\nu_1^2-\nu^2}{\nu_+^2-\nu^2}\right]\delta, \tag{15}$$

since

$$(n^2-1)/(n^2+2)=P_1+P_2+P_+=P_1[1+(P_2/P_1)+(P_+/P_1)].$$

Division of Eq. (15) by $(n^2-1)^2/(n^2+2)^2$ and multiplication by $(n^2-1)^2/2n$ gives us finally

$$n_{||}'-n_\perp'=-\frac{(n^2-1)^2}{2n}\frac{4.007}{f_1}\left\{\frac{\left(1+\dfrac{P_2}{P_1}\dfrac{\nu_1^2-\nu^2}{\nu_2^2-\nu^2}-\dfrac{P_+}{P_1}\dfrac{\nu_1^2-\nu^2}{\nu_+^2-\nu^2}\right)}{\left(1+\dfrac{P_2}{P_1}+\dfrac{P_+}{P_1}\right)^2}\right\}\delta. \tag{16}$$

It should be noted that in deriving Eqs. (6), (15) and (16) no account was taken of the change in N, the number of molecules per cubic centimeter. To do so would have introduced a term in δ^2. For both kinds of crystal $|\delta|$ is of the order of magnitude of 10^{-6}. Hence δ^2 is negligible compared with δ.

Calculations and Tables

Numerical calculation of Eq. (16) has been made for three wave-lengths by using the formulae of Herzfeld and Wolf. The value of δ was obtained from the paper by Herzfeld as were the terms calculated by him from Eq. (6) which we have added to our result to obtain the complete difference $(n_{||}-n_\perp)$. The experimental values for this difference were also taken from the same paper.

Two tables are included, the first for sodium chloride, the second for potassium chloride. Column I gives the wave-length for which the calculations were made; column II gives the numerical values of the terms calculated by Herzfeld; column III gives those calculated here from Eq. (16) multiplied by 10^7; column IV gives the sum of II and III, namely $(n_{||}-n_\perp)10^7$; column V gives the corresponding experimental results; lastly, column VI gives the ratio of V to IV.

TABLE I. *Sodium chloride. Negative pressure of 1 kg per square centimeter.*

I λ	II Last two terms of Eq. (6) $\times 10^7$	III Eq. (16) $\times 10^7$	IV $(n_{\parallel}-n_{\perp})10^7$ Calc.	V $(n_{\parallel}-n_{\perp})10^7$ Obs.	VI $\frac{\text{Obs.}}{\text{Calc.}}$
4358	1.382	−12.388	−11.006	2.197	−0.20
5461	1.185	−11.419	−10.234	2.059	−0.20
5790	1.152	−11.245	−10.093	1.922	−0.19

TABLE II. *Potassium chloride. Negative pressure of 1 kg per square centimeter.*

I λ	II Last two terms of Eq. (6) $\times 10^7$	III Eq. (16) $\times 10^7$	IV $(n_{\parallel}-n_{\perp})10^7$ Calc.	V $(n_{\parallel}-n_{\perp})10^7$ Obs.	VI $\frac{\text{Obs.}}{\text{Calc.}}$
4358	−12.98	−10.43	−23.40	−2.973	0.13
5461	−12.67	− 9.70	−22.37	−2.900	0.13
5790	−12.56	− 9.57	−22.13	−2.895	0.13

There is no agreement between experiment and theory except the order of magnitude. Experiments made in this physical laboratory recently by Mr. A. Smith and calculations by Joseph E. Mayer[8] seem to indicate that the results which Herzfeld and Wolf got for the position of the main absorption by evaluating the dispersion formula are wrong. As long as no better values are known, it is impossible to say how far this accounts for the failure of the calculations shown in the tables.

QUANTUM THEORY

Consider an ion in the undisturbed crystal. The Schrödinger equation of a dispersion electron is

$$(h^2/8\pi^2 m)\Delta\psi+(V-E)\psi_0=0.$$

We now add the perturbation function due to the potential dip,

$$\begin{aligned} V' &= \mp(4\pi N/2)e^2\delta[(\alpha_{\parallel}-\beta_{\parallel})z^2+(\alpha_{\perp}-\beta_{\perp})(x^2+y^2)] \\ &= \mp 2\pi Ne^2\delta[(\alpha_{\parallel}-\beta_{\parallel}-\alpha_{\perp}+\beta_{\perp})r^2\cos^2\vartheta+(\alpha_{\perp}-\beta_{\perp})r^2] \\ &= \pm 2\pi Ne^2\delta[4{,}007r^2\cos^2\vartheta-2{,}174r^2]. \end{aligned} \tag{17}$$

In the last line the sign is the sign of the ion. This perturbation function has cylindrical symmetry and accordingly the appropriate undisturbed wave functions are the ones that occur in the Stark effect.

The unexcited state has, of course, spherical symmetry and is, therefore, not degenerate. Call the undisturbed wave function ψ_0, then the ground state is not split up.

We assume that the unperturbed wave function can be written

$$\psi_j=\left(\frac{(2l+1)(l-m)\,!}{4\pi(l+m)\,!}\right)^{\frac{1}{2}} P_l{}^m(\cos\vartheta)e^{+im\varphi}F(j,\,l) \tag{18}$$

where $F(j, l)$ depends on r only and is so normalized that

$$\int |F(j,\,l)|^2 r^2 dr=1. \tag{18'}$$

The perturbation matrix is given by

$$V(j,\,l,\,m;\,k,\,l',\,m')=\int\tilde{\psi}_j V'\psi_k d\tau. \tag{19}$$

From the form of V' (17) it follows that (19) is different from 0 only if $m'=m$; $l'=l$ or $l'=l\pm 2$. Furthermore, the transition probabilities in (5), $f(i,\,l,\,m;\,j,\,l',\,m')$ are different from zero only if

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[8] Joseph E. Mayer, J. Chem. Phys. **1**, 270 (1933).

$l'=l\pm 1$ and either $m'=m$ (for light polarized parallel to z) or $m'=m\pm 1$ for light polarized normal to z. Each member of the mol-refraction formula (5) will be changed by

$$\Delta\frac{f(0;j)}{\nu_j^2-\nu^2}=\frac{f(0;j)}{\nu_j^2-\nu^2}\left(-\frac{\nu_j^2+\nu^2}{\nu_j^2-\nu^2}\frac{\Delta\nu_j}{\nu_j}+\frac{\Delta|p(0;j)|^2}{|p(0;j)|^2}\right), \tag{20}$$

where we have put

$$f(0;j)\sim\nu_j|p(0;j)|^2; \tag{21}$$

we have the same selection rule for the electric moment p as we stated before for f.

It is true that there will also appear formerly "forbidden" lines, but their amplitude is of the first order in V', their intensity therefore quadratic.

Now the application of the general theory of perturbations[9] together with the properties of V' and the selection rules leads to the following formula:

$$\Delta|p(0;j,1,m)|^2=2p(0;j,1,m)\sum_k\left\{\frac{V(0;k,0,0)}{W_0-W_k}p(k,0,0;j,1,m)-\frac{V(k,1,m;j,1,m)}{W_k-W_j}p(0;k,1,m)\right.$$
$$\left.+\frac{V(0;k,2,0)}{W_0-W_{k,2}}p(k,2,0;j,1,m)\right\}. \tag{22}$$

Here we have made use of the fact that the p's can be chosen real.[10] From (22) we get therefore:[11]

$$h\Delta\sum_j\frac{f(0;j)}{\nu_j^2-\nu^2}=-\sum\frac{\nu_j^2+\nu^2}{(\nu_j^2-\nu^2)^2}[V(j,1,m;j,1,m)-V(0;0)]p^2(0;j,1,m)$$
$$+2\sum_j\sum_k{}'\frac{W_j-W_0}{\nu_j^2-\nu^2}\left\{\frac{V(0;k,0,0)}{W_0-W_k}p(0;j,1,m)p(k,0,0;j,1,m)\right.$$
$$\left.-\frac{V(k,1,m;j,1,m)}{W_k-W_j}p(0;j,1,m)p(0;k,1,m)+\frac{V(0;k,2,0)}{W_0-W_{k,2}}p(0;j,1,m)p(k,2,0;j,1,m)\right\}$$
$$=-\sum_j\sum_k\frac{\nu_j\nu_k+\nu^2}{(\nu_j^2-\nu^2)(\nu_k^2-\nu^2)}V(k,1,m;j,1,m)p(0;j,1,m)p(0;k,1,m)$$
$$+V(0;0)\sum_j\frac{\nu_j^2+\nu^2}{(\nu_j^2-\nu^2)^2}p^2(0;j,1,m)$$
$$-2\sum_j\sum_k{}'\frac{\nu_j}{\nu_k}\frac{1}{\nu_j^2-\nu^2}V(0;k,0,0)p(0;j,1,m)p(k,0,0;j,1,m)$$
$$-2\sum_j\sum_k\frac{\nu_j}{\nu_k}\frac{1}{\nu_j^2-\nu^2}V(0;k,2,0)p(0;j,1,m)p(k,2,0;j,1,m). \tag{23}$$

Define now

$$\overline{r^2}(j,l,m;k,l',m)=\int F(j,l,m)r^2F(k,l',m)r^2dr, \qquad A=\mp 2\pi Ne^2\delta.$$

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[9] See, for example, M. Born and P. Jordan, *Elementare Quanten Mechanik*, p. 198, Eq. (22), Berlin, 1930.

[10] J. H. Van Vleck, *Electric and Magnetic Susceptibilities*, p. 273, Oxford, 1932.

[11] The prime on the double sum means $j\neq k$.

We have then

$$\begin{aligned} V(k,1,0;j,1,0) &= A\ \ 0{,}231\ \ \bar{r}^2(k,1;j,1), \\ V(k,1,\pm1;j,1,\pm1) &= -A\ \ 1{,}373\ \ \bar{r}^2(k,1;j,1), \\ V(0;k,2,0) &= A(2/15)5^{\frac{1}{2}}\cdot 4{,}007\ \ \bar{r}^2(0;k,2). \end{aligned} \tag{24}$$

We have for light polarized in the z direction, $m=0$; for light polarized in the x-direction, $m=\pm1$ and, as each of these corresponds to circularly polarized light

$$p_x^2 = \tfrac{1}{2}\{p^2(0;j,1,+1)+p^2(0;j,1,-1)\} = p^2(0;j,1,+1) = p^2(0;j,1,0) = p_z^2, \tag{25}$$

the latter because of the "law of spectroscopic stability."

Therefore, if we form for (23) the difference between light polarized parallel and at right angles to z (designating this difference with Δ'), the second and third terms drop out.

Furthermore, we have[12]

$$\begin{aligned} p^2(k,2,0;j,1,0) &= 2/5\ p_z^2(k,2;j,1), \\ p_x^2(k,2,0;j,1) &= \tfrac{1}{2}\{p^2(k,2,0;j,1,+1)+p^2(k,2,0;j,1,-1)\} = 1/10\ p_z^2(k,2;j,1). \end{aligned} \tag{26}$$

$p(k,2,0;j,1,+1)$ and $p(0;j,1,+1)$ have opposite signs because the increase of m by 1 is in the former case accompanied by a decrease, in the latter by an increase in l. The corresponding is true for $m=-1$. On the other hand $p(k,2,0;j,1,0)$ has the same sign as $p(0;j,1,0)$, because no change in m occurs.

The final formula for the difference in refractive index due to the potential dip, apart from the Lorentz-Lorenz force, is:

$$\Delta' n = \frac{(n^2-1)(n^2+2)}{6n}\,\frac{4\pi Ne^2\delta}{5h}\,4{,}007\left\{\sum_j \frac{f(0;j,1)}{\nu_j^2-\nu^2}\right\}^{-1} \sum_j\sum_k a_{jk}\left\{\left(\frac{f(0;j,1)}{\nu_j}\,\frac{f(0;k,1)}{\nu_k}\right)^{\frac{1}{2}} \frac{\nu^2+\nu_j\nu_k}{(\nu_j^2-\nu^2)(\nu_k^2-\nu^2)}\,\bar{r}^2(j,1;k,1) + \left(\frac{2\nu_j f(0;j,1) f(j,1;k,2)}{\nu^2(0;k,2)\nu(j,1;k,2)}\right)^{\frac{1}{2}} \frac{1}{\nu_j^2-\nu^2}\,\bar{r}^2(0;k,2)\right\}. \tag{27}$$

Here a_{jk} is $+1$ if the absorption lines j and k both belong to the negative ion
is -1 if the absorption lines j and k both belong to the positive ion
is zero if the absorption lines j and k belong to different ions.

While the first sum includes $j=k$, this is excluded in the second sum. Comparing with the classical expression (16), one sees

$$\frac{\Delta' qu}{\Delta' kl} \sim \frac{n^2+2}{3(n^2-1)}\,f_1\,\frac{1}{\nu_1}\,\frac{4\pi Ne^2}{5h}\,\bar{r}^2(1;1) = 0{,}84\,\frac{n^2+2}{n^2-1}\,\frac{Ne^2\overline{r^2}(1;1)}{h\nu_1}\,f_1.$$

As $N=1/2r_0^3$, where r_0 is the distance between two adjacent ions

$$\frac{\Delta' qu}{\Delta' kl} \sim 0{,}42\,\frac{n^2+1}{n^2-1}\,\frac{e^2}{r_0}\,\frac{\bar{r}^2(1;1)}{r_0^2}\,\frac{1}{h\nu_1}\,f_1.$$

Now $h\nu_1$ is somewhat larger than the lattice energy 1.74 e^2/r_0, therefore this expression is probably <1, although of this order of magnitude.

One sees from Tables I and II, that (27) should be about $-1/10$ of column III for rocksalt, -1 of column III for KCl to give the experimental values. Whether that is possible cannot be determined

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[12] Born and Jordan, reference 9, p. 160.

until more is known about the absorption spectrum and the atomic states in crystals, so that the different expressions can be calculated. The difference between the classical and quantum results is primarily due to the use of a more general dynamical model in the latter. When the matrix amplitudes involved in (27) are specialized to the harmonic oscillator, the quantum formula is the same as the classical one.

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