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# Calculation of the Refractive Indices of Sodium Bicarbonate from the Atomic Arrangement

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## I. Introduction

IN the following we will attempt to calculate the optical properties of sodium bicarbonate directly from the atomic arrangement given in the preceding article.

Two methods for calculating the refractive indices from the crystal lattice have been described.[1] The crystal lattice of sodium bicarbonate is characterized by as many as 18 degrees of freedom, so that the numerical calculation involved in the Born-Ewald method becomes forbidding, and we will therefore use the Bragg method which is more simple. In spite of the success of Bragg's attempts to account for the optical properties of calcite and aragonite structures, very little attention has been paid to this interesting and useful method. Recently it was tried to find a correlation between prominent optical characters of crystals and striking features in the atomic arrangements.[2] Certain definite relationships were actually established. It is of interest to note that these empirical correlations without exception can be directly and simply deduced by application of Bragg's method, a fact which strangely enough was completely overlooked.

In the following chapter we will give a brief resumé of the principles upon which Bragg based his methods.

## II. W. L. Bragg's Method for Calculation of Refractive Indices

When a crystal is placed in an electric field it will become polarized, and the well-known relation (1) will hold.

$$EK = E + 4\pi P \tag{1}$$

where $E$ is the intensity of the field, $K$ the dielectric constant and $P$ the total polarization per cc. The total polarization represents the sum of all the induced dipole moments. For not too strong fields the moment induced is proportional to the intensity of the field, the proportionality factor being defined as the polarizability of the particle. Hence we can write

$$P = N\Sigma m = N\Sigma \delta F \tag{2}$$

where $N$ is the number of molecules per cc, $\Sigma m$ the sum of the dipole moments per molecule, $\delta$ the polarizability and $F$ the intensity of the field acting upon the particle. The field $F$ consists of the field $E$ and the field due to all the surrounding dipoles in the crystal.

Let us draw a sphere around the particle under consideration sufficiently large to include a great number of polarized atoms, but small enough so that $E$ does not vary appreciably over distances compared with it. All the dipoles lying on or outside this sphere will then be responsible for a field at the center of intensity $4/3\pi P$. The dipoles within the sphere will, however, create a field at the center whose intensity depends upon the spatial arrangement of the dipoles. Suppose that the sphere contains $n$ dipoles $m_1 m_2 \cdots m_n$ with components of moments $m_{1,\,x}\, m_{1,\,y}\, m_{1,\,z}$ up to $m_{n,\,x}\, m_{n,\,y}\, m_{n,\,z}$ and with coordinates $x_1 y_1 z_1$ up to $x_n y_n z_n$. Let subscript one refer to the atom at the center of the sphere which is the origin of our coordinate system. The dipole $m_p$ will produce a field at origin whose intensity in the $x$-direction is given by:

$$f_{1,\,p}{}^x = \frac{3x_p{}^2 - r_p{}^2}{r_p{}^5}\, m_{px} + \frac{3x_p y_p}{r_p{}^5}\, m_{py} + \frac{3x_p z_p}{r_p{}^5}\, m_{pz}, \tag{3}$$

where $r_p$ is the radius vector, for the $y$ and $z$ components of the created field analogous expressions hold. If now the $x$-direction is chosen in the di-

[1] M. Born, *Atomtheorie des festen Zustandes*, Leipzig, 1923. W. L. Bragg, Proc. Roy. Soc. (London) **A105**, 370 and **A106**, 346 (1924).

[2] W. A. Wooster, Zeits. f. Krist. **80**, 495 (1931).

rection of the field $E$, the dipole moments $m_1$ will be determined by the three equations:

$$m_{1,x} = \delta_{1,x}[E + (4\pi/3)P + \sum_p f_{1,p}{}^x],$$

$$m_{1,y} = \delta_{1,y} \sum_p f_{1,p}{}^y,$$

$$m_{1,z} = \delta_{1,z} \sum_p f_{1,p}{}^z. \qquad (4)$$

Analogous equations will hold for all the other dipoles so that we get a system of $3n$ equations. We are interested in finding the $x$-components of the dipole moments. In order to solve the $3n$ equations of the type (4) the polarizabilities must be known. Let us now suppose that the polarizability of a particle is independent of the direction of the local field, i.e., $\delta_x = \delta_y = \delta_z$ and let us assume that the polarizabilities can be found by other methods. The solutions of Eqs. (4) may then be found and may be given in the form:

$$m = \delta q(E + (4\pi/3)P). \qquad (5)$$

Hence the total polarization per unit volume is $P = N\Sigma \delta q(E + (4\pi/3)P)$, which together with Eq. (1) gives us:

$$K - 1 = n^2 - 1 = 4\pi N\Sigma \delta q/(1 - (4\pi/3)N\Sigma \delta q). \qquad (6)$$

Knowing the polarizabilities we are thus able to calculate the dielectric constants, respectively the refractive indices for infinite wave-lengths. The refractive indices for any given wave-length may be calculated from Eq. (6) provided that we know the polarizabilities for the corresponding frequency.

The optical anisotropy enters through the factors $q$, which depend upon the atomic arrangement and the orientation of the electric vector, (and also upon the polarizabilities).

### III. Application of the Method on Sodium Bicarbonate

In order to carry through the calculations outlined in the previous chapter the polarizabilities of the atoms building up the crystal lattice must be known. We will assume that the polarizabilities of hydrogen and carbon can be considered as negligible. (This assumption does not necessarily imply that we consider carbon to be present as a $C^{+4}$ ion.) The polarizability of an oxygen atom in the $NaHCO_3$ lattice we will take to be the same as for an oxygen atom in carbon dioxide, hence $\delta_0 = 1.29 \times 10^{-24}$.[3] For $Na^+$ we will assume a polarizability of $0.28 \times 10^{-24}$, which corresponds to Wasastjerna's mole refraction value for $Na^+$ in crystals.[4] The polarizability of the sodium ion recently deduced from spectral term values by J. E. Mayer and M. G. Mayer[5] is somewhat lower, namely $0.18 \times 10^{-24}$. This latter value, however, refers to a free cation. The polarizabilities given should correspond strictly to Na light.

In order to simplify the numerical calculations the following approximations were made:

I. The sodium ions are polarized to the same extent as if they were in an isotropic medium, i.e., $q_{Na} = 1$. This approximation is justified since each sodium ion is surrounded in the first sphere of coordination by six oxygen atoms which occupy the corners of a slightly distorted octahedron. These six oxygen atoms will therefore create a field with negligible intensity in the sodium dipole. The field due to oxygen dipoles still further away will be negligible for the same reason and also because the intensity of the field created by a dipole is inversely proportional to the cube of the distance.

II. For an oxygen dipole we will take into consideration the influence of the surrounding sodium and oxygen dipoles which are less than 5.5A away. In reality this means that we take into account the 35–40 nearest dipoles.

III. Components at right angles to the field will be neglected for all dipoles more than 3.0A away.

As the procedure of the numerical calculations has been discussed in detail in Bragg's original papers, we will give only the results. For information about the atomic arrangement the preceding article should be consulted.

The sodium bicarbonate crystals are monoclinic so that the orientation of the tensor ellipsoid is not completely determined by the symmetry. By actual calculation we were able to show that one of the axes of the ellipsoid is exactly normal to the plane of the $CO_3$-groups, which are all oriented parallel to each other. It was further

[3] W. L. Bragg, reference 1.

[4] J. H. Wasastjerna, Soc. Scient. Fenn. Comm. Phys. Math. 1, 37 (1923).

[5] J. E. Mayer and M. G. Mayer, Phys. Rev. 43, 605 (1933).

found that this axis corresponds to the smallest refractive index, $\alpha$. The second axis in the ellipsoid because of the monoclinic symmetry must coincide with the twofold axis. This axis corresponds to refractive index $\beta$. Thus the symmetry plane must contain the two optical axes. Numerically the calculations gave the following values for the three principal refractive indices: $\alpha = 1.393$; $\beta = 1.480$; $\gamma = 1.583$. Consequently the birefringence is negative in character.

In Table I the calculated and observed optical properties are given:

TABLE I.

| Calculated | Observed[6] |
|---|---|
| Plane containing optical axes is (010) | Plane containing optical axes is (010) |
| Acute bisectrix normal to (101) | Acute bisectrix normal to (101) |
| Optically negative 1.393   1.480   1.583 | Optically negative 1.380   1.500   1.586 |
| Angle between the optical axes: 92° | Angle between optical axes: 102° (directly observed) 110° (calculated from observed indices) |

## IV. DISCUSSION OF THE RESULTS

We wish to emphasize the fact that the calculations were carried out on the basis that the observed values were considered to be completely unknown. That is to say the constants in our equations were not adjusted so as to make the calculated and observed value for one of the refractive indices coincide. It is of interest to note that the calculated and observed orientation of the tensor ellipsoid is exactly the same. The numerical agreement is also as good as may be ex-

[6] Compare the preceding article, Zachariasen, J. Chem. Phys. **1**, 634 (1933).

pected with the approximative character of the method itself.

The differences between observed and calculated refractive indices can only in part be ascribed to our approximations I, II and III. The principal source of inaccuracy no doubt is introduced by the assumption that the polarizability of a particle in the crystal lattice is independent of the direction. Furthermore we have also assumed that all the oxygen atoms in the crystal have the same value for the polarizability in spite of the fact that there actually are three kinds of oxygen atoms. (See the preceding article.)[6]

Most other biaxial carbonates in which the $CO_3$-groups are parallel are approximately uniaxial (optical axial angle close to 180°, i.e., $\beta$ and $\gamma$ nearly equal). This is not true for $NaHCO_3$ and the fact that this abnormal behavior is accounted for by the calculations is worthy of special notice.

## SUMMARY

The optical properties of sodium bicarbonate crystals are calculated directly from the known atomic arrangement, when using the method developed by W. L. Bragg.

The results of the calculations and the observed properties are given in Table II.

TABLE II.

|  | Calculated | Observed |
|---|---|---|
| Plane containing optical axes | (010) | (010) |
| Optical character | Negative | Negative |
| Direction of acute bisectrix | $\perp$ (101) | $\perp$ (101) |
| $\alpha$ | 1.393 | 1.380 |
| $\beta$ | 1.480 | 1.500 |
| $\gamma$ | 1.583 | 1.586 |
| $2V$ | 92° | 110° |