LATTICE-THEORY OF ALKALINE EARTH CARBONATES.

Part IV. Elasticity Constants of Calcite.

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Received December 11, 1936.
(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

Introduction.

The three previous papers,¹ under the same title, will be quoted herein as I, II and III respectively. In this part we proceed with the calculation of such elasticity constants of calcite, as do not essentially depend on ionic deformations. The method is exactly the same as used in II for the calculation of the elasticity constants of aragonite. Thus $c_{ij}$ consists of two parts $c_{ij}^e$ and $c_{ij}^r$ due, respectively, to the electro-static and the repulsive forces. These two parts will be calculated separately.

§1. Systems of Parallel Neutral Planes.

Fig. 1 gives the projection of the crystal on $x$–$y$ plane and Fig. 2 on the

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y–z plane. The numbers in the figures denote the “heights” as multiples of c and a [III (1, 1)], above the planes z = 0 and x = 0 respectively.

We take the following three systems of parallel neutral planes:

(1) all planes perpendicular to the x-axis,
(2) all planes perpendicular to the y-axis,
and (3) all planes perpendicular to the line in the plane y = z making an angle \( \theta \) with the z-axis, where \( \theta \) is given by

\[
\tan \theta = \frac{b}{c} \quad (1, 1)
\]

First System.—In this the distance between consecutive planes is given by

\[
d = \frac{a}{2} \quad (1, 2)
\]

In a unit cell of each neutral plane, there are six lattice-points. Fig. 3 shows the arrangement of the ions in the planes at \( x = O, \pm a, \pm 2a, \ldots \pm na, \ldots \).
The $y$ and $z$ co-ordinates of the 6 lattice-points are given by

\begin{align*}
  k = 1, \text{ calcium ion } & (0, 0); \quad k = 4, \text{ CO}_3 \text{ ion } \left(0, \frac{c}{2}\right) \\
  k = 2, \ldots \quad & \left(\frac{b}{3}, \frac{c}{3}\right); \quad k = 5, \ldots \quad \left(\frac{b}{3}, \frac{5c}{6}\right) \\
  k = 3, \ldots \quad & \left(\frac{2b}{3}, \frac{2c}{3}\right); \quad k = 6, \ldots \quad \left(\frac{2b}{3}, \frac{c}{6}\right)
\end{align*}

(1, 3)

The ionic arrangement in the planes at $x = \pm \frac{a}{2}, \pm \frac{3a}{2}, \ldots, \pm \frac{2n+1}{2}a, \ldots$ is similar to this except that there is a displacement of the ions through a distance $\frac{b}{2}$ along $Oy$.

**Second System.**—In this the distance between consecutive planes is given by

\[ d = \frac{b}{6} \]  

(1, 4)

The unit cell of each plane consists of only two lattice-points.

Fig. 4 shows the arrangement of the ions in the plane $y = 0$. The $x$ and $z$ co-ordinates of the lattice-points are

\[ k = 1, \text{ calcium ion } (0, 0) \text{ and } k = 2, \text{ CO}_3 \text{ ion } \left(0, \frac{c}{2}\right) \]  

(1, 5)

The successive planes are similar in the ionic arrangement except that each is displaced through distances $\frac{a}{2}$ and $\frac{2c}{3}$ along $Ox$ and $Oz$ respectively.
Third System.—In this the distance between consecutive planes is given by

\[ d_\theta = \frac{bc}{2 \sqrt{b^2 + c^2}} \]  

(1, 6)

For the representation of this system we choose a system of co-ordinates \(x_\theta, y_\theta, z_\theta\); such that \(Ox_\theta\) coincides with \(Ox\) and \(Oz_\theta\) is perpendicular to the system of parallel planes. The dimensions of a unit cell of the plane lattice are given by

\[
\begin{align*}
    a_\theta &= a \\
    b_\theta &= \frac{\sqrt{b^2 + c^2}}{3}
\end{align*}
\]

(1, 7)

Fig. 5 shows the arrangement of the ions in the plane \(Z_\theta = 0\). A unit cell of the lattice consists of two points only, whose \(x_\theta\) and \(y_\theta\) co-ordinates are given by

\[ k = 1, \text{ calcium ion } (0, 0) \; ; \; k = 2, \text{ CO}_3 \text{ ion } \left( \frac{a_\theta}{2}, \frac{b_\theta}{2} \right); \]

(1, 8)

The ionic arrangement in successive planes is similar except that each is displaced through distances \(\frac{a_\theta}{2}\) and \(\frac{b_\theta}{4}\) along \(Ox_\theta\) and \(Oy_\theta\) respectively.
Lattice-Theory of Alkaline Earth Carbonates—IV

Denoting the elasticity constants in directions perpendicular to these three systems by $c_{11}$, $c_{22}$ and $c_{33}^\theta$ respectively; we have as in II (1, 9)

\[
\begin{align*}
c_{11} &= c_{11}^\epsilon + c_{11}^\gamma \\
c_{22} &= c_{22}^\epsilon + c_{22}^\gamma \\
and c_{33}^\theta &= c_{33}^\epsilon + c_{33}^\gamma
\end{align*}
\]

\[\text{(1, 9)}\]

§2. Evaluation of $c_{11}^\epsilon$, $c_{22}^\epsilon$ and $c_{33}^\epsilon$.

As derived in II (2, 12) we have

\[
c_{11}^\epsilon = \frac{4\pi^2}{b^2c^2} 4\varepsilon^3 \sum_{j=1}^{\infty} \left\{ \frac{a_{l,m}}{2\pi} \left| j \frac{d}{c} \right| e^{-a_{l,m} \left| j \frac{d}{c} \right|} \sum_{k} \left[ F_{l,m}^j (k) \right] \right\}
\]

\[\text{(2, 1)}\]

where

\[
a_{l,m} = 2\pi \left| \frac{l}{b} + \frac{m}{c} \right|
\]

\[\text{(2, 2)}\]

The function $F_{l,m}^j (k)$ depends, as shown in II [§2, refer equation (2, 5) — (2, 10)] on the ionic arrangement of the planes.

The functions $a_{l,m}$ and $F_{l,m}^j$ will be different in the 3 cases.

In the first system, only two adjoining planes need to be considered.

The bracketed expression on summation is found to be

\[-0.267; (2, 3)\]

In the second case, only five adjoining planes have to be considered.

\[-0.085; (2, 4)\]

In the third case, the summation yields the value

\[-0.1048; (2, 5)\]

Substituting these in the proper formula we get

\[
c_{11}^\epsilon = \frac{16\pi^2\varepsilon^2}{b^2c^2} (-0.267) = -0.176 \times 10^{12} \text{ dynes/cm}^2; (2, 6)
\]

\[
c_{22}^\epsilon = \frac{16\pi^2\varepsilon^2}{c^2a^2} (-0.085) = -0.169 \times 10^{12} \text{ dynes/cm}^2; (2, 7)
\]

and

\[
c_{33}^\theta = \frac{16\pi^2\varepsilon^2}{a^2b^2} (-0.1048) = -0.916 \times 10^{12} \text{ dynes/cm}^2; (2, 8)
\]

§3. The Nature of the Repulsive Forces.

The change in the potential due to the repulsive forces is given by III (2, 1)

\[2 \frac{\beta}{\delta^n}; (3, 1)\]

where, as in I (3, 4)

\[
\beta = \frac{ae^2}{n} \delta^{n-1}; (3, 2)
\]

$\delta$ is defined in III (1, 24).
The force between two dissimilar ions is \( \frac{b_{12}}{r^n} \) and \( \frac{b_{11}}{r^n} \) or \( \frac{b_{22}}{r^n} \) between two similar ions. Let

\[
b_{11} = b_{22} = -kb_{12};
\]

As in II (§3) we consider only the close neighbours of any ion; in fact we take only such neighbours of which the distances from the ions are less than \( \delta \), defined in III (1, 24). Further from III (1, 1) we get

\[
b = 8.63
\]

Thus \( b \) may be taken roughly equal to \( c \). Putting

\[
\begin{align*}
\frac{1}{r_1^2} &= \frac{b_2^2}{4}; & s_1^2 &= a^2; \\
\frac{1}{r_2^2} &= \frac{b_2^2}{(\frac{7}{4} + \frac{\delta}{c})}; & s_2^2 &= \frac{b_2^2}{(\frac{7}{4} + \frac{\delta}{c})}; \\
\frac{1}{r_3^2} &= \frac{b_2^2}{(\frac{7}{4} + \frac{\delta}{c})}; & s_3^2 &= \frac{b_2^2}{(\frac{7}{4} + \frac{\delta}{c})}; \\
\frac{1}{r_4^2} &= \frac{b_2^2}{(\frac{7}{4} + \frac{\delta}{c})};
\end{align*}
\]

The potential due to the repulsive forces is given by

\[
V_\Delta = 12 \frac{b_{12}}{b_2} \left\{ \frac{2}{r_1^n} + \frac{6}{r_2^n} + \frac{6}{r_3^n} + \frac{6}{r_4^n} - k \left( \frac{6}{s_1^n} + \frac{6}{s_2^n} + \frac{12}{s_3^n} \right) \right\}
\]

\( n \) has been found in III (Table II) to be 6.5.

Expressing the distances in terms of \( \delta \)

\[
V_\Delta = \frac{12 b_{12}}{\delta^{6.5}} \left( 1275.6 - 332 k \right)
\]

Comparing this with (3, 1)

\[
\frac{2ae^2 \delta^{6.5}}{6.5} = 12 b_{12} \left( 1275.6 - 332 k \right)
\]

whence

\[
b_{12} = \frac{ae^2 \delta^{6.5}}{6 \times 6.5 \left( 1275.6 - 332 k \right)}
\]

Substituting this in (3, 6)

\[
V_\Delta = 2 \frac{ae^2 \delta^{6.5}}{6.5 \left( 1275.6 - 332 k \right)} \left\{ \frac{2}{r_1^{6.5}} + \frac{6}{r_2^{6.5}} + \frac{6}{r_3^{6.5}} + \frac{12}{r_4^{6.5}} - k \left( \frac{6}{s_1^{6.5}} + \frac{6}{s_2^{6.5}} + \frac{12}{s_3^{6.5}} \right) \right\}
\]

\( V \), the potential per unit volume, is given by

\[
V = \frac{V_\Delta}{\delta^3}
\]

For \( c_{12} \), \( c_{22} \) and \( c_{33}^{\delta} \) we take formula similar to those given in II (3, 11) and (3, 12).

The value of \( k \) is determined, as in the case of aragonite, by comparison with the observed value of \( c_{12} \).
Evaluation of $k$ and $c_{\theta\theta}$.

Carrying out the differentiations and then substituting the numerical values of the $r$'s and $s$'s and their components in the respective directions we get:

$$c_{11}^r = \frac{a e^2}{\delta^4} \frac{1870.3 - 363.8 k}{1275.6 - 332 k} \quad (4, 1)$$

$$c_{22}^r = \frac{a e^2}{\delta^4} \frac{1870.3 - 363.8 k}{1275.6 - 332 k} \quad (4, 2)$$

$$c_{33}^\theta = \frac{a e^2}{\delta^4} \frac{2478.6 - 455.1 k}{1275.6 - 332 k} \quad (4, 3)$$

From (4, 1) and (4, 2)

$$c_{11}^r = c_{22}^r \quad (4, 4)$$

and since from (2, 6) and (2, 7) we have $c_{11}^r$ and $c_{22}^r$ approximately equal, we obtain by calculation the observed result

$$c_{11}^r = c_{22}^r \quad (4, 4)$$

The value of $c_{11}$, as experimentally determined by Voigt, is $1.37 \times 10^{12}$ dynes/cm.$^2$

Hence from (1, 9) and (2, 6)

$$c_{11}^r = 1.546 \times 10^{12} \text{ dynes/cm}.^2 \quad (4, 5)$$

Substituting the proper values of $e$ and $\delta$, and the value of $a$ from III (1, 28) we get

$$1.03 \frac{1870.3 - 363.8 k}{1275.6 - 332 k} = 1.546 \quad (4, 7)$$

whence

$$k = 0.353 \quad (4, 8)$$

Substituting this value of $k$ in (4, 3)

$$c_{33}^\theta = 2.06 \times 10^{12} \text{ dynes/cm}.^2 \quad (4, 9)$$

The value of the elasticity constant in the direction $Oz_\theta$ is not directly measured. As in II (5, 1) this can be obtained with the transformation formula given by Voigt. We get

$$c_{33}^\theta = 1.109 \times 10^{12} \text{ dynes/cm}.^2 \quad (4, 10)$$

Substituting from (4, 9) and (2, 8) in (1, 9) the calculated value is given by

$$c_{33}^\theta = 1.148 \times 10^{12} \text{ dynes/cm}.^2 \quad (4, 11)$$

The agreement between the two values is quite satisfactory.

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Summary.

The electro-static parts of the elasticity constants $c_{11}$, $c_{22}$ and $c_{33}^\theta$ are calculated by the same method as used for aragonite. The nature of the 'repulsive' forces is further completely determined by comparison with the observed value of $c_{11}$. The value of $c_{33}^\theta$ is then determined and found to agree well with the experimental value.