LATTICE-THEORY OF ALKALINE EARTH CARBONATES.

Part IV. Elasticity Constants of Calcite.

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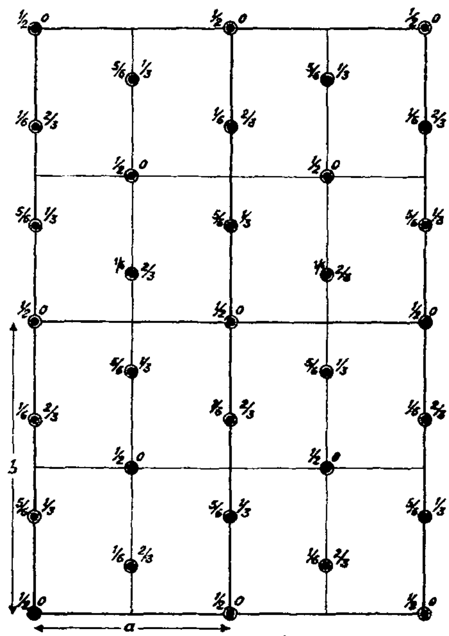
Introduction.

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}^{ϵ} 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



The numbers on the right refer to Calcium ●
" " " left " CO_3 ○
Fig. 1.

[1] B. Y. Oke, *Proc. Ind. Acad. Sci.*, 1936, **4**, 1, 514 and 525.

y–z plane. The numbers in the figures denote the " heights " as multiples 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 $y\,o\,z$ making an angle θ with the z-axis, where θ is given by

$$\tan\theta = \frac{b}{c} \tag{1, 1}$$

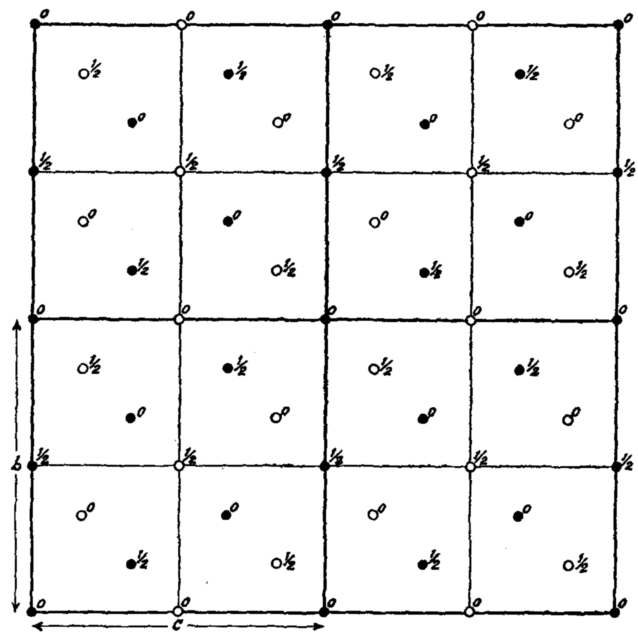


Fig. 2.

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

$$d = \frac{a}{2} \tag{1, 2}$$

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 $x = O, \pm\, a, \pm\, 2a, \ldots\ldots \pm\, na, \ldots\ldots$

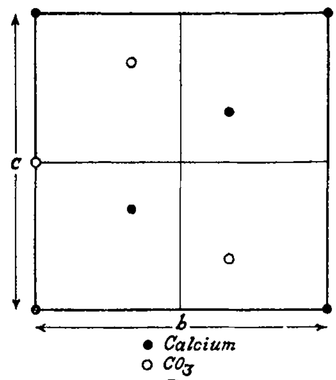


Fig. 3.

The y and z co-ordinates of the 6 lattice-points are given by

$$\left.\begin{array}{llll} k=1, \text{ calcium ion} \left(0,\ 0\right); & k=4, \ CO_3 \text{ ion} \left(0, \frac{c}{2}\right) \\ k=2, \quad ,, \quad ,, \left(\frac{b}{3}, \frac{c}{3}\right); & k=5, \quad ,, \quad ,, \left(\frac{b}{3}, \frac{5c}{6}\right) \\ k=3, \quad ,, \quad ,, \left(\frac{2b}{3}, \frac{2c}{3}\right); & k=6, \quad ,, \quad ,, \left(\frac{2b}{3}, \frac{c}{6}\right) \end{array}\right\} \qquad (1, 3)$$

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

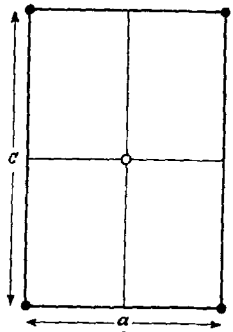
$$d = \frac{b}{6} \qquad (1, 4)$$

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

$$k = 1, \text{ calcium ion } (0, 0) \text{ and } k = 2, \ CO_3 \text{ ion} \left(0, \frac{c}{2}\right) \qquad (1, 5)$$

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.



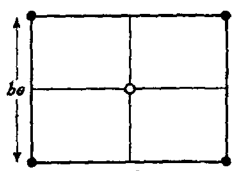
• Ca
o CO_3
Fig. 4.

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

$$d_\theta = \frac{bc}{2\sqrt{b^2+c^2}} \tag{1, 6}$$

For the representation of this system we choose a system of co-ordinates x_θ, y_θ, z_θ ; such that Ox_θ coincides with Ox and Oz_θ is perpendicular to the system of parallel planes. The dimensions of a unit cell of the plane lattice are given by

$$\left.\begin{aligned} a_\theta &= a \\ b_\theta &= \frac{\sqrt{b^2+c^2}}{3} \end{aligned}\right\} \tag{1, 7}$$



• Calcium
o CO_3
Fig. 5.

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_θ and y_θ co-ordinates are given by

$$k = 1, \text{ calcium ion } (0, 0) \ ; \ k = 2, \ CO_3 \text{ ion } \left(\frac{a_\theta}{2}, \frac{b_\theta}{2}\right); \tag{1, 8}$$

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_θ and Oy_θ respectively.

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

$$\left.\begin{aligned} c_{11} &= c^{e}_{11} + c^{r}_{11} \\ c_{22} &= c^{e}_{22} + c^{r\theta}_{22} \\ \text{and } c^{\theta}_{33} &= c^{e}_{33} + c^{r\theta}_{33} \end{aligned}\right\} \qquad (1,\ 9)$$

§2. *Evaluation of* c^{e}_{11}, c^{e}_{22} *and* c^{e}_{33}.

As derived in II (2, 12) we have

$$c^{e}_{11} = \frac{4\pi^2}{b^2c^2}\, 4e^2 \sum_{j=1}^{\infty} \left\{ \frac{a_{l,m} \mid jd \mid}{2\pi}\; e^{-a_{l,m} \mid jd \mid} \sum_{k} [\mathrm{F}_j^{l,m}(k)] \right\} \qquad (2,\ 1)$$

where
$$a_{l,m} = 2\pi \left| \frac{l}{b} + \frac{m}{c} \right| \qquad (2,\ 2)$$

The function $\mathrm{F}_j^{l,m}(k)$ 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 $\mathrm{F}_j^{l,m}$ 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

$$-\ 0 \cdot 267\ ; \qquad (2,\ 3)$$

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

$$-\ 0 \cdot 085\ ; \qquad (2,\ 4)$$

In the third case, the summation yields the value

$$-\ 0 \cdot 1048\ ; \qquad (2,\ 5)$$

Substituting these in the proper formula we get

$$c^{e}_{11} = \frac{16\pi^2e^2}{b^2c^2}(-\ 0 \cdot 267) = -\ 0 \cdot 176 \times 10^{12} \text{ dynes/cm.}^2\ ; \qquad (2,\ 6)$$

$$c^{e}_{22} = \frac{16\pi^2e^2}{c^2a^2}(-\ 0 \cdot 085) = -\ 0 \cdot 169 \times 10^{12} \text{ dynes/cm.}^2\ ; \qquad (2,\ 7)$$

and
$$c^{e\theta}_{33} = \frac{16\pi^2e^2}{a_\theta^2 b_\theta^2}(-\ 0 \cdot 1048) = -\ 0 \cdot 916 \times 10^{12} \text{ dynes/cm.}^2\ ; \qquad (2,\ 8)$$

§3. *The Nature of the Repulsive Forces.*

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

$$2\, \frac{\beta}{\delta^n}\ ; \qquad (3,\ 1)$$

where, as in I (3, 4)

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

δ 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

$$b_{11} = b_{22} = -kb_{12}; \tag{3, 3}$$

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 δ, defined in III (1, 24). Further from III (1, 1) we get

$$b = 8 \cdot 63 \tag{3, 4}$$

Thus b may be taken roughly equal to c. Putting

$$\left.\begin{array}{ll} r_1^2 = \frac{b^2}{4}; & s_1^2 = a^2; \\ r_2^2 = b^2\left(\frac{1}{9}+\frac{1}{36}\right); & s_2^2 = b^2\left(\frac{1}{9}+\frac{1}{9}\right); \\ r_3^2 = b^2\left(\frac{4}{9}+\frac{1}{36}\right); & s_3^2 = b^2\left(\frac{1}{9}+\frac{4}{9}\right); \\ r_4^2 = b^2\left(\frac{1}{3}+\frac{1}{4}\right); & \end{array}\right\} \tag{3, 5}$$

The potential due to the repulsive forces is given by

$$V_\triangle = 12\, b_{12} \left\{\frac{2}{r_1^n} + \frac{6}{r_2^n} + \frac{6}{r_3^n} + \frac{12}{r_4^n} - k\left(\frac{6}{s_1^n} + \frac{6}{s_2^n} + \frac{12}{s_3^n}\right)\right\} \tag{3, 6}$$

n has been found in III (Table II) to be 6·5.

Expressing the distances in terms of δ

$$V_\triangle = \frac{12\, b_{12}}{\delta^{6.5}} \{1275 \cdot 6 - 332\, k\} \tag{3, 6'}$$

Comparing this with (3, 1)

$$\frac{2\, ae^2\, \delta^{5.5}}{6 \cdot 5} = 12\, b_{12}\, (1275 \cdot 6 - 332\, k) \tag{3, 7}$$

whence

$$b_{12} = \frac{a\, e^2\, \delta^{5.5}}{6 \times 6 \cdot 5\, (1275 \cdot 6 - 332\, k)} \tag{3, 8}$$

Substituting this in (3, 6)

$$V_\triangle = 2 \frac{ae^2\, \delta^{5.5}}{6 \cdot 5\, (1275 \cdot 6 - 332\, k)} \left\{\frac{2}{r_1^{6.5}} + \frac{6}{r_2^{6.5}} + \frac{6}{r_3^{6.5}} + \frac{12}{r_4^{6.5}} - k\left(\frac{6}{s_1^{6.5}} + \frac{6}{s_2^{6.5}} + \frac{12}{s_3 r^{6.5}}\right)\right\} \tag{3, 9}$$

V, the potential per unit volume, is given by

$$V = \frac{V_\triangle}{\delta^3} \tag{3, 10}$$

For c_{11}^r, c_{22}^r and $c_{33}^{r\theta}$ 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_{11}.

§4. *Evaluation of* k *and* $c^{r}_{33}\theta$.

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 :—

$$c^{r}_{11} = \frac{\alpha e^2}{\delta^4} \frac{1870 \cdot 3 - 363 \cdot 8\, k}{1275 \cdot 6 - 332\, k} \tag{4, 1}$$

$$c^{r}_{22} = \frac{\alpha e^2}{\delta^4} \frac{1870 \cdot 3 - 363 \cdot 8\, k}{1275 \cdot 6 - 332\, k} \tag{4, 2}$$

$$c^{r}_{33}\theta = \frac{\alpha e^2}{\delta^4} \frac{2478 \cdot 6 - 455 \cdot 1\, k}{1275 \cdot 6 - 332\, k} \tag{4, 3}$$

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

$$c^{r}_{11} = c^{r}_{22}$$

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

$$c_{11} = c_{22} \tag{4, 4}$$

The value of c_{11}, as experimentally determined by Voigt,[2] is $1 \cdot 37 \times 10^{12}$ dynes/cm.^{2}

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

$$c^{r}_{11} = 1 \cdot 546 \times 10^{12} \text{ dynes/cm.}^2 \tag{4, 5}$$

$$\therefore \quad \frac{\alpha e^2}{\delta^4} \frac{1920 \cdot 8 - 327 \cdot 8\, k}{1215 \cdot 6 - 332\, k} = 1 \cdot 546 \times 10^{12} \text{ dynes/cm.}^2 \tag{4, 6}$$

Substituting the proper values of e and δ, and the value of α from III (1, 28) we get

$$1 \cdot 03 \frac{1870 \cdot 3 - 363 \cdot 8\, k}{1275 \cdot 6 - 332\, k} = 1 \cdot 546 \tag{4, 7}$$

whence

$$k = 0 \cdot 353 \tag{4, 8}$$

Substituting this value of k in (4, 3)

$$c^{r}_{33}\theta = 2 \cdot 06 \cdot \times 10^{12} \text{ dynes/cm.}^2 \tag{4, 9}$$

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

$$c^{\theta}_{33} = 1 \cdot 109 \times 10^{12} \text{ dynes/cm.}^2 \tag{4, 10}$$

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

$$c^{\theta}_{33} = 1 \cdot 148 \times 10^{12} \text{ dynes/cm.}^2 \tag{4, 11}$$

The agreement between the two values is quite satisfactory.

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[2] W. Voigt, *Lehrbuch der Kristallphysik*, p. 754.

Summary.

The electro-static parts of the elasticity constants c_{11}, c_{22} and c^{θ}_{33} 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^{θ}_{33} is then determined and found to agree well with the experimental value.