

ENERGY CHANGES BY A VARIATION FROM
THE CRYSTALLOGRAPHIC GROUP

BY H. M. EVJEN

CALIFORNIA INSTITUTE OF TECHNOLOGY, PASADENA

(Received October 11, 1929).

ABSTRACT

The purpose of the paper may be briefly stated as follows: To investigate the possibility of energy minima by a systematic departure from the perfectly symmetrical crystalline lattice. A geometrically simple variation is considered. The surface (100-plane) of a heteropolar crystal of the face-centered type is contracted uniformly in patches, and the interior planes are likewise contracted in patches by amounts decreasing linearly with the distance from the surface. In this way a "mosaic" structure of a type previously suggested in the literature¹ is obtained. A numerical calculation of the change in potential energy is carried out for rock-salt with certain simplifying assumptions. The change in energy is obtained as a power series in terms of the maximum displacement of the ions. Due to the slow convergence of this alternating series an approximate remainder term is introduced to take care of powers higher than the third. The series contains two parameters, namely the linear extension of the patches and the depth of the cracks. The function, in general, is found to have two minima with respect to the displacement of the ions, one at zero displacement, and a second at a finite displacement. The second minimum, depending on the parameters, may be negative with respect to the former. The function also has minima with respect to the two parameters, thus proving the static stability of a mosaic structure of definite dimensions. These considerations with only minor changes, are also applicable to a mosaic structure in the interior of the crystal.

THE potential energy of two ions may be written in the form:

$$E = -(e^2/r) + A/r^\alpha \quad (1)$$

where the first term represents the energy due to the inverse square Coulomb forces, and the second term phenomenologically stands for the energy due to the repulsive forces between ions, which are necessary for static equilibrium. A and α in general depend on the kind of ions considered.² In the following, however, we shall confine our attention to crystals of the rock-salt type and shall assume that these constants are the same for each of the three combinations of ions which occur. This greatly simplifies the calculations, and is permissible in first approximation, in as much as we are not primarily interested in quantitative results. In the case of rock-salt then, the best value of α will be that corresponding to a Na-ion against a Cl-ion, namely 9.² With this constant fixed and the value of the lattice constant known, the value of A may be computed in the usual manner from the minimum energy condition. With Bragg's³ value for the lattice constant of rock-salt, namely 2.81×10^{-8} cm, we obtain $A = 25.8 \times 10^{-82}$.

¹ F. Zwicky, Proc. Nat. Acad. Sci. **15**, No. 3, March, 1929.

² Lennard-Jones and Dent, Proc. Roy. Soc. **A121**, 247 (1928).

³ Bragg, X-Rays and Crystal Structure, 306, (1924).

This calculation is based on the assumption of an infinite space lattice, perfectly symmetrical, with a lattice constant everywhere the same. Needless to say, this assumption has been amply justified in the case of a great number of physical properties. In the case of certain other properties,⁴ there has been a great discrepancy between theory and facts, a discrepancy which has recently led to a questioning of the above mentioned assumption.⁵ It is then a matter of considerable interest to investigate the energetic aspects of a systematic departure from the space lattice of perfect symmetry. As to the type of variation to be considered there are several possibilities. These might perhaps be classified as follows: (1) Variations utilizing the loss in potential energy by contraction of planes, lines, and dipoles, from the lattice constant of the solid to that of the plane, line, or dipole respectively. (2) Variations utilizing the loss in energy by expansion of planes of homogeneous polarity. (3) Variations utilizing the former two principles in combination with a rearrangement of the ions leading to losses in energy comparable with the heat of sublimation. The most favorable variation probably would be of the third type, and probably would be geometrically somewhat complicated. If, however, we can establish the existence of energy minima outside of the crystallographic group by a geometrically simple variation of the first type, our main purpose will be fulfilled. Very reliable quantitative results can hardly be expected anyway, except perhaps as to order of magnitude, since the existence of energy minima outside of the crystallographic group would in some measure invalidate our previous computation of the ionic constants α and A , constants which we shall have to use in the establishment of the minima.

The following variation, then, will be considered: Starting with an ideal rock-salt crystal, a boundary 100-plane will be contracted in square patches, the contraction of two neighboring ions being everywhere the same, namely $d/(p-1) = \delta$, except at the edges where the displacement will be d . p is the number of ions in a line element of the patch. During this first step of the variation the interior lattice planes are kept rigid. The resulting change in energy will be due to two sources: (1) Change due to the ions in the contracting plane, and (2) change due to the ions of the interior planes. As a second step in the variation the interior planes are similarly contracted by amounts decreasing linearly with the distance from the surface.

The energy of an isolated plane, contracted as outlined above, may be written:

$$E = \frac{1}{2} \sum_{l=-\infty}^{\infty} \sum_{m=-\infty}^{\infty} \sum_{r=1}^p \sum_{s=1}^p \left[\frac{(-1)^{l+m} e^2}{[(la - k_1\delta)^2 + (ma - k_2\delta)^2]^{1/2}} + \frac{A}{[(la - k_1\delta)^2 + (ma - k_2\delta)^2]^{\alpha_2}} \right] \quad (2)$$

where a is the lattice constant, and k_1 and k_2 are integers depending on l and r , m and s respectively in a manner such that

⁴ See f. ex. F. Zwicky, *Phys. Zeits.* **24**, 131 (1923).

⁵ See reference 1.

$$\begin{aligned}
\frac{1}{p} \sum_{r=1}^p k_1^2 &= R\left(\frac{l}{p}\right) \left[p - R\left(\frac{l}{p}\right) \right] \\
\frac{1}{p} \sum_{s=1}^p k_2^2 &= R\left(\frac{m}{p}\right) \left[p - R\left(\frac{m}{p}\right) \right] \\
\frac{1}{p} \sum_{s=1}^p k_2^3 &= -R\left(\frac{m}{p}\right) \left[p - R\left(\frac{m}{p}\right) \right] \cdot \left[p - 2R\left(\frac{m}{p}\right) \right]
\end{aligned} \tag{3}$$

where the symbol $R(m/p)$ stands for remainder in m/p .

The change in energy now may be obtained by expanding the expression 2 in powers of $d/a = \delta_e$, and summing the pure number series occurring as coefficients in this expansion. The expansion converges for $d/a < 1$. The coefficients of the three first terms in this expansion have been evaluated.⁶ The higher orders in the expansion may, to good approximation, be said to arise entirely from the ions forming the boundaries of the patch. This enables us to replace the higher orders by an approximate remainder,⁶ so that for reasonably great values of p ($p > 10$) the following functional relation is obtained between the average change in energy per ion, ΔE and δ_e :

$$\begin{aligned}
pa\Delta E/e^2 &= 1.9417 - 1.4753\delta_e + \{1.14p/(p-1) - 0.6235\}\delta_e^2 \\
&\quad - \{0.04 - 7.66/(p-1)^2\}\delta_e^3 - 2/(1+\delta_e) + 0.0583/(1+\delta_e)^9 \tag{4}
\end{aligned}$$

In addition to this there will be a decrease in energy due to polarization caused by the asymmetries of the mosaic configuration. This change in energy will be given by:

$$p^2\Delta E = -\frac{\alpha}{2} \sum_{t=1}^p \sum_{q=1}^p \{\overline{\Delta X^{qt^2}} + \overline{\Delta Y^{qt^2}}\}$$

where the first term in a Taylor expansion gives:⁶

$$\Delta X^{qt} = - \sum_{l=-\infty}^{\infty} (-1)^l \cdot \frac{2ek_1}{a^3 l^3} \delta + \sum_{l=-\infty}^{\infty} \frac{e\delta}{a^3} \frac{k_1(m^2 - 2l^2) - 3k_2lm}{[l^2 + m^2]^{5/2}} \cdot (-1)^{l+m}$$

so that the second order change in energy will be:

$$pa\Delta E/e^2 = -0.366(p/p-1)^2 \cdot \delta_e^2 \tag{5}$$

α being the average polarizability of the ions.⁷

The higher orders here may be neglected, so that the change in energy due to the ions of the contracting plane may be written:

$$\begin{aligned}
pa\Delta E/e^2 &= 1.9417 - 1.4753\delta_e + \{1.14p/(p-1) - 0.366(p/p-1)^2 - 0.6235\}\delta_e^2 \\
&\quad - \{0.04 - 7.66/(p-1)^2\}\delta_e^3 - 2/(1+\delta_e) + 0.0583/(1+\delta_e)^9 \tag{6}
\end{aligned}$$

The energy of a displaced ion in the surface due to the interior of the crystal may be written:

⁶ H. M. Evjen, Thesis, California Institute of Technology, 1929.

⁷ Born and Heisenberg, Zeits. f. Physik. **23**, 388, (1924).

$$E = \sum_{l=1}^{\infty} \sum_{m=-\infty}^{\infty} \sum_{n=-\infty}^{\infty} \left[\frac{(-1)^{l+m+n} e^2}{[(la)^2 + (ma - h_1 \delta)^2 + (na - h_2 \delta)^2]^{1/2}} + \frac{A}{[(la)^2 + (ma - h_1 \delta)^2 + (na - h_2 \delta)^2]^{\alpha_2}} \right] \quad (7)$$

where h_1 and h_2 depend on p in such a way that

$$\frac{1}{p} \sum_{r=1}^p h_r^2 = \frac{1}{p} \sum_{s=1}^p h_s^2 = \frac{(p^2 - 1)}{12}. \quad (8)$$

Again an expansion by the binominal theorem gives the change in energy. Only even powers of d occur in this expansion. The second order change has been evaluated.⁶ If account is taken of the Lennard-Jones contraction perpendicular to the surface,² it is:

$$pa\Delta E/e^2 = 0.0228p(p+1)/(p-1)\delta_e^2 \quad (9)$$

The total change in energy by the first step in the variation now may be written:

$$\begin{aligned} pa\Delta E/e^2 = & 1.9417 - 1.4753\delta_e + \{1.14p/(p-1) - 0.366(p/p-1)^2 \\ & - 0.6235 + 0.0228p(p+1)/(p-1)\}\delta_e^2 \\ & - \{0.04 - 7.66/(p-1)^2\}\delta_e^3 - 2/(1+\delta_e) \\ & + 0.0583/(1+\delta_e)^9. \end{aligned} \quad (10)$$

From which it is seen that this first step in the variation, which in itself forms a highly artificial variation out of the crystallographic group, already gives rise to energy minima. For certain values of p the change in energy may be represented as depicted in Fig. 1. The function also will be seen to

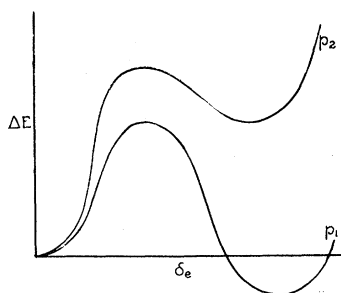


Fig. 1. Change in energy by a variation from the crystallographic group.

possess a minimum with respect to p , showing that the patches, if formed in this way, would tend to assume a definite size.

The simultaneous minimum in δ_e and p , however, falls outside of the region of convergence of the expansion, so that the value of p for which this occurs can only be roughly estimated. It is of the order of 10.

The smallness of the patches formed in this way is due to the restraining influence of the fixed space lattice represented by Eq. (9), which is distinguished by the fact that it contains p to a higher power than the contribution of the plane, (Eq. 6). When we carry out the second step of our variation this restraining influence will be seen to be practically annihilated. That is, when the boundary plane is already contracted, the forces of interaction between the planes will tend to contract the neighboring interior planes. It is not deemed necessary, therefore, actually to compute the energy of interaction between the planes by the second step of the variation, as an upper limit to the total change in energy of interaction is given by the expression (9) divided by the number of planes contracted; and this will be seen to be a rather small contribution, since the term now has lost its distinction of containing p to a higher power than the contribution of the planes. In the place of the actual value of this positive contribution we shall therefore use the upper limit.

Aside from this small change in energy due to the interaction between the planes, the change will be made up of a sum of expressions of the type 6. If this expression be denoted by $f(\delta_e)$, the sum in question will be:

$$S = \sum_{q=1}^n f(\delta_e \cdot q/n). \quad (11)$$

In summing the last two terms of $f(\delta_e \cdot q/n)$, the summation may be replaced by an integration, so that, writing $p = xn$, the total change in energy by the complete variation may be written:

$$pa\Delta E/e^2 = 1.9417 - 0.7376\delta_e + 0.502\delta_e^2 - 0.0116\delta_e^3 \\ - (2\ln(1+\delta_e))/\delta_e + (0.0073/\delta_e)[1 - 1/[1+\delta_e]^8] + \phi(n, x) \quad (12)$$

where

$$\phi(n, x) = 0.0228x\delta_e^2 + \frac{\delta_e}{n} \left[-0.736 + \left(0.121 + \frac{0.136}{x}\right)\delta_e + (0.02 + 0.26/x \right. \\ \left. + 0.014/x^2)\frac{\delta_e}{n} \right] - \left[0.022 - \frac{(1.915/x^2 - 0.022)}{n} \right] \frac{\delta_e^3}{n} \quad (13) \\ - \frac{2}{\delta_e} \ln \left(1 + \frac{\delta_e}{n} \right) - \frac{2}{n\delta_e} \ln \frac{1+\delta_e}{1+\delta_e/n} \\ - \frac{n}{n-1} \frac{0.0073}{\delta_e} \left[1 - \frac{1}{(1+\delta_e/n)^8} \right] + \frac{0.0073}{n\delta_e} \left[1 - \frac{1}{[1+\delta_e]^8} \right]$$

This functional relation again may be represented graphically by the type of curves shown in Fig. 1. The function possesses minima with respect to x and n as well as δ_e , showing that the mosaic structure, if formed in this way, would have definite dimensions. Again the absolute minimum occurs outside of the region of convergence, and the values of x and n for which maximum stability obtains can be only roughly estimated. x seems to be of

the order 1, and n of the order 25, which agrees roughly with previous phenomenological estimates.⁸

If the previous calculation had been carried out for planes very far removed from the boundaries of the crystal the final result would have been essentially the same. The only difference in the calculation would have been the introduction of factor 2 in the constant of expression 9, which again would mainly have the effect of decreasing somewhat the value of the ratio x at the absolute minimum, an effect which we should expect.

Beyond establishing the possibility of energy minima outside of the crystallographic group, the previous calculation is of interest in that it suggests the possibility of a coexistence of different modifications of the same crystallographic group below certain temperatures.

⁸ A. Smekal, *Zeits. f. techn. Physik* **7**, 535 (1926); **8**, 561 (1927) and reference 1.