THE INFLUENCE OF THE ELECTRIC POLARIZABILITY ON THE GLIDING STRENGTH OF CRYSTALS

HANS MÜLLER, *Dept. of Physics, Mass. Institute of Technology.*

In a recent paper M. J. Buerger[1] discovered an interesting relation between the electric polarizability of the ions of face centered cubic crystals and their mode and ease of translation-gliding. Buerger's results of his investigation of the translation-gliding on 12 different isometric crystals of the NaCl type can be summarized as follows:

(a) If the sum of the polarizabilities of the two kinds of ions is small, the crystal has a high gliding strength, and glides only along the (110) plane. (Examples NaCl, NaF, MgO).

(b) The larger the sum of the polarizabilities, the smaller the gliding strength (the greater the plasticity) and the smaller the gliding strength for gliding in the (001) plane, relative to the strength for gliding in the (011) plane. Crystals with ions of large polarizability (PbTe, PbS, KI) have a small gliding strength and glide only along the (001) plane, while crystals with ions of medium polarizability (NaI, KBr, NaBr, KCl) have a medium gliding strength and glide along both planes.

(c) The gliding in either plane takes place in the direction $[1\bar{1}0]$, which is the direction of shortest distance between two ions of the same kind. Fig. 1 illustrates the two possible modes of gliding in a crystal of the type NaCl.

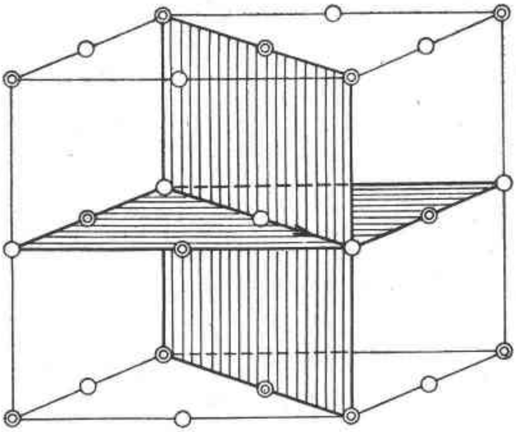

FIG. 1.

---

[1] M. J. Buerger, *Am. Mineralogist*, Vol. **15**, Nos. 2, 5, 6 (1930).

These results lead to the following relations between the gliding strengths in the two respective planes and the sum of the polarizabilities:

(1) If the ions are not polarizable, the gliding strength for the (001) plane is much larger than this for the (011) plane.

(2) Both gliding strengths decrease with increasing polarizability, but the decrease must be faster for the (001) plane.

Fig. 2 illustrates the type of relationship which must exist between gliding strength and polarizability according to Buerger's measurements.

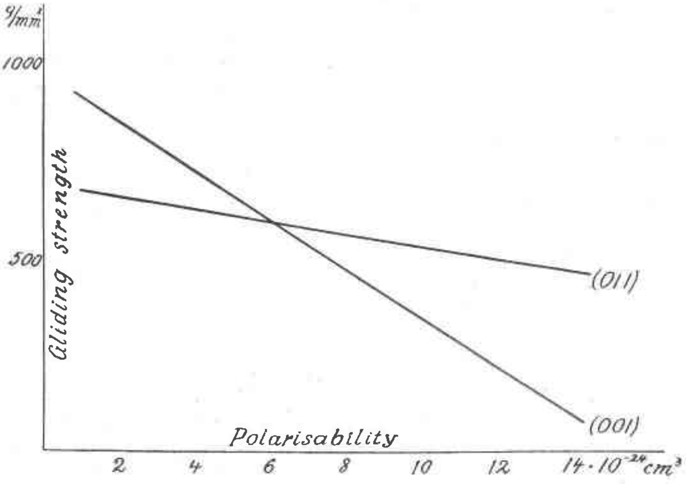

FIG. 2.

A rigorous theoretical treatment of the gliding of crystals encounters great difficulties. They arise from two sources. First, it is extremely difficult to picture the molecular arrangement during gliding. The most simple assumption would be to consider the gliding as a relative translation of two ideal half crystals. If this picture were correct, the distance of gliding would be a multiple of the closest distance of two equal ions, and the crystal would after gliding represent again an ideal lattice. The fact, however, that plastic deformation increases the tensile strength of a crystal indicates, and the X-ray diagrams show it directly, that after gliding the lattice arrangement is disturbed. The second difficulty arises from the limited knowledge of the forces acting between the ions of the crystal. These forces are generally considered to be the electrostatic forces between the ionic charges and certain repulsive forces which are due to the finite size of the ions. Unsöld has given an explanation of the origin of these repulsive forces with the help of wave mechanics. It is generally assumed that they are spherically symmetric and decrease with the inverse 9th or 11th power of the distance. Lennard-Jones[2] and his collaborators have investigated the values of n and A in a power law, $F = A/r^n$ for a large number of ions. It is however most probable that this approximation holds only if the ions are in the normal lattice distance. The approximation is sufficient to calculate elastic and equilibrium constants of the crystal, but is not sufficient to calculate the gliding strength, since during gliding the ions separate considerably. The value of the gliding strength depends very much on the choice of the repulsive forces, and since we have no definite information about them, it is entirely hopeless to calculate accurate values for the gliding strength.[3] It is in particular impossible to explain the experimental fact, that the gliding strength along the (001) plane is larger than the one along the (011) plane, if the ions are not polarizable.

Frenkel[4] attempted to calculate the gliding strength of NaCl, but his results are of no value (negative gliding strength for the 011 plane) since his assumptions about the repulsive forces are obviously too simple. Here we will only estimate the order of magnitude of the gliding strength, assuming the ions are not polarizable. For this purpose we consider the gliding as a relative translation of two halfcrystals, and calculate the component of the force between these two halfcrystals which acts in the direction of gliding. The maximum value of this force per unit area of the gliding-surface is the gliding strength. The total force between the two halfcrystals is the sum of all the forces between the ions of one halfcrystal and all the ions of the other halfcrystal. Since however all forces decrease quickly with increasing distance we only take into account the forces between the two layers on both sides of the gliding plane.[5] The order of magnitude of the distance between these two layers

---

[2] Lennard-Jones, *Proc. of the Royal Society*, Vol. **109**, (1925).

[3] We have carried out calculations using Lennard Jones' data and also by replacing the inverse powerlaw by an exponential decrease of the repulsive forces. The results vary much with the assumption and do not agree with the observations. The calculations give in many cases a negative gliding strength. The few valuable conclusions resulting from these calculations are mentioned in this paper.

[4] Frenkel, *Zeit. für Physik*, Vol. **37**, 572 (1926).

[5] A more accurate calculation shows that this approximation involves an error of less than 10%.

is the lattice distance a, hence the order of magnitude of the electric force between two ions is e^2/a^2, where e is the charge of the ions, and since the number of ions per unit area is of the order of magnitude of $1/a^2$ the total electrostatic force has the order of magnitude of e^2/a^4. The repulsive forces are of the same order of magnitude, since in equilibrium they balance the Coulomb forces, and the same holds for the maximum of the component in the gliding direction. Hence the gliding strength G should be:

$$G = \gamma \frac{e^2}{a^4}$$

where γ depends on the gliding plane and the gliding direction, and it depends very much on the law for the repulsive forces. Using the results of Lennard-Jones we find that γ may vary between 0.01 and 1. Since a is for most crystals about 6.10^{-8} cm. we should expect the gliding strength to be of the order of magnitude $2\gamma.10^{+10}$ dyne/cm.$^2 = 2.10^{+3} - 10^5$ gr/mm^2. The only quantitative determination has been performed by Joffe, Kirpitchewa and Levitzky.[6] They find for the gliding of NaCl along the (011) plane at 0°C a gliding strength of 10^3 gr/mm^2. Our estimate is made for absolute zero, neglecting the zero point energy. The experiments of Joffé and his collaborators show that the gliding strength increases rapidly with low temperatures. While there are no measurements at temperatures below 0°C we can estimate by extrapolation of Joffé's curves, that for 0°, K the gliding-strength, is of the order of 10^4 gr/mm.^{2}, which agrees with our theoretical estimate. Contrary to other statements[7] we find that Born-Madelung's lattice theory of crystals can account for the observed order of magnitude of the gliding strength.

The influence of the polarizability of the ions on the gliding strength as observed by Buerger is particularly interesting because it presents the only example where the polarizability influences a mechanical property of a regular crystal.

The ions of the crystals investigated by Buerger have the spherical symmetric structure of the atoms of inert gases. In the equilibrium state and during elastic deformation every ion of a crystal of the NaCl type is a center of symmetry. Consequently the polarizability of the ions does not play a rôle either for the equilibrium

---

[6] Joffé, M. W., Kirpitchewa, and M. A. Levitzky. *Zeit. f. Physik*, Vol. **22,** (1924).

[7] F. Zwicky, *Helvetical physica acta*, Vol. **3,** 269 (1930).

energy or for the elastic constants. During gliding however the ions on both sides of the gliding plane are no longer symmetrically surrounded by the other ions. The sum of the electro-static forces exerted by the surrounding ions is no longer zero as in the symmetrical case, but the electric field strength has a finite value of the order of magnitude e/a^2. Now an ion is an atomic system consisting of a positive nucleus surrounded by negative electrons. If there is no outer field acting on this system the electron distribution is spherically symmetric. An electric field disturbes this symmetry in such a way that the negative electrons are displaced in the direction opposite to the field. In this state the center of gravity of the electrons no longer coincides with the position of the nucleus. The ion is polarized and represents an electric dipole. Such a system can be characterized by its dipole moment μ, which is the product of the total displaced charge and the average displacement. Since this displacement is proportional to and in the direction of the field, the dipole moment induced by a field of the strength K will be proportional to K and we can write:

$$\mu = \alpha K \tag{1}$$

α depends on the structure of the ion and is called the electric polarizability of the ion. This constant plays an important role for the dielectric constant of the crystal and can and has been determined for a large number of ions from measurements of refractive indices. The order of magnitude of α is 10^{-24} cm^3.

The dipole moment μ is a vector, pointing from the center of gravity of the negative charges towards the nucleus (opposite to the direction of the displacement of the electrons) and has therefore the direction of the field vector K. We have, therefore, for the components:

$$\begin{aligned} \mu_x &= \alpha K_x \\ \mu_y &= \alpha K_y \\ \mu_z &= \alpha K_z. \end{aligned} \tag{1'}$$

Due to this electrical polarization of the ions an additional force acts between the two halfcrystals in the state of gliding. This force is the sum of the forces between the electric charges of one halfcrystal and the dipoles of the other halfcrystal. (The forces between the dipoles are of smaller order of magnitude.) To estimate the order of magnitude of this force we have only to consider the ions again in the two planes along which the gliding takes place.

The force acting on a dipole of the moment μ in an electric field is proportional to the rate of change of the field strength, which is of the order of magnitude of e/a^3, and to the dipole moment which is of the order of magnitude of $\alpha e/a^2$. Hence the additional force per ion is of the magnitude $\alpha e^2/a^5$, and since α is about 10^{-24} cm.^{3} and a about 10^{-8} cm. we see that this force is of the same magnitude as the Coulomb force e^2/a^2, and can therefore have an appreciable influence on the gliding-strength.

In order to decide whether the influence of these dipole forces is an increase or a decrease of the gliding strength, we have to calculate the component of the force in the gliding direction. For this purpose let us consider a dipole, represented by a negative charge $-\epsilon$ at the point (xy) and a positive charge $+\epsilon$ at the point $(x+\Delta x, y+\Delta y)$ (Fig. 3). The dipole moment has the components:

$$\begin{aligned} \mu_x &= \epsilon\Delta x \\ \mu_y &= \epsilon\Delta y. \end{aligned} \tag{2}$$

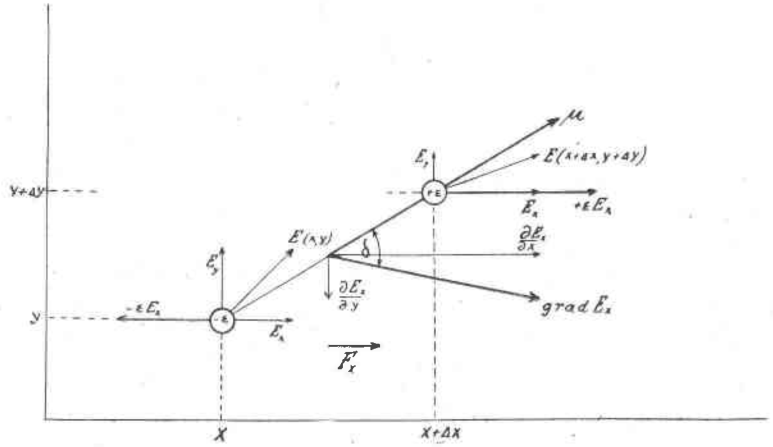

FIG. 3.

This dipole is placed in an electric field with the components, E_x, E_y, which are functions of x and y. The x direction shall be the gliding direction and we will calculate the force on the dipole in the gliding direction. The force on the negative charge $(-\epsilon)$ is evidently $-\epsilon E_x(x,y)$ while the force on the positive charge is $+\epsilon E_x(x+\Delta x, y+\Delta y)$. Since Δx and Δy are small we can develop:

$$E_x(x+\Delta x,\ y+\Delta y) = E_x(x,\ y) + \frac{\partial E_x}{\partial x}\Delta x + \frac{\partial E_x}{\partial y}\Delta y$$

The sum $\epsilon E_x(x+\Delta x, y+\Delta y)-\epsilon E_x(x, y)$ gives the total force on the dipole, and we have therefore:

$$F_x = \frac{\partial E_x}{\partial x}\epsilon\Delta x + \frac{\partial E_x}{\partial y}\epsilon\Delta y$$

or

$$F_x = \frac{\partial E_x}{\partial x}\mu_x + \frac{\partial E_x}{\partial y}\mu_y \tag{3}$$

$\delta E_x/\delta x$ and $\delta E_x/\delta y$ can be considered as the x and y components of a vector which is called grad E_x and a simple calculation shows that (3) can also be written (the scalar product of two vectors)

$$F_x = \left|\text{grad } E_x\right| \cdot \left|\mu\right| \cos\delta \tag{3'}$$

where where δ is the angle between the two vectors grad E_x and μ, and $|\text{grad } E_x|$ and $|\mu|$ are the absolute values of these vectors. This force is positive or negative according to whether the angle δ is smaller or larger than 90°. A positive force acts in the gliding direction and therefore decreases the gliding strength, a negative force however means an increase of the gliding strength.

In the crystal the field E is the Coulomb field of the ions of the other halfcrystal. The dipole moment μ is induced by the field K which is the Coulomb field of the ions of both halfcrystals. Since μ and K have the same direction, δ is also the angle between the vectors E and K. Since a negative ion is always, even during gliding, surrounded in the same way by positive ions just as the negative ions surround a positive one, the direction of E, E_x, grad E_x and K for a negative ion are all opposite in direction to E, E_x, grad E_x and K for a positive ion, and consequently the angle δ is the same for each ion. To find the influence of the polarizability on the gliding strength we have therefore to consider any one ion in the gliding plane of one halfcrystal. The polarizability produces an increase or a decrease of the gliding strength according to whether the angle between K and grad E_x is larger or smaller than 90°. K is the electric field strength on the ion due to all the ions of both halfcrystals, while E_x is the component in the gliding direction of the field strength due to the ions of the other halfcrystal only.

We shall consider the two ways of gliding separately. (1) The gliding along the (001) plane.

We will consider the lower halfcrystal as fixed and the upper halfcrystal gliding. Since $[0\bar{1}1]$ is the gliding direction the ions move in the $(\bar{0}11)$ plane. Fig. 4 shows the molecular arrangement in this plane during gliding. Due to the symmetry of the crystal it is evident that in this plane the vectors E, K and grad E_x have no components normal to this plane. We introduce a system of coordinates with the x direction in the direction of gliding and the y direction pointing away from the fixed halfcrystal. We consider a negative ion which is originally at the point A and reaches its next equilibrium position at B. The path between A and B could be calculated if we knew the exact forces. Considering the ions as rigid spheres

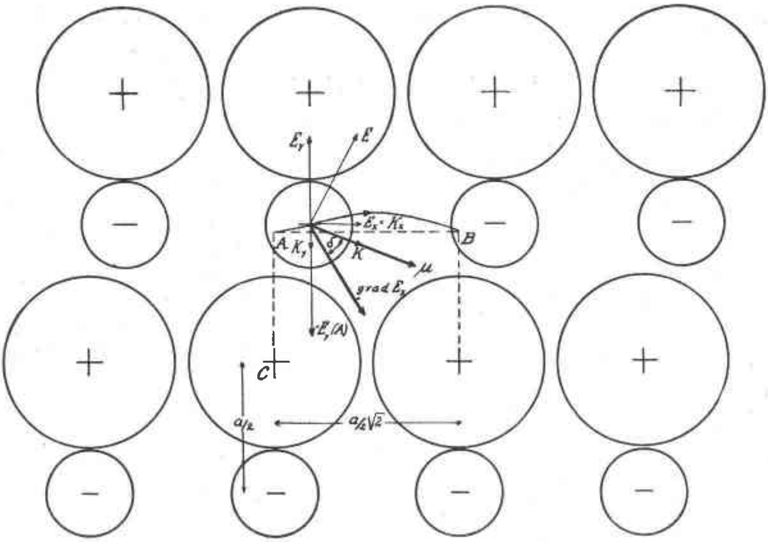

FIG. 4.

Buerger comes to the conclusion that the path can be a straight line except if the ratio of the radii of the two kinds of ions is smaller than 0.63. For ratios smaller than this value there must be a lift. From the symmetry of the crystal we conclude that the force on the ion will change periodically with the period $AB = a/2\sqrt{2}$, hence the maximum force will be reached for $x = AB/4 = a/8\sqrt{2}$. Independent of the form of the path we will have in the region $x \leqq a/8\sqrt{2}$

$$E_x > 0$$

$$E_y > 0$$

E_x and E_y will decrease with increasing distance from the fixed halfcrystal, and E_x will increase with increasing x while E_y will decrease. All these conclusions follow from the fact that the Coulomb forces decrease with the inverse square of the distance, hence the direction and the change of the field is determined by the nearest ion, which in this case is the positive ion in the point C. Hence we have:

$$\frac{\partial E_x}{\partial x} > 0, \quad \frac{\partial E_x}{\partial y} < 0.$$

Therefore the vector grad E_x will be in the fourth quadrant of the system of coordinates.

To find the direction of K, the field due to all ions of both halfcrystals, we can consider it as the sum of three field-strengths, namely the field E due to the ions of the fixed crystal, the field due to the ions in the same layer as the ion, and the field due to the rest of the moving halfcrystal. The ions in the same layer surround the considered ion symmetrically and therefore give no field. The rest of the moving halfcrystal gives a field which is equal and opposite to the field E at the point A. Hence:

$$K_x = E_x$$
$$K_y = E_y(x, y) - E_y(A).$$

Since $\delta E_y/\delta x<0$ and $\delta E_y/\delta y<0$ we always have $E_y(x, y)<E_y(A)$. Hence:

$$K_x > 0$$
$$K_y < 0.$$

Whence the vector K is also in the fourth quadrant of the system of coordinates, and the angle δ between the vectors K and grad E_x is necessarily smaller than 90°. Consequently, *the polarizability of the ions always decreases the gliding strength along the (001) plane.* This holds independent whether there is a lift or not.

(2) The gliding along the (011) plane.

In this case the ions move in the (001) plane (Fig. 5) and again the vectors E, K, grad E_x have no component normal to this plane. The path of the ion from A to B is certainly not a straight line, since the ion cannot penetrate the ion at the point C. It is more natural to assume that the path is approximately a circle around the point C. We choose the x direction in the direction of gliding and the y

direction normal to the fixed halfcrystal. The maximum force will again be reached for $x=a/8\sqrt{2}$. We consider a negative ion. From the crystallographic arrangement we conclude, that for $x \leqq a/8\sqrt{2}$ we have:

$$E_x < 0 \qquad \frac{\partial E_x}{\partial x} < 0$$

$$E_y > 0 \qquad \frac{\partial E_x}{\partial y} > 0.$$

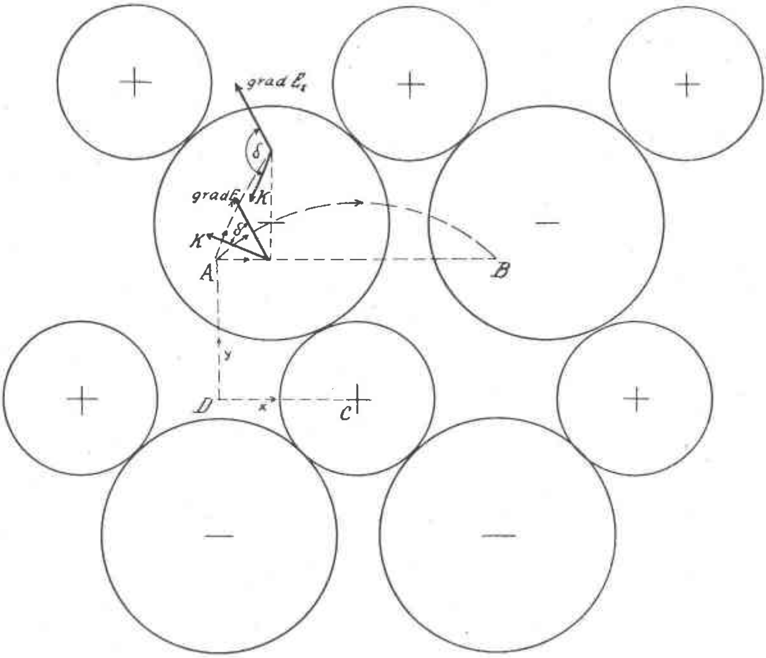

FIG. 5.

Hence the vector grad E_x is in the second quadrant of the system of coordinates. The vector K is again:

$$K_x = E_x < 0$$

$$K_y = E_y(x,\ y) - E_y(A).$$

If the path would be a straight line we would necessarily have $E_y(x, y) > E_y(A)$ and hence $K_y > 0$. For this case the vector K is also in the second quadrant and the angle δ is smaller than 90°.

The polarizability would therefore produce a decrease of the gliding strength. However, there must be a lift connected with the gliding along the (011) plane. For a very large lift $E_y(x, y)$ becomes very small, hence $K_y = -E_y(A) < 0$, and the vector K is now in the third quadrant. Therefore, there exists the possibility that with lift the angle δ is larger than 90°, and that the polarizability of the ions produces an increase of the gliding strength along the (011) plane. There will be a path between A and B along which the angle δ is 90° and along which the polarizability of the ions will not influence the gliding strength. If the actual path lies below this critical path, the polarizability results in a decrease of the gliding strength, but if the actual path lies above it the polarizability increases it.

In order to determine this critical path we need to know the value of E_x and E_y. They can be calculated by a method given by Madelung. Frenkel has given the electrostatic potential of a half-crystal limited by a (011) plane, and from it we find as a first approximation:

$$E_x = -\frac{32\pi e}{a^2}\cdot\frac{1}{\sqrt{3}}\cdot\frac{e^{-2\pi y/a\sqrt{3}}}{1-e^{-\pi\sqrt{3/2}}}\cdot\sin\frac{4\pi}{a\sqrt{2}}x$$

$$E_y = \frac{16\pi e}{a^2\sqrt{2}}\cdot\frac{e^{-2\pi y/a}}{1+e^{-\pi\sqrt{1/2}}} - \frac{32\pi e}{a^2\sqrt{2}}\cdot\frac{e^{-2\pi y/a\sqrt{3}}}{1-e^{-\pi\sqrt{3/2}}}\cdot\cos\frac{4\pi}{a\sqrt{2}}x$$

where x and y are the coordinates with respect to the point D. The dipole force vanishes according to (1′) and (3) if

$$K_x\frac{\partial E_x}{\partial x} + K_y\frac{\partial E_x}{\partial y} = 0 \tag{4}$$

where $K_x = E_x$ and

$$K_y = E_y - E_y(A) = \frac{16\pi e}{a^2\sqrt{2}}\cdot\frac{1}{1+e^{-\pi\sqrt{1/2}}}\left[e^{-2\pi y/a} - e^{-\pi\sqrt{1/2}}\right]$$

$$-\frac{32\pi e}{a^2\sqrt{2}}\cdot\frac{1}{1-e^{-\pi\sqrt{3/2}}}\left[e^{-2\pi y/a\sqrt{3}}\cos\frac{4\pi}{a\sqrt{2}}x - e^{-\pi\sqrt{3/2}}\right].$$

Introducing these expressions in (4) we find, after a rather long but elementary calculation, that the dipole force vanishes for $x=0$ and if

$$e^{-2\pi y/a\sqrt{3}}\cos\frac{4\pi}{a\sqrt{2}}\,x-\frac{3}{2}\,\frac{1-e^{-\pi\sqrt{3/2}}}{1+e^{-\pi\sqrt{1/2}}}\cdot e^{-2\pi y/a}$$
$$=3e^{-\pi\sqrt{3/2}}-\frac{3}{2}\,\frac{1-e^{-\pi\sqrt{3/2}}}{1+e^{-\pi\sqrt{1/2}}}\cdot e^{-\pi\sqrt{1/2}}$$

or

$$e^{-2\pi y/a\sqrt{3}}\cos\frac{4\pi}{a\sqrt{2}}\,x-1.325e^{-2\pi y/a}+0.0798=0.$$

Since $y>a/4\sqrt{2}$ the first term is always very much smaller than the two others and can therefore be neglected, and we find that the dipole force vanishes if:

$$y=-\frac{a}{2}\log\text{nat.}\frac{0.0798}{1.325}=0.447,\ a=\frac{a}{4}\sqrt{2}+0.093a.$$

Consequently, the electric polarization of the ions increases or decreases the gliding strength according to whether the lift in the point of maximum gliding force is smaller or larger than $0.093a$.

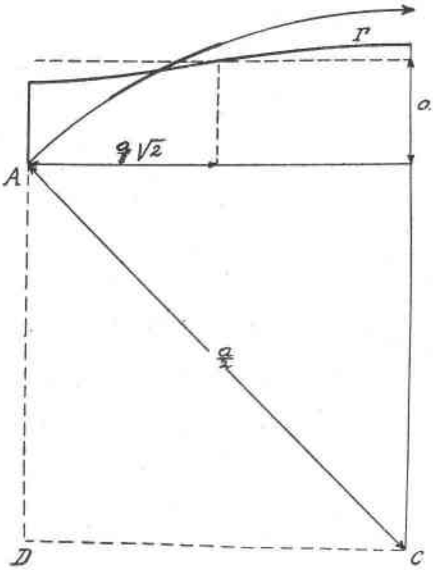

FIG. 6.

Fig. 6 shows the curve Γ along which the dipole force vanishes (calculated without neglecting the first term). The forces acting between the ions during gliding are not large enough to produce an appreciable compression of the ions. Hence we must assume that the path of the ion must be a circle with C as center. The periodicity of the crystal structure leads to the conclusion that the maximum gliding force occurs for a shift $x=a/8\sqrt{2}$. The figure shows that at this point the lift is larger than $0.093a$. A more careful consideration of the repulsive forces shows that the maximum gliding force may occur for a shift $x<a/8\sqrt{2}$ but still at a point near the curve Γ. We conclude therefore that: *The polarizability of the ions has a very small influence on the gliding strength along the (011) plane.* Whether it is an increase or a decrease depends on the law governing the repulsive forces.

SUMMARY

The gliding strength of crystals cannot accurately be calculated since it depends largely on the unknown law for the repulsive forces between the ions. The order of magnitude of the observed gliding strength is in agreement with the estimated theoretical value. The experiments show that for crystals with ions of small polarizability the gliding strength along the (011) plane is smaller than along the (001) plane.

The theory leads to the conclusion that the electric polarizability of the ions decreases the gliding strength along the (001) plane but does not appreciably change the gliding strength along the (011) plane.

This consideration explains the observation (Fig. 2) of Buerger that crystals whose ions have a large polarizability glide along the (001) plane.