# The Molecular Process of Crystal Growth in Hexagonal Metals. Deposition upon Monocrystalline Hemispheres of Zinc

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The growth of a single crystal rod of zinc is allowed to proceed from a small orifice into a mass of molten zinc and the monocrystalline hemisphere thus formed isolated by rotation of the apparatus. The hemisphere is subjected to uniform bombardment by zinc vapor and observation of the growth on its surface forms the basis for a study of the variation of depositional rate with crystal surface structure. It is assumed, with Kossel and Stranski, that the force acting upon an atom which has struck the crystal surface is qualitatively proportional to the number of contiguous lattice atoms and a "force series" is drawn up listing the relative depositional energies for eleven typical positions of different crystal surface structure. With the aid of this force series the macroscopically observed growth on the experimental crystal is interpreted in terms of atom-by-atom deposition.

WE DEFINE the term "molecular process of crystal growth" as the process by which a macroscopic crystal takes atoms or molecules from its environment and incorporates them into its lattice.[1] To describe this process we have to answer the specific question: what is the influence of the geometric arrangement of atoms at any given point of the crystal surface upon the probability that an atom striking the crystal at that point will condense and become an integral part of the lattice? The bombarding atom may come from the gaseous or liquid phase or from an adjacent crystal of different orientation (recrystallization phenomena).

The molecular process of crystal growth has been studied from both the theoretical[2] and experimental[3] angles in the cases of certain heteropolar salts but the investigation of the metals from this point of view has scarcely been begun.[4] Stranski[5] recently has extended his method of theoretical treatment to metals of simple cubic lattice type. With the exception of the work of Volmer and Estermann on mercury[6] little if any experimental work has been done under conditions permitting direct and unambiguous interpretation of the experimental observations.

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* During the course of this work, National Research Fellow in Physics.

[1] The mechanism of formation of crystal nuclei is regarded, at least formally, as a distinct problem.

[2] Kossel, Leipziger Vorträge, 1928. Hirzel, Leipzig; Stranski, Zeits. f. physik. Chem. **136**, 259 (1928).

[3] Kossel, reference 2, gives a resumé of this work.

[4] The great mass of information which has been accumulated in metallographic research throws little light upon the fundamental crystal growth mechanism. The initial conditions are generally so imperfectly defined as to preclude analysis of the observations in terms of the fundamental growth process.

[5] Stranski, Zeits. f. physik. Chem. B **11**, 342 (1930).

[6] Volmer and Estermann, Zeits. f. Physik **7**, 13 (1921).

Of all the possible schemes for the study of crystal growth one involving deposition upon a monocrystalline sphere or hemisphere is peculiarly adapted to furnish the maximum amount of information directly interpretable in terms of the elementary process of atom-by-atom growth.[7] If we subject a spherical monocrystalline surface which is free from oxide or other impurities to uniform bombardment from a disperse phase slightly supersaturated with respect to the crystal temperature any observed differences in growth rate at different points of the crystal surface can be traced with some degree of confidence to the structure of the crystal substratum at these points; the initial conditions are otherwise impartial to growth in any given direction.[8] Since, furthermore, every possible crystal zone is potentially developable from a sphere or hemisphere a comprehensive survey of the effect of substratum structure upon growth is obtainable in a single experiment.

## EXPERIMENTAL

### Method

The essential features of the method may be described as follows: A single crystal rod is grown by Bridgman's method[9] in a narrow tube, *C* Fig. 1, which projects into a mass of molten zinc contained in a wider tube, *B*. The growth of the rod is carried beyond the orifice of *C*; a hemispherical crystal-liquid boundary is thus formed and upon quickly rotating the tube through 180° a monocrystalline hemisphere, strain-free and with an oxide-free mirror-smooth surface, is left exposed to the bombardment of zinc vapor furnished by the pool of metal at the other end of the tube. Regulation of the rate of growth on this hemisphere is effected by a simple regulation of the temperature difference between crystal and vapor source. Continuous visual observation of the growth is secured by using an open-wound glass tube *F* as the heating furnace.

### Apparatus and procedure

The apparatus described here is that used in our first experiments. Some obvious refinements, notably the addition of an evacuated glass cylinder for shielding the tube from irregular air currents, and more exact control of the temperature gradient between crystal and vapor source by a thermocouple acting upon a galvanometer-photocell-thyratron circuit[10] so far have been found to have no decided effect upon the results and are not mentioned further.

Fig. 1 is a diagrammatic cross sectional sketch of the essential parts of the apparatus: a Pyrex glass tube *ABC* blown in the form shown and the Pyrex

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[7] Kossel, reference 2.

[8] The anisotropic nature of the thermal conductivity in noncubic crystals is probably significant only when the growth rate is rapid. Gliding of "adsorbed" atoms over the crystal surface with final condensation at a point other than the point of impact is a factor which must, however, be considered.

[9] Bridgman, Proc. Am. Acad. Arts Sci. **60**, 307 (1925).

[10] A slight modification of the arrangement described by the writer in Rev. Sci. Insts. **1**, 764 (1930).

furnace tube *F*. *ABC* made a sliding fit in *F*. *F* was wound with 3 mm nichrome ribbon spaced 3 mm between turns, total resistance about 20 ohms, and the winding secured with narrow vertical bands of talc-water glass cement. The winding was divided into two sections, $S_1$ and $S_2$, by an adjustable contact clamp. *T* was a thin-walled brass tube cemented over the end of *C*. The open end of *F* was stopped with a transite disk and the whole arrangement mounted on laboratory clamps in such a way that, from an initial vertical position, it could be rotated through 180° about a horizontal axis.

Highly purified zinc[11] in the form of small lumps and in quantity sufficient to fill *C* and about one third of *B* with molten metal, was placed in the chamber *A* and *V* then connected by flexible metal vacuum tubing and cooled sealing wax joints with a Hyvac pump, McLeod gauge, mercury trap, and a reservoir containing nitrogen over liquid sodium-potassium alloy. After repeated evacuation and washing of *ABC* with nitrogen the zinc was melted in vacuum and degassed by swashing the molten metal about in *A* under full vacuum. After continuing this treatment for two hours enough nitrogen was admitted to force the metal slowly through the 0.2 mm capillary filter connecting *A* and *B*. *A* was reevacuated while the capillary was still sealed by a small quantity of molten zinc and the tube sealed off from the pump. The molten metal in *B* showed no traces of floating oxide and retained the appearance of clean mercury after being held continuously in the molten state

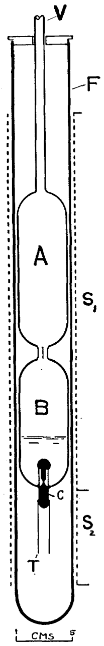

Fig. 1. Experimental arrangement for preparing monocrystalline hemispheres and subjecting them to deposition from the vapor phase.

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[11] Total impurities under 0.001 percent. Kindly furnished to me by Mr. H. M. Cyr of the New Jersey Zinc Company.

for periods as long as five days. Improvement of the outgassing vacuum from $10^{-3}$ to $10^{-6}$ by addition of a three-stage mercury diffusion pump and double liquid air trap had no appreciable effect upon the results.

Crystallization in $C$ was started by slowly decreasing the current in section $S_2$. The beginning of crystallization and its growth upwards toward the orifice was followed by the characteristic change in light reflection attending solidification and the final stage in the development of the hemisphere determined by trial and error: the tube was rotated sufficiently to expose the orifice and the position of the solid meniscus observed. By suitable readjustment of the heating currents in $S_1$ and $S_2$ and of the position of the tube $ABC$ relative to the temperature gradient between $S_1$ and $S_2$ the crystal-liquid interface was moved out into the bulk of molten metal until it took the desired position. Two or three trials were usually sufficient and the interface position could then be held practically constant for hours at a time. The heating currents in $S_1$ and $S_2$ and the tube position for this steady state, which is designated "setting I", were recorded, the apparatus rotated and fixed in the inverted position, and the currents again adjusted until the crystal was held just below and the pool of zinc just above the melting point, "setting II". This latter adjustment was made by determining the currents for which the crystal just began to melt and the pool to solidify, then slightly decreasing the one and increasing the other. Having once determined these settings growth experiments could be carried out repeatedly on different crystal hemispheres with the same tube.[12] The procedure for each growth experiment was, now, (1) the zinc in $C$ and $B$ was remelted completely, the current in $S_1$ set at the value for setting *I*, and the crystal hemisphere grown by gradually decreasing the current in $S_2$ to the value for setting II. The stem and hemisphere were usually grown in about one hour but the process could be speeded up to half an hour or slowed down to two hours without apparent influence on subsequent observations. (2) The tube was rotated and the currents brought immediately to setting II.

To secure an estimate of the temperature difference between the crystal surface and the vapor source during deposition a dummy tube, identical to $ABC$ with the exception that a thermocouple well was punched in $B$, and $C$ blown in such a way as to allow of introducing a thermocouple junction just below the surface of the hemisphere,[13] was put through adjustments identical to those in the determination of settings I and II. The temperature difference in this tube was found to be about 5°C and in the actual growth experiments the difference was, presumably, of this order. It should be emphasized at once that an extremely small temperature gradient inducing growth at a rate so low as to approach the equilibrium or zero-growth-rate state is a desirable experimental condition and that the rather primitive apparatus employed here is not capable of the exact control required for the study of extremely slow growth. The results which have been obtained show, however, that infor-

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[12] Crystallization and remelting of zinc in a Pyrex tube does not crack the tube provided the temperature is maintained near the melting point.

[13] In this case the hemisphere was polycrystalline.

mation regarding some of the main features of growth may be gotten by this simple method and the consequences of a proposed theory of growth are checked sufficiently to warrant the conclusion that the general method of attack is sound.

## Results

Deposition on the hemisphere began immediately after rotation of the tube. The phenomena observed are grouped in stages, progression to a new stage connoting in general the point at which a significant feature of growth first became visually observable.

*Stage 1:* During the first half-hour the only effect observed was a slight, apparently uniform, dulling of the initially mirror-smooth surface of the hemisphere.

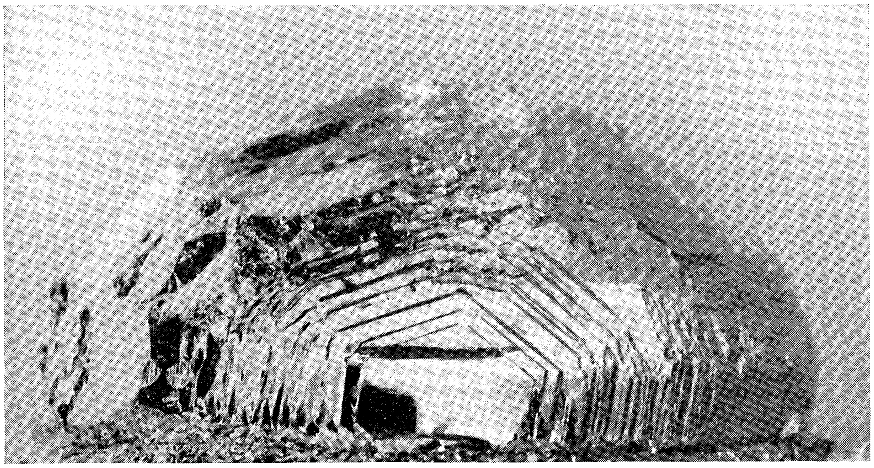

Fig. 2. Photograph of a typical experimental crystal after two and one-half hours deposition. Principal crystal axis approximately normal to plane of paper.

*Stage 2:* A small patch, about half a millimeter in diameter when first observed, plane, circular, and brilliantly reflecting, appeared against the duller background of the crystal surface.

*Stage 3:* The small patch increased continuously in diameter and clearly showed itself to be a plane truncating the sphere. After a total elapsed time of an hour three narrow brilliant bands, equidistant and comparable to the longitudinal lines of a terrestrial globe map, appeared. These bands converged at the center of the "polar" plane patch. This stage was especially striking and beautiful to watch.

*Stage 4:* The polar plane continued to increase in diameter; it was no longer circular but imperfectly hexagonal with the corners of the hexagon undeveloped. Below the polar plane a series of step-like plane-surfaced shoulders developed, each hexagonal in form.

Further growth was a continuation of stage 4 with each feature noted there progressively developing. Fig. 2 is a photograph of a hemisphere after two and a half hours deposition; the heating current was shut off and the crystal broken out of the cold tube. This crystal was chosen for its particularly favorable orientation and is, otherwise, somewhat less perfect than most of the crystals which have been made. In ten of the twelve hemispheres grown the major crystal axis was approximately normal to the tube axis, a tendency which has been observed in single crystal rods by Bridgman and others and which is consistent with the theory of growth suggested later in this paper.

### Interpretation of results

Fig. 3 is a photograph of a model, built up from steel ball-bearings secured with rubber cement, which has proved useful in visualizing the initial surface structure of the zinc hemisphere and in reducing the observed growth to its origin in single-atom deposition. With the aid of suitable guides this model was built in such a way that it duplicated the model which would be obtained by filling a spherical cavity with balls arranged in the system of hexagonal closest packing, dividing this sphere through the equatorial basal crystal plane, and finally quartering the hemisphere. The exposed side elevation of the model then represents fairly acccurately a portion of the surface of a single crystal sphere of ideal close packed hexagonal type some 5 $\mu\mu$ in diameter. The differentiation in surface structure clearly shown between (1) the uniquely regular surface $B$ representing the 0001 basal cleavage plane, (2) the bands $P$ with the characteristic alternate-row regularity of the prismatic and pyramidal zones, and (3) the irregular regions $K$, furnish the starting point for interpreting the experimental observations. It is clear that in the actual crystal corresponding to a model of impracticable size $K$ spreads out over practically the entire surface; $B$ and $P$ would very nearly but, on purely geometric grounds, never entirely disappear. What, now, is to be expected when a hemisphere of this surface structure is subjected to bombardment by gaseous metal atoms? The white balls in Fig. 3 represent atoms which have struck the

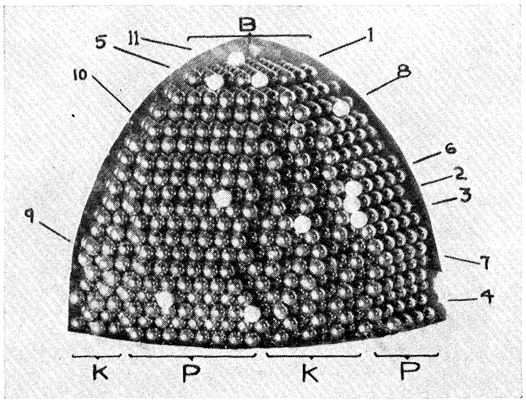

Fig. 3. Model of spherical crystal surface in its initial state. Numbered white balls represent atoms from vapor which have struck at points of different surface structure. Principal crystal axis normal to base of model.

crystal at points of different surface structure. Which of these atoms is most likely to be held, which to reevaporate immediately?

Table I lists these "white" atoms, a description of their positions in terms of the surface geometry of the crystal, and the number of lattice atoms contiguous to each. The effective diameter of a lattice atom is set equal to unit length and only the four innermost shells with radii 1, $2^{1/2}$, $(8/3)^{1/2}$, and $3^{1/2}$ about the condensed atom are taken into account. The environment of any given atom may be described by a symbol of the form 6/3/1/9 which is equivalent to the statement that the atom is question has six "neighbors" at unit distance (direct contact), three at distance $2^{1/2}$, one at $(8/3)^{1/2}$, and nine at $3^{1/2}$. We now make the assumption, analogous to that previously used by Kossel and by Stranski in their theoretical discussion of growth in cubic crystals, that the force acting upon an atom which has struck the crystal surface is the sum of four force terms, each of which is proportional to the number of neighbors in a given shell and each of which is weighted by the radius of that shell. The symbol 6/3/1/9 then becomes a measure of the relative magnitude of the force acting upon the atom in question. Quantitative weighting, which

TABLE I. *Relative depositional energies as a function of crystal surface structure.*

| Designation of position. Fig. 3 | Description of position | Number of contiguous atoms at distances: | | | | Symbol |
|---|---|---|---|---|---|---|
| | | 1 | $2^{1/2}$ | $2(2/3)^{1/2}$ | $3^{1/2}$ | |
| 1 | Edge of incomplete 0001 lattice plane. | 6 | 3 | 1 | 9 | 6/3/1/9 |
| 2 | Edge of incomplete $10\bar{1}2$ pyramidal face. position 6 previously filled. | 6 | 3 | 1 | 7 | 6/3/1/7 |
| 3 | Ditto of 2. Position 2 previously filled. | 6 | 3 | 1 | 7 | 6/3/1/7 |
| 4 | Edge of incomplete $10\bar{1}0$ prismatic face. | 6 | 2 | 1 | 9 | 6/2/1/9 |
| 5 | Edge of complete 0001 lattice plane. | 5 | 3 | 1 | 9 | 5/3/1/9 |
| 6 | Edge of incomplete $10\bar{1}2$ pyramidal face. Position 2 not previously filled. | 5 | 3 | 1 | 7 | 5/3/1/7 |
| 7 | Ditto of 6 | 5 | 3 | 1 | 7 | 5/3/1/7 |
| 8 | On $10\bar{1}1$ pyramidal face. | 5 | 3 | 1 | 7 | 5/3/1/7 |
| 9 | On prismatic $10\bar{1}0$ face. | 4 | 4 | 0 | 7 | 4/4/0/7 |
| 10 | On $10\bar{1}2$ pyramidal face. | 4 | 2 | 1 | 9 | 4/2/1/9 |
| 11 | On basal 0001 face. | 3 | 3 | 1 | 6 | 3/3/1/6 |

would be impossible at present, generally turns out to be unnecessary. Table I is arranged as a force series; it is also an energy series and a condensation probability series. The atom at the head of the table is acted upon by the maximum, that at the foot by the minimum, force and the probability of permanent condensation decreases from top to bottom.

Reexamination of the experimental observations in the light of this force table and the crystal model from which it is derived yields the sought for interpretation of the macroscopically observed growth process in terms of atom-by-atom deposition. If the force table is valid deposition will occur at the maximum rate, position 1, along the edges of the rudimentary polar plane, *B* Fig. 3, and of the 0001 lattice layers which form a series of steps below *B* in the polar region of the hemisphere. The maximum rate is maintained until all except the corner atoms of the hexagon in each of these layers are laid down; the corner atoms are bound by the slightly smaller force 6/3/1/8. For the beginning of a new row along the edge of one of these hexagons the force drops to 5/3/1/9, position 5, and since the force is still less at the corners of the completed hexagons, 5/3/1/7, growth will be directed toward rather than away from these corners. The imperfect corners exhibited by the experimental crystal, Fig. 2, show agreement between theory and experiment on this point. In contradistinction to the maximum rate parallel to the 0001 plane, the growth rate normal to *B* should be a unique minimum, position 11. Isolated atoms initiallly present on *B* will evaporate and atoms striking the face of *B* will either reevaporate relatively rapidly or glide to an edge and there condense.[14] Growth in this region of the hemisphere should be relatively very rapid parallel to, and slow normal to, the 0001 plane; the rudimentary plane *B* should grow until it eventually develops into a uniquely perfect macroscopically visible polar plane truncating the hemisphere, conclusions which are strikingly borne out by the experimental results.[15]

The next most favored positions of growth lie along the edge of a *P* band, positions 4 and 6, or in one of the zigzag furrows which initially cover practically the entire surface of the hemisphere, position 7. Because of the greater depositional energy at position 4 the first atom will most probably be laid down near the "equator". After a single atom is deposited in any one of these positions the force acting upon the next atom jumps to 6/3/1/7, Positions 2 and 3, and this force is maintained until a complete vertical row is deposited. The first effect of this deposition to be observed experimentally is an increase in the width and depth of the furrows. The furrows are initially sufficiently minute to permit specular reflection of visible light and the hemisphere appears optically smooth. As the dimensions of the furrows approach the wave-length of visible light scattering sets in and the hemisphere is "dulled", stage 1 above. The mechanism of this coarsening is indicated in Fig 4, which is a model of part of a single 0001 lattice plane comprising a *K*

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[14] The reality of this gliding hypothesis is being investigated by a direct method in this laboratory.

[15] See stages 2 and 3 of the experimental observations. We have here an explanation for the results of Volmer and Estermann on mercury, reference 6.

region bounded by two *P* bands. Each vertical row deposited at the edge of a *P* band or in a furrow contributes one atom to each 0001 plane. The black-dotted white balls represent the atoms which are laid down first; deposition then follows along the direction of the arrows. As two columns of condensing atoms, moving toward each other at an angle of 120°, meet at a corner the depositional energy drops sharply and growth at that corner is halted until succeeding columns moving up en echelon meet at the corner and halt in their turn. The net effect is the progressive coarsening observed experimentally.

An atom striking at any point on the face of a *P* band, positions 8, 9, 10, is held by forces which are everywhere less than the minimum force at the edge of the band and the effect of this differentiation upon growth should be a progressive widening of the rudimentary bands while their surfaces remain "flat", i.e., everywhere parallel to a hexagon circumscribing the equatorial great circle of the sphere. Stage 3 of the experimental observations may be interpreted as the stage of growth at which the widening of these bands becomes visible. Since the band surfaces are relatively regular in structure they appear as the brilliant "longitudinal lines" against the duller background of the *K* regions. The result of continued growth along the preferred tangential direction is shown by the experimental crystal, Fig. 2. Positions 8, 9, and 10 are, of course, only typical of a multiplicity of surface structures which are presumably present initially along a *P* band. A consideration of the variation in depositional energy between these few positions is, however, sufficient to bring out one or two more important features of growth. From the large value of the force term for position 8 relative to positions 9 and 10 we should conclude that the $10\bar{1}1$ surface structure wherever initially present should be filled in. The filling-in process will leave a minute shoulder or ledge bounded by a 0001 plane and a low-energy pyramidal or prismatic plane. In general

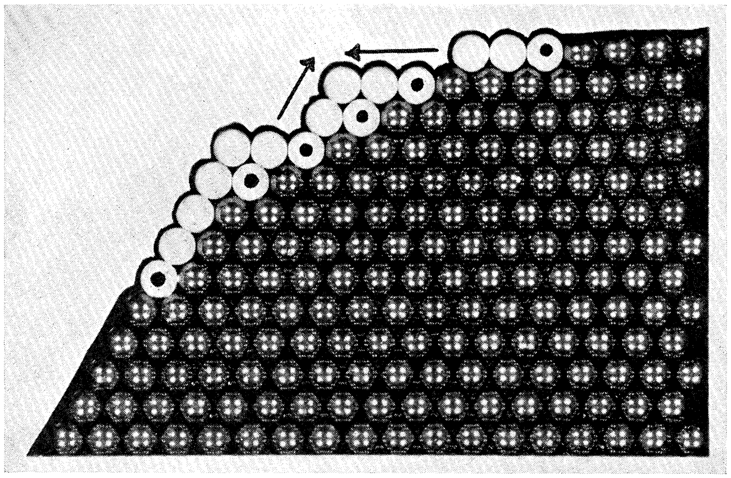


Fig. 4. Model of a single 0001 lattice plane of the hesmisphere. Dark balls: initial structure. White balls: condensed atoms.

such a ledge will be formed wherever a high-energy surface adjoins a low-energy surface and since, on geometric grounds and as indicated by the model, an alternation of high and low energy surfaces is to be expected along a rudimentary $P$ band the first effect of growth on the surface of these bands should be the formation of a series of ledges. The crystal hemisphere is converted, in effect, into a stack of crystal plates, each plate paralleling the 0001 crystal plane. The edge of a shoulder is relatively impregnable to further deposition and growth must be directed from the inner corners of the shoulders toward the edges. The result will be a progressive increase in the width and depth of the shoulders similar to the coarsening of the furrows discussed above. The development of these shoulders was easily followed during deposition on the hemisphere from the first appearance of the longitudinal lines, which under a low-power lens showed a surface structure similar to the edge of an imperfectly aligned pack of cards, to the point at which some of the shoulders attained a depth and width of the order of a millimeter, Fig. 2. A further consequence implicit in this interpretation is: high-energy pyramidal faces should not appear on the final crystal. While goniometric measurements have not been made for lack of the necessary instruments, rough visual examination with a low-power microscope is sufficient to distinguish between pyramidal faces of high $d/a$ axial ratio (low-depositional energy according to our force series) and those of low $d/a$ ratio (high energy). Such examination of the experimental crystals has failed to show a single face of low ratio among hundreds of high ratio.

## General significance of the results

The study of the molecular process of crystal growth is essentially a study, under peculiarly simple conditions, of crystal surface forces as a function of surface structure and as such is capable of throwing light on related problems involving the action of the surface forces of solids. The hypothesis of "active centers" which has played such a prominent part in the development of the theory of adsorption and catalysis at solid-gas and solid-liquid interfaces may be given definite form in terms of relative depositional energies. The forces which determine crystal growth, and for which the bombarding atoms are in effect probes, must enter also as the variable factor which, for a given system, determines the effect of surface structure upon adsorption. Stranski[16] has already pointed out that in solids of simple cubic lattice type the high adsorptive power of homopolar relative to heteropolar crystals may be accounted for by the juxtaposition of high energy positions peculiar to the homopolar crystal lattice. It is clear from the preceding discussion that this juxtaposition is characteristic, also, of zinc. In zinc the active centers are of course those positions which rank near the top of the force series, Table I, and the variation of the heat of adsorption with surface structure may be expected to parallel the variation in the depositional energy of zinc atoms themselves.[17]

[16] Stranski, reference 5, p. 348.

[17] Interesting possibilities, not discussed further, are encountered in considering the adsorption of polyatomic molecules; e.g., the modifying effect of the dissociation energy, the influence of the space configuration of the gaseous molecule, and the orienting effect to be expected from fitting one end of the molecule into contiguous positions on the crystal surface.

Particularly significant results may be expected from combining the findings of molecular growth studies with those of the reflection of molecular rays from monocrystalline surfaces, whether the reflection be of specular or of cosine type. Cosine reflection, true condensation succeeded by reevaporation in the sense of the original theory of Langmuir and Wood, may evidently be treated by methods identical to those used in the present work, and the accommodation coefficient, to which the effect of crystal surface structure is relegated in the Langmuir theory, invested with specific physical significance in terms of the relative depositional energy.

The major part of this investigation was done at the Jefferson Physical Laboratory of Harvard University in 1929–30. I should like to record my great obligation to Professor P. W. Bridgman for his interest and advice during the course of the work.

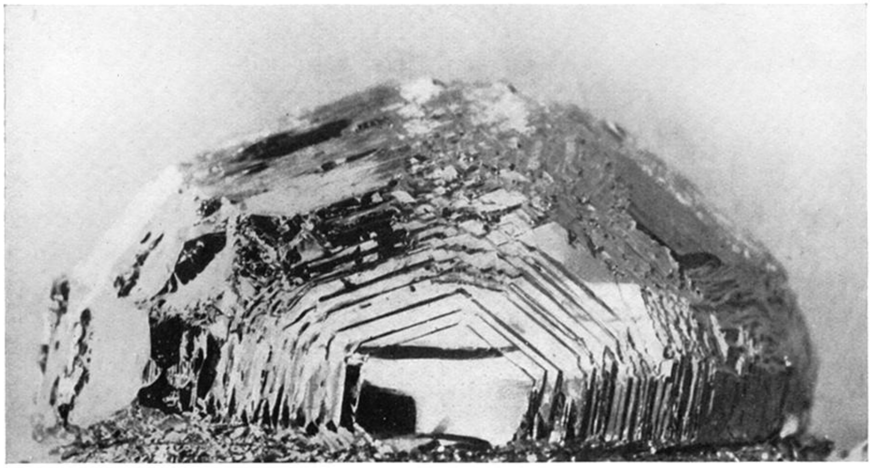
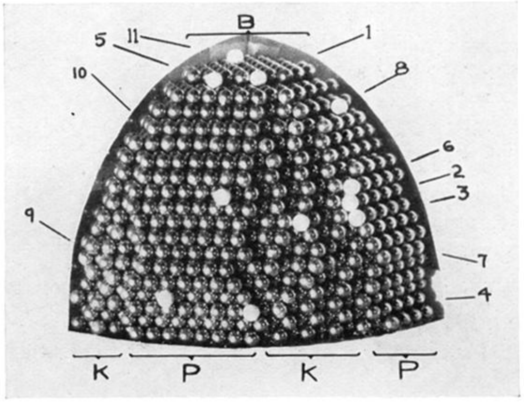


Fig. 2. Photograph of a typical experimental crystal after two and one-half hours deposition. Principal crystal axis approximately normal to plane of paper.



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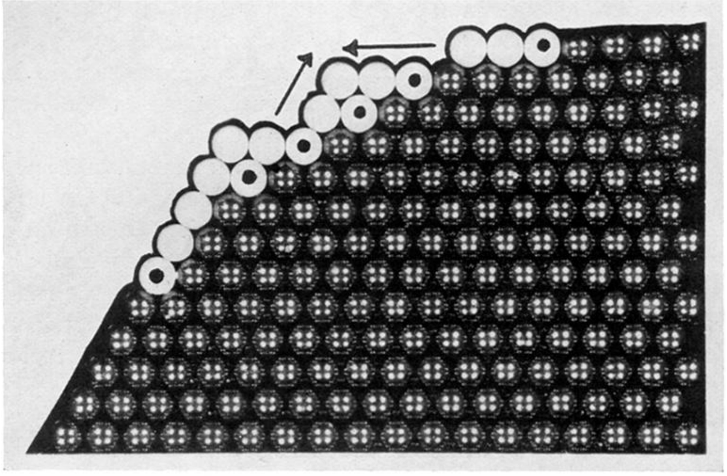

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