THE SIGNIFICANCE OF "BLOCK STRUCTURE" IN CRYSTALS

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ABSTRACT

An apparent subdivision into block-like subunits in almost parallel orientation is very common in crystals. It is shown that actually the subunits are not separate blocks or grains, but are continuous with each other by way of the parent crystal nucleus, forming a rudely spherically-symmetrical, tree-like structure. The term *lineages* is introduced to cover such crystal subdivisions. The origin of lineages is ascribed to structural distortions, which, in turn, are surmised to arise either from the Zwicky surface cracks in crystals or from improperly distributed solid solution impurities. A much larger spacing is ascribed to the Zwicky cracks while the crystal is immersed in its depositing solution.

Lineage boundaries are loci of negative crystals and voids, and probably localize exsolution and replacement.

Anyone who has attempted to find flawless material for gliding experiments can not have helped making the observation that in the ideal sense genuinely continuous single crystals of some species are not obtainable in anything but the smallest bits. A similar observation must have been made by all those who have attempted to make goniometric measurements on the surface planes of crystals. The writer has had occasion to observe that galena, natural and artificially grown alkali halides, pyrite, and marcasite, especially, cause not a few experimental difficulties because of imperfections in this respect.[*]

The condition is apparent in two very striking ways. First, the surface of a crystal (certain Joplin galena and marcasite, and certain pyrite display it well) often has the appearance of being composed of many smaller crystals stacked together in almost parallel position, but with enough difference in orientation so that its cumulative effect sometimes gives rise to a twisted appearance of the major unit. The individual subunits may in themselves display all the forms common for the mineral in that locality,[1] (see Figures 1–4). Mild cases of this condition (as distinct from vicinal faces) are an annoyance to the goniometer investigator.

[*] This statement does not imply that this feature is peculiar to the crystals mentioned. Once one's attention has been called to the condition described beyond, it can be recognized on almost any crystal whatever.

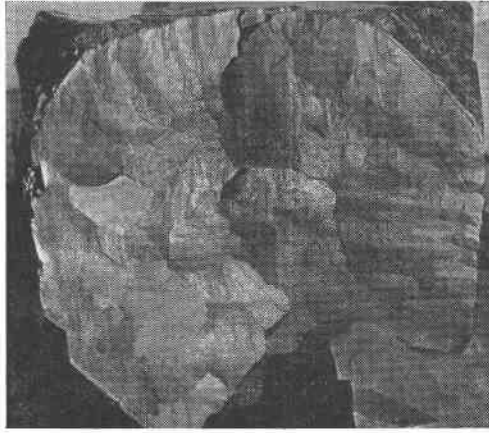[1] There need be no confusion of this feature with certain types of natural etching.

FIG. 1. Galena from Joplin, $\frac{2}{3}$ natural size. The specimen was illuminated so that the lineage development is brought out. The peripheral regions of the top and right, especially, illustrate the radial tendency of lineages. Some of the larger blocks, as the one in the center, are in themselves composed of a number of lineages, each a descendant within a family, so to speak, from the parent lineage represented by the block.
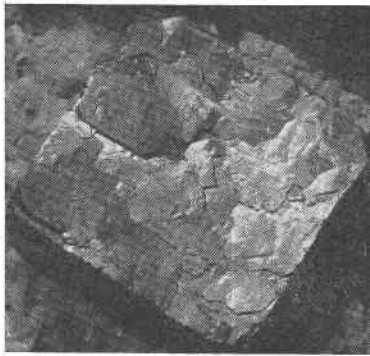

FIG. 2. Galena crystal on dolomite, with chalcopyrite; Joplin, natural size. The cube has been illuminated to bring out some of the surface evidences of lineage structure. Sharp shadows mark the crystal off into blocks of cubo-octahedral outline. These are the major lineage families. Each of these is further subdivided into the less conspicuous individual lineages made visible by mottling. This feature is more easily observed by actually rotating the specimen and observing the changes in illumination.

Second, minerals with good cleavage like galena allow one to examine this feature in the interior. Head[2] has recently noted this characteristic in the Joplin galena. Superficially, it appears that the crystal is simply an inter-growth of separate individuals in almost parallel position. The whole cleavage surface is an irregular mosaic of different grains. For the most part, the grains are de-
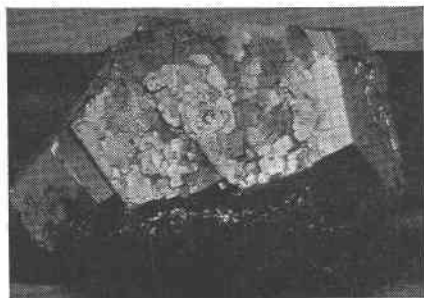

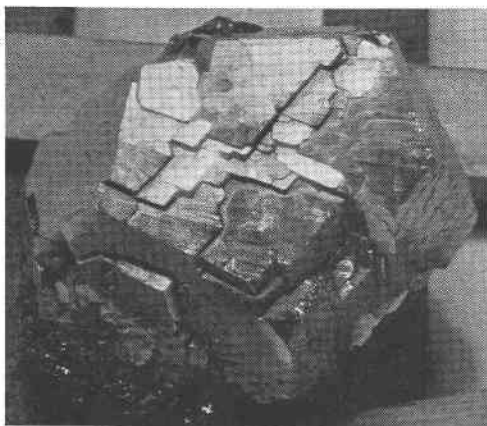FIG. 3. Pyrite from Elba, natural size. Mosaic of lineages on pentagonal face of pyritohedron.

FIG. 4. Pyrite from Elba, natural size. The pyritohedral face is clearly cut up into sharp blocks which represent families of lineages. The individual lineages within the family blocks are indicated by a faint mottling. This is most apparent in the upper block.

[2] R. E. Head, The Cleavage Surfaces of Galena: *American Mineralogist*, **16**, 1931, 345–351.

cidedly elongated, and as Head has remarked, they have a distinctly radial arrangement. The grain boundaries are visible almost wholly because adjacent grains differ slightly in orientation and therefore the cleavage of each grain (the aggregate of all of which make the ordinary galena cleavage) differs very slightly in slope from that of its neighbors. With diffuse light, this condition is not striking, but with a sharp source of light it can not be missed.

FIG. 5. Photomicrograph of galena cleavage surface, ×43. This photograph was taken with normal illumination using a metallographic microscope, with the cleavage surface tipped slightly so as to give a maximum contrast between several lineages. The parent crystal stock is at the bottom of the photograph. Between a quarter and half way up, this splits into four branches, a dark one at the left, another dark one in the center, and alternating light ones. Degree of illumination is a measure of degree of deviation from the parent orientation. This illustration is especially introduced to indicate the derivation of the central dark lineage from the parent stock and its gradual change in orientation. The square motif is the cubic cleavage traces. The fine lines on the surface will be discussed in a later paper.

If the observation goes no farther than this the intrinsic nature of the situation is overlooked. The key to the explanation of the phenomenon is found in the fact that the orientation discrepancies between neighboring blocks are least near the center of the crystal and increase toward the edges, and, most important, grains which are discrete near the periphery of the crystal, when followed back

to the center are found to join in one and the same parent grain.[3] Figure 5 gives photographic proof of this. In other words, the different "grains" are not actually different grains in the ordinary sense, but are really one and the same grain, connecting by way of the original nucleus. Figure 6 illustrates this relationship diagrammatically for the two-dimensional analog of a crystal.

The writer proposes the name *lineages* for all such "grains" whose orientations descend continuously from the same parent nucleus but whose mutual orientations may differ. Some such term is plainly called for since in the strictest sense all descendants from
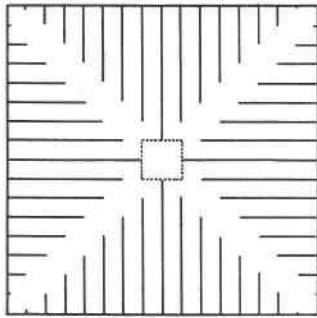

FIG. 6. Two dimensional analogue of a cube subdivided into lineages. All lineages are descended from the central (dotted) nuclear cube, and all are parts of a continuous structure. This illustration is highly diagrammatic and much too simple, partly because the third dimension complicates the structure and partly because natural lineages are much less regular. The scheme, however, is intrinsically correct. The parallel peripheral lineages may be seen in the galena of Figure 1.

the same nucleus are the same grain and in the best sense they are also the same crystal. In this nomenclature, the discontinuities which mark the cleavage surfaces of a single crystal, such as those under discussion for galena, are *lineage boundaries*.

The reason for the "parallel" part of the sub-parallel grouping is clear: the orientation is inherited by direct line of descent from the original crystal nucleus, with slight modification. One of the characteristics of the modification is that it is continuous and does not suffer sudden breaks. It appears evident without the necessity of any special argument that the only thing capable of causing a

[3] Because of the three dimensional nature of the crystal, all neighboring grains can not be followed to a common single source for most of the joining takes place at some other depth than that of the cleavage surface under observation.

continuous change in orientation from parent nucleus to final crystal exterior is a structural distortion (so-called "lattice distortion").

The question arises, what causes structural distortion? It appears that it may arise from two distinct sources, which may be briefly designated *surface effect* and *solid solution*. It further appears that neither of these two effects is sufficient to cause lasting distortion unless crystallization takes place under essentially non-equilibrium conditions.

Surface Effect

The evidence for the existence of cracks in crystal surfaces has been reviewed by Zwicky in one of his earlier papers on the mosaic structure in crystals.[4] The presence of these flaws has been suggested along two main lines of independent evidence: the discrepancies in expected and experimental strengths of solid materials, and the calculated surface contraction in ionic crystals.

It has been realized for some time that the experimental strength of solid materials, including polycrystalline aggregates, single crystals, and even glass, is not of the order of magnitude demanded by theoretical considerations of various sorts, but is much too small.

Having in mind particularly polycrystalline aggregates and glass, Griffith[5] has suggested and given very convincing argument in support of the thesis, that the subnormal experimental strength owes its origin to surface cracks. Zwicky[6] adopted this hypothesis for the preliminary form of his mosaic crystal theory, with rather special application to single crystals.

A second line of evidence is derived from direct calculations. Lennard-Jones and Dent[7] have shown that the surface layers of the sodium chloride structural type crystals (and this includes galena, admitting that the latter is ionic) must contract linearly some five odd per cent. They conclude, in part (p. 258):

[4] F. Zwicky, On the Imperfections of Crystals: *Proc. Nat. Acad. Sci.*, **15**, 1929, 253–259.

[5] A. A. Griffith, The Theory of Rupture: *Proc. of the First Int. Cong. for Applied Mechanics*, Delft, **1925**, 55–63.

[6] *Op. cit.*

[7] J. E. Lennard-Jones and Beryl M. Dent, The Change in Lattice Spacing at a Crystal Boundary: *Proc. Royal Soc.*, (A) 121, **1928**, 247–259.

> The general tendency will ... be toward contraction and this may lead to cracking at the surface.

This opinion was pronounced quite independently of any knowledge of Griffith's conclusions, the research being undertaken for the purpose of investigating whether or not the surface contraction which was apparently required by the results of experiments on electron scattering by crystals, was to be expected.

In order to gain a visual conception of how surface cracks may account for distorted structure, Figure 7 is introduced. This represents a (100) cross-section of an NaCl-type crystal. Because of the surface contraction necessary for a crystal of this type, the surface is in equilibrium only if the contraction strains are relieved by checking as indicated by the wedging cracks. For ionic crystals the order of magnitude of the spacing between cracks, is controlled, to a first approximation, by the fact that the greatest differential contraction between a pair of (001) planes A and B must not bring an ion in the upper plane opposite one of like sign in the lower plane. For most of the simple ionic crystals, like, say, the alkali halides, this gives the following relation:

$$\frac{\Delta c}{2} \sim \frac{a}{2} \tag{1}$$

where Δc is the maximum differential contraction between a pair of planes, and a is the length of a unit cell.

Taking Δc as of the order of magnitude of the total contraction, c,

$$\frac{c}{2} \sim \frac{a}{2} \tag{2}$$

Introducing the 5 per cent contraction calculated by Lennard-Jones and Dent, this leads to

$$\frac{5}{100}d \sim a \tag{3}$$

where d is the spacing between cracks.

or $$d \sim 20a \tag{4}$$

For the alkali halides and galena, this amounts to a spacing between cracks of about 100Å. This far we essentially follow Zwicky with regard to the checking of crystal surfaces.

The writer will presently propose an abnormal development of surface checking as an origin of lineage boundaries. In the present form of the theory of checking, however, the correlation is not very

obvious because the distance expected between cracks, some 100Å, is not of the order of magnitude of the lineage boundary spacings, which can be measured in millimeters in the alkali halides and galena. Zwicky's approximations, however, require additional considerations, all of which tend to increase the spacing of the cracks:
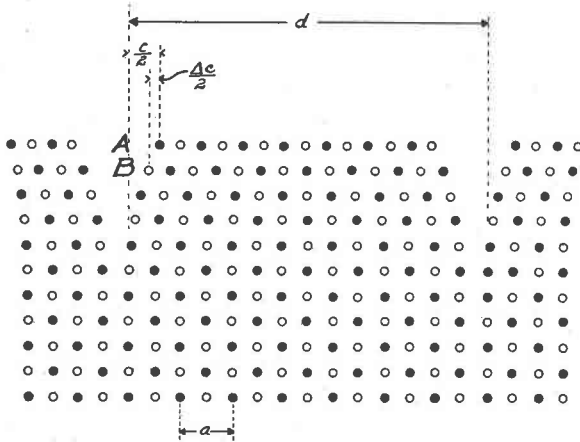

Fig. 7. Cross section of an NaCl-type structure on (100), showing cracks resulting from contraction of surface planes. Highly diagrammatic, simplified, and not to scale.
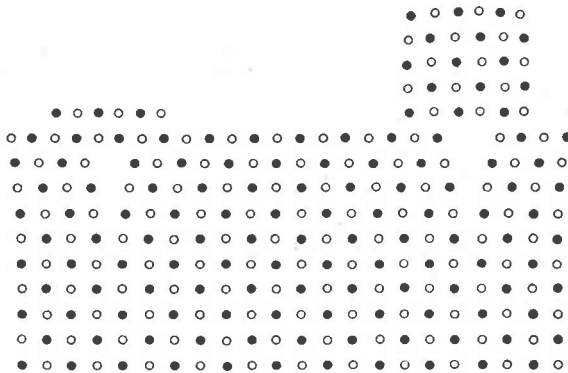

Fig. 8. The keying of the cracks shown in Figure 7, to form permanent distortions and lineages. Crack at left keyed by deposition of two layers of ions; crack at right keyed by precipitation of crystalline block. Diagrammatic.

(1) Lineages are developed during the actual growth of the crystal. In a majority of the cases which come up for consideration,

especially in the mineral kingdom, the crystal is deposited from some sort of liquid solution. The degree of surface contraction calculated by Lennard-Jones and Dent must be considerably modified if one takes account of this more complicated condition. In the absence of any very exact knowledge of the mechanism of crystallization, it is not easy to see just the extent of the modification, but it is to be expected that the direction of the change will be such as to decrease the quantity of contraction by a very considerable amount. The calculations have been made for a completely isolated single plane. The authors[8] say in this connection:

> A full investigation of this effect, taking into account the influence of the rest of the crystal, is not attempted here, but some indication of its magnitude may be obtained by considering the spacing in a single isolated layer. This will give an *upper limit* to the effect. [Italics by M.J.B.]

and also:

> The decrease is seen to be of the order of 5 or 6 per cent. The actual decrease in the surface layer will, of course, be less than this owing to the restraining influence of the lower layers.

Now, if not only the body of the crystal under the isolated plane is taken into account, but also the "restraining influence" of the mass of quasi-crystalline material, both solute and solvent, in the saturated layer just at the surface of the crystal, the situation is quite different. The external plane in question finds itself in an environment which is more like the normal interior of a crystal than like that of an isolated plane, and the contraction must not only be less, but, as a guess, must be orders of magnitude less, than that calculated for an isolated plane.

This effects the spacing of cracks in two ways. First, the coefficient 5/100 in (3) becomes very much smaller, hence the spacing, d, proportionally larger. Second, the surface plane is no longer in a region of such a sharp gradient in the field, because of the fact that the crystal bits, coordinated groups, or molecules of the solute, and molecules of the solvent as well, all oriented near this surface, effect a more gradual change in the field than is the case when the crystal is in contact with, let us say, air. For this reason, the differential contraction at the two surface layers is not vastly greater than that of the next pair of planes. In other words, the differential contraction gradient follows the field gradient and this is relatively gradual in the region of the crystal boundary. There-

[8] Lennard-Jones and Dent. *Op. cit.*, 256 and 258.

fore, the differential contraction of the two surface layers can no longer be taken as of the order of magnitude of the total contraction, but will be of a lower order, for the contraction is more uniformly distributed among the planes. This still further lowers the order of magnitude of the coefficient given as $5/100$ in (3), and consequently raises the order of magnitude of the spacing, d.

Apparent confirmation of the suggestion that contact with the solvent increases the crack spacing, is to be found in the experiments of Joffé[9] and his collaborators. Like other substances, rock salt shows an experimental strength inferior to its theoretical strength. The experimental strength is greater than usual, however when tested on pieces of the order of magnitude of 10^{-5} or 10^{-6} cms., from which it has been concluded that this is about the spacing of the surface cracks. When, however, the experimental strength is measured on specimens which are normal except that they have a wetted surface, Joffé finds that the strength approaches the theoretical limit. This anomalous increase appears to be in harmony with a large increase in the spacing of the cracks when in contact with a solvent.

(2) For crystals capable of easy translation-gliding, it is not absolutely necessary that the condition be obeyed which limits the maximum differential contraction to the length of a unit cell. A contraction of more than this amount would be no more serious to the stability and the solidity of the crystal than the condition of a crystal after bend-gliding.[10] For any crystal which can translation-glide, it is easy to imagine a condition of checked surface such that the lengths of the checks are indefinitely large (or possibly limited by some minimum energy condition) in a translation-gliding direction and of the width indicated by relation (4). In this case the cracks transverse to the gliding direction would attain major proportions, while those parallel to it would be of normal width. In the case of crystals composed of highly polarizable ions, and having, therefore, unusual translation-gliding possibilities, such as galena with translation $T=\{001\}$, $t=[100]$,[11] the checks might be of extranormal extent in all directions.

[9] Abram F. Joffé, The Physics of Crystals: *New York,* **1928,** especially pages 62–66.

[10] M. J. Buerger, Translation-gliding in Crystals: *American Mineralogist,* **15,** 1930, 50–51.

[11] M. J. Buerger, Translation-gliding in Crystals of the NaCl structural type: *American Mineralogist,* **15,** 1930, 235–236.

These considerations would appear to indicate that the cracking of a crystal surface, following the main theme developed by Zwicky, might in part, at least, be a cause of lineage formation, simply because the checking of the surface separates the crystal into lineage-like blocks which speculation indicates may be of the same general order of size as the observed lineages. Furthermore, the structure in the region of a crack is considerably distorted. Under normal conditions the distortion can not be cumulatively inherited by crystal substance yet to be deposited, for the simple reason that as the crystal grows, the crack closes behind as new layers are added ahead. Under normal conditions, therefore, the crack is lasting but insignificant, while the distortion at any given spot is ephemeral.

Under near-equilibrium conditions of crystallization, therefore, one would not expect lineages to form, and this is apparently just the case. The ideal crystals which are a pleasure to handle on the goniometer would be of this near-equilibrium grown type. Every crystallographer knows how rare such material is, a situation in line with one's expectancy of near-equilibrium conditions of crystallization.

Under conditions of rapid crystallization, there appear ways of maintaining the separation of the crystal into the branches (*i.e.*, lineages) produced by the cracks, and ways of maintaining the structural distortion caused by the crack. To gain a visual picture of this, suppose that addition of new material to the surface of the crystal takes place by the attachment of ions or coordination groups. A crack is bound to be bridged by this rather plastic juvenile material as indicated in Figure 8, and before it has a chance to compete, as in normal equilibrium, for a more secure perch, it is covered by another layer which seals the whole arrangement. The same would be expected to come about if new material is added to the surface as minute crystal blocks (Figure 8). This latter possibility is rather suggested for crystallizations from a viscous substance, from supercooled liquids,[12] and possibly for ordinary crystallizations.[13] Each crack-bounded surface patch, with cracks so keyed, becomes a possible lineage, both because of splitting of the original structure and because of the splitting

[12] J. T. Randall, H. P. Rooksby and B. S. Cooper, X-ray Diffraction and the Structure of Vitreous Solids-I: *Zeit. Kristallographie*, **75**, 1930, 196–214.

[13] E. W. Skinner, Diffraction of X-rays in Liquids: Effect of Temperature: *Physical Review*, **36**, 1930, 1625–1630.

which becomes necessary from the distortion introduced by the keying. It follows that the width between lineage boundaries formed according to this theory can not be less than the width between cracks. This extreme condition prevails when every crack is keyed, a condition to be expected under very rapid growth. Once completely keyed in this fashion, no more cracks could form until the volume growth of the crystal provided a materially larger surface, for the development of lineages automatically splits the crystal up into grain-like patches whose surface contraction does not exceed the ability of the surface to contract as an entity. This state of affairs seems in harmony with what is observed on galena cleavages, where the sizes of the lineages are more or less uniform for a given crystal, and their shapes are prism-like, the prism extending from the center and branching peripherally.

Finally, with conditions between the extremely rapid growth and near-equilibrium growth, one would expect fewer cracks keyed, and larger lineages. In other words, the more slowly a crystal is grown, the more nearly it should conform to the ideal single crystal from the point of view of continuity of structure.

Solid Solution

A second possible cause for structural distortions serious enough to give rise to lineages, is solid solution. Since no two species of atoms are alike in properties, especially in the property, effective size, or in the more fundamental properties, polarizability, deformability, etc., it follows that if one species[14] proxies for another in solid solution, it must be distributed either with complete regularity or with complete randomness in order that a cumulative structural distortion may not arise. If neither condition is fulfilled, a distortion must appear commensurate with the lack of uniformity. Upon growth of the crystal, a point will eventually be reached where, instead of continuing as a severely distorted continuous medium, there will be a possibility of the structure splitting into two branches (lineages) to ease the strain of the accumulating distortion. Energy conditions will dictate when the latter must occur.

[14] Isotopes can not rightly be excluded from the category of an atom species which proxies for another in solid solution, although, from what is known of isotopes, the indications are that the effect of this sort of solid solution in distorting the structure would not rank as of the same order of magnitude as the effect due to solid solution of actual foreign atoms.

Unless the crystal is precipitated under equilibrium conditions, its impurity content does not have a chance to acquire a regular distribution. Under extreme circumstances, the first position occupied by an atom is its final position because it becomes immediately covered with another layer which protects it from the competition for most suitable position which must go on in crystallization under equilibrium.

Furthermore, if a gradient or directional effect of any kind is present at the time of crystallization, it may have an effect on orienting an incoming unit about to attach itself to the growing structure, or it is likely to effect a sorting action on the incoming matter so that slightly different amounts of impurities reach different places, *i.e.*, a composition gradient in the crystal is established.

As in the case of the surface crack possibility, a structure tolerant to gliding distortion may be expected to be tolerant to solid solution distortions and hence to split and give rise to lineages less frequently, *i.e.*, to grow larger lineages.

Discussion

It has just been shown that a definite "mosaic" structure is present in crystals, and it has been demonstrated that this structure does not partake of the nature of individual blocks, but rather partakes of the nature of a tree with branches arranged in a rudely spherically-symmetrical manner. Theoretical arguments have been advanced for considering this feature a result of too rapid growth to permit of the expected ideally continuous crystal. The fundamental cause of the lineages has been surmised to be either a keying-open of the Zwicky cracks or a branching of the crystal structure due to the distortions arising from misplaced solid solution impurities. Doubtless both of these effects contribute to lineage formation.

While the discussions of the possible causes of lineages have implied an application to ionic crystals, especially in the case of cracking of crystal surfaces, there is no reason why the general ideas would not apply equally to crystals bonded by other than ionic forces. In a certain sense, valence bonded crystals should prove capable of enduring a severe distortion of internal origin, for the bonding in this case is of the nature of a linking together of atoms in chains, nets, and solid meshworks. Superficially, it would

appear that distortion of these chains etc. would be rather easily tolerated; the lineages would, therefore, be expected to be rather large. The large lineages of pyrite and marcasite, minerals which are quite intolerant to gliding distortions and which are not ionic, seem to favor this view.

Crystals in parallel position and dendrites can only be regarded as special cases of lineage growth. The beginnings of parallel groupings can be seen in Figures 1–4. Both these conditions evidently arise due to still more rapid growth conditions than are required to produce simple lineages, dendrites being characteristic of the most rapid growth. The essential difference between simple lineages and exaggerated cases of parallel growth is that in the former, the structure is bathed by a solution of more or less uniform concentration on all sides, so that the space between lineages is kept filled with precipitated material and the lineages are able to keep pace with the growth of one another, while in the latter case, the rapid growth allows material to be added only to the growing ends of the separated lineages, the regions of the lineage boundaries not receiving much material for growth, because it is all precipitated on the leading tips.

Interlineage boundaries appear to have an important place in theoretical mineralogy. They are often the locus of negative crystals and cavities of irregular shape,[15] which may house samples of the solution from which the mineral was deposited.[16] It also appears probable that due to the character of lineage boundaries as discontinuities in the structure of the crystal and of communicating throughout its interior, they may provide means of ingress of solutions which effect mineralogical replacement. They may also form convenient starting places for the lodging of foreign material thrown out by the process of exsolution. If this should prove to be the case, the textures of the unmixing structures and replacement structures may be based on the pattern of the lineage boundaries.[17]

[15] M. J. Buerger, The Cleavage Surfaces of Galena: To appear in a later issue of *The American Mineralogist.*

[16] M. J. Buerger, The Negative Crystal Cavities of Certain Galena, and their Brine Content: To appear in a later issue of this Journal.

[17] If both unmixing and replacement patterns are inherited from the same source, their anomalous similarity finds an explanation: W. H. Newhouse, An Examination as to the Intergrowth of Certain Minerals; *Ec. Geology,* **21,** 1926, 68–69.

That most crystals must have some sort of mosaic imperfection has long been recognized by x-ray investigators[18] who customarily allow for its effects in the calculation of the intensities of x-ray reflections. There appears to be really very little actually known about mosaic imperfections of this type, except that if allowance is made approximately for an imperfection, the intensities of x-ray reflection come out more nearly correct than if no allowance is made.[19,20] The writer submits that mosaic structure in this sense may in part be due simply to structural distortions and in part to actual lineage development, perhaps sometimes on a scale too small to be readily detected.

[18] A very easy introduction to the situation is given by R. W. James, X-ray Crystallography, *London*, pages 63 and 64.

[19] See, however, the very interesting paper by Alexander Goetz, On the experimental evidence of the Mosaic Structure of Bi Single-crystals: *Proc. Nat. Acad. Sci.*, **16**, 1930, 99–105.

[20] A considerable literature on evidences in support of a mosaic structure, has appeared too late to be included in this article. The bearing of these data on the theory of lineages will be discussed in another paper.