A phase-contrast microscopic study of the surface structure of blende crystals.

(With Plates III and IV.)

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Summary.—The surface structure of blende crystals from Joplin, Jasper County, Missouri, U.S.A., has been explored by the application of phase-contrast microscopy and light-profile microscopy. Attention has been specially directed to the small-scale features with thicknesses (or depths) of molecular dimensions.

Some growth features of special interest were observed. A large number of beautifully developed growth spirals were observed on the tetrahedral face of a blende crystal. These are in accord with the dislocation theory of Burton, Cabrera, and Frank. The high visibility of these growth spirals is possibly due to the preferential deposition of some impurity, or etching, which also gives a mottled appearance to the entire surface. In addition, an extensive microscopic structure has been observed on some crystal faces. Triangular growth terraces and markings are seen, both orientated parallel to the edges of the crystal. Some triangles, inverted with respect to the latter, have been explained on similar lines to the well-known 'growth trigons' on the octahedral faces of diamond as arising from imperfect dislocations.

An attempt has been made to explain the growth features in the light of known theories of crystal growth.

THE surface structure of mineral and other crystals has been studied from time to time by several workers, and these observations have helped us to understand the mode of growth of crystals. Most of the work has been done microscopically, using bright field illumination or polarized light. Recently Seager (1953) examined the surfaces of a large number of mineral crystals for the study of growth structures but utilized only a metallurgical type of microscope using low powers (usually 1 inch objective). Improved optical and interferometric techniques are now available. Tolansky (1948) and his co-workers have used multiple-beam interference fringes extensively for the study of the surface topography of crystals such as quartz, mica, diamond, silicon carbide, &c. Until recently phase-contrast microscopy has received only slight attention for the study of minerals, but some uses have been described by Bennett, Jupnik, Osterberg, and Richards (1946), and by Smithson (1946, 1948), the latter confining himself mainly to thin sections of rocks. But lately, mainly

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because of the interest stimulated by the dislocation theory of crystal growth (Frank 1949*a*; Burton, Cabrera, and Frank, 1951), a closer examination of surface structure has been carried out for a large number of crystals and minerals by several workers. Over the past few years the author has also been carrying on a study of the topography of crystals, including minerals, utilizing a combination of multiple-beam interferometry and phase-contrast microscopy, with high magnifications. The different minerals that have been studied have been chosen mainly from the collection at the British Museum (Natural History). The choice of crystals has often been dictated by the demands of interferometry which requires crystals with almost perfectly plane faces. Attention has particularly been directed to the study of small-scale features with thicknesses of only molecular dimensions. A phase-contrast microscopic study of zinc-blende crystals is now presented. The multiple-beam interferometric study of some minerals will be described in a later communication.

Experimental methods.

Phase-contrast microscopy is a well-established technique and it is not proposed to give any detailed account here. Its principles were enunciated by Zernicke (1934), and recently an account of this branch of microscopy, including its applications and an extensive bibliography, has been given by Bennett, Jupnik, Osterberg, and Richards (1951). We give below some of the special features pertaining to the present investigation.

The microscopic study of the crystal surfaces has been carried out on phase-contrast equipment which can be fitted on to a Vickers projection microscope manufactured by Cooke, Troughton, and Simms. Since the crystals studied were opaque, only the reflection type of equipment has been used, which has an additional advantage that for two features differing in level by t the path difference becomes $2t$ in reflection and hence has a greater sensitivity as compared with transmission. A diagrammatic scheme of the general arrangement is shown in fig. 11. An annular diaphragm D serves as the entrance pupil of the optical system consisting of the field lens, the microscope objective, and the reflecting surface of the specimen. The field lens and the objective form an image D_1 of the field diaphragm just below the surface of the specimen The reflected light passes through the objective and forms a real image D_2 (shown by solid lines) of the diaphragm D. Image D_2 is the exit pupil and the place where the phase plate is placed. In the present equipment the optical assembly, consisting of the microscope objective lenses, 45° inclined beam splitter, and the phase plate, is all mounted on the objective. Objectives of focal

length 25 mm., 16 mm., 8 mm., 4 mm., and 2 mm. (oil immersion) were available. The equipment used was a positive phase contrast with the phase retardation of $\pi/2$, the absorption of the phase plate being equal to 80 %. Whenever permission could be obtained for silvering the surface of the specimen this was always done, since silver truly contours the

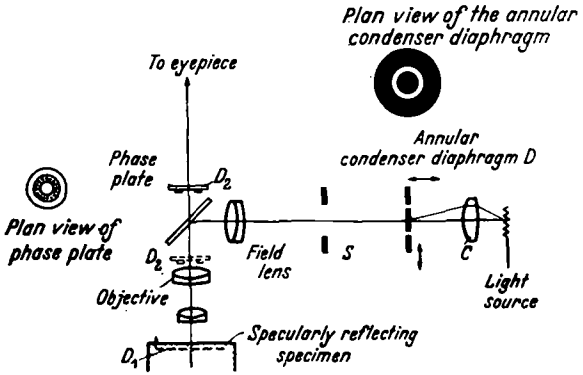

FIG. 11. Diagrammatic sketch of the arrangement for phase-contrast microscopy by reflected light.

surface and does not impose any topography of its own, but cuts down the exposure time and thus reduces the background fogging of the photographic plate. The same silvered crystal can then also be used for multiple-beam interferometric studies or light-profile microscopy. The thin layer of silver deposited on the crystal is usually 400 500 Å. thick, giving a reflectivity of 80 90 %. The silvering is done *in vacuo* in a commercial evaporating unit manufactured by Edwards & Co.

When dealing with rough surfaces, as in the present case of blende crystals, the interferometric techniques cannot be adequately applied. For such specimens having surface features of heights (or depths) ranging from a fraction of a micron to a few microns and requiring the use of high-power or even oil-immersion objectives, the technique of light-profile microscopy is specially suitable (Tolansky, 1952).

Results of observation (pls. III and IV).

Of a large number of blende crystals examined, one group was found to show several interesting surface features, and all the following illustrations refer to them. They all come from Joplin, Jasper County, Missouri, U.S.A., and form a part of the Trechmann collection of the British

Museum. The Pb–Zn ores of Joplin are of low-temperature metasomatic origin. On the matrix of some of the specimens small crystals of pyrite were observed. The first crystal (crystal no. 1) has one fairly well-developed face of a tetrahedron of which the sign was not determined, together with a face of the form {100}. The appearance of this tetrahedral face is shown in pl. III, fig. 1, which is a low-power photomicrograph taken with bright field illumination using the green line, $\lambda 5461$, of a mercury arc. To the naked eye the face shows somewhat dark metallic lustre, the surface appearing quite polished and smooth but showing some interference colours; some interference fringes can be seen in fig. 1. On examining this tetrahedral face by the phase-contrast microscope without silvering it, the whole surface appeared mottled, though according to Miers (1929) this mineral is exceptionally free from tarnish. However, on this messy background several surface features could be observed and are discussed below. Crystal no. 2, which also showed some interference tints, has one prominently developed cube face nearly 7 mm. $\times$ 8 mm., together with faces of {111} and {$\bar{1}$11}. Pl. III, figs. 4 and 5, refer to crystal no. 2, all others to crystal no. 1.

The observed surface structures may be summarized as follows:

The commonly observed triangular growth terraces and lines may be seen in pl. III, figs. 3, 4, and 6; the triangular shape of these hills on tetrahedral faces is in conformity with the general observation that growth layers show the same degree of symmetry as the face on which they grow.

Growth spirals on the tetrahedral face of crystal no. 1 are observable on the mottled background in pl. IV, figs. 7, 8, and 10.

Small triangular markings can be seen at the bottom of fig. 7, and are shown enlarged, using high power, in fig. 9; these triangular markings are, throughout the surface of the crystal, orientated in the same direction as the edges of the tetrahedral face of fig. 1.

A hexagonal area (see fig. 2, which shows a part of fig. 1 under high power) is completely free from the messy background. This hexagonal area does not appear to be orientated in any simple crystallographic direction with respect to the edges of the growth terraces, which continue into or right across the figure. To decide whether this smooth hexagonal area is an elevation above or a depression below the general level of the crystal surface around it, a light-profile photomicrograph was taken; the shift of the profile line showed it to be a depression. Thus the possibility that it is an overgrowth can be ruled out. Perhaps a small adherent crystallite protected the surface underneath during the last

phase of growth and was dislodged afterwards; it may have been an inclusion of calcite or galena.

An extensive system of substructure was seen on the tetrahedral faces of crystals 1 and 2 (figs. 6 and 4). It appears as if these figures were produced as a result of solution, but it is not possible to verify this since permission could not be obtained to etch these crystals. However, according to Gebhardt (1933), etching experiments give sharply defined triangular or hexagonal pits on (111) and no figures on ($\bar{1}11$).

Fig. 5 shows several deep triangular pits on a tetrahedral face on crystal number 2.

Perfect screw dislocations and growth spirals.

The formation of a perfect screw dislocation in a crystal creates on the surface a terminated step with a height equal to (or an integral multiple of) the X-ray unit cell. When growth proceeds on this step it winds itself into a spiral shape, giving rise to growth spirals with molecular step heights (Burton, Cabrera, and Frank, 1951). These predicted growth spirals have been observed on several crystals (for a detailed list of references see Verma, 1953). A growth spiral originating from a unit dislocation in a blende crystal would not be easy to observe because of the small size of the unit cell ($a = 5{\cdot}42$ Å.). However, it has been observed that a deposit of a suitable impurity along the growth edges can often lead to a remarkably high visibility (Verma, 1951; Vand, 1951; Forty and Frank, 1953). The growth spirals of figs. 7 and 10, which have possibly unimolecular step heights, may have been revealed by this 'decoration effect' of the impurities. However, it is not possible to measure the step heights of these growth spirals by multiple-beam interferometry because of the extensive background on the surface of the crystal. Applebe and Kaye (1953) attributed the exceptional visibility of small steps on beryl crystals to etching, since they found a high concentration of pits along the step edges.

To discover the nature of the surface layer of the crystal it was examined by electron diffraction methods;[1] it was found to be amorphous. It is possible that this amorphous impurity layer was formed on the surface of the crystal in the last phase of growth, or it could be due to chemical alteration after growth, either by natural processes underground or by atmospheric attack after it was mined. Indeed, the surface of the crystal, though highly reflecting, shows interference colours, and these interference fringes with monochromatic light can be seen in fig. 1;

[1] The author is indebted to Dr. H. Wilman for this examination.

they are proof of the presence of a thin layer on the crystal surface. But it is at once clear that the growth spirals are not built of the impurity atoms since a regular arrangement of the impurity atoms over the extension of the growth spirals would give them a crystalline arrangement. Moreover, the growth spirals take crystallographic shape, the spiral edges tending to become straight lines that are orientated at simple crystallographic angles (e.g. 90°) with respect to the edges of the triangular growth hills. The structure of the underlying ZnS and the growth spirals thus appears to be alike.

The behaviour of the spiral growth steps originating from different dislocations is similar to that observed on other crystals. A compound growth pattern, from two dislocations of the same hand close to each other, is illustrated at the bottom right of fig. 7 (pl. IV). Another noteworthy observation, which is in striking similarity to an observation on silicon carbide crystals (Verma, 1951), is that in any one region of the crystal the dislocations are usually of the same sign. Thus in fig. 7 there are some twenty growth spirals, all of which appear to be right-handed. Different parts of the crystal were therefore searched and, as seen in fig. 10, the top left corner contains several left-handed growth spirals: this region being separated from the rest of the crystal by a boundary marking a region containing triangular markings of the type shown in fig. 9. Examples of two dislocations of opposite hand close together can also be seen in fig. 10. The predominant occurrence of dislocations of the same sign in any one region of the crystal has been explained by Frank (1951) on an hypothesis about the mechanism of the creation of the dislocations. According to this the initial crystal plate formed by the nucleation process gets self-stressed, through inhomogeneous distribution of impurities. When this stress reaches the yield stress, the plate will buckle and shear, raising terminated steps that will not be of constant height all along, and macroscopically speaking will taper away. Every time the step height is reduced by one unit cell a dislocation will be left behind, and these will obviously be all of the same hand. During growth these dislocations will repel each other and spread over the surface of the crystal. The above observation on zinc-blende crystals thus lends support to Frank's hypothesis about the creation of dislocations. Few other crystals have shown a large density of individual dislocations on the same crystal plate.

Imperfect dislocations and growth trigons.

The triangular growth terraces of fig. 3 represent a triangular growth hill, as is easily seen from the positive phase-contrast image showing a

white border on the edge of the step towards the higher level side. In addition to this, a closer examination of the step edge shows some 'trigons' in different stages of formation. These trigons are pits, oppositely orientated to the triangular growth hills. A small completed trigon can be seen nearly in the right middle of the bottom growth layer (it is indicated by arrows). Several incomplete trigons, which were still in the process of formation when growth ceased, can be seen at the top right-hand end of the figure. The formation of several oppositely orientated trigons can be seen in fig. 4 also. These trigons closely resemble similar features on diamond. Indeed, this is to be expected since the structure of blende and diamond are very similar: the Zn and S atoms are each arranged on a face-centred cubic lattice, and by replacing both Zn and S by C we get a structure like that of diamond. As was shown by Tolansky and Wilcock (1946, 1947), these oppositely orientated triangular pits on the octahedral faces of diamond are not the result of an etching but are 'growth trigons' arising from the meeting of the three systems of growth layers advancing at 60° to each other. Halperin (1954) has put forward a theory about the formation of trigons and has explained them on the basis of the presence of imperfect dislocations, which arise by the transfer of atoms from lattice positions to twin lattice positions (Frank, 1949*b*). The strength of these dislocations, i.e. the displacement of the atoms, is only a fraction of the lattice unit, and imperfect steps result. These steps are thought by Halperin (loc. cit.) to be formed as a result of accumulations of interstitial faults in the lattice. It is therefore possible to explain the formation of oppositely orientated trigons in zinc-blende arising from imperfect dislocations, since stacking faults can be easily created in the *ABC* sequence of the hexagonal close-packed layers which form the face-centred cubic blende crystal. It should be noted that the triangular growth hills are not of this origin. If growth takes place on imperfect dislocations zinc-blende may also be thought to exhibit 'polytypism' of the type shown by silicon carbide crystals (Thibault, 1944). This has recently been reported by X-ray diffraction studies (Strock and Brophy, 1955; Buck and Strock, 1955). The step lines originating from two imperfect dislocations cannot fuse with one another crystallographically, and a surface of lattice discontinuity marking out a fault surface should be formed; some of the markings separating growth spirals in figs. 7 and 10 may be of this origin.

The creation of dislocations by buckling and slip mechanism may also create some slip steps on the surface of the crystal. Votava, Amelinckx, and Dekeyser (1953) have carried out microscopic studies of (111) faces

of deformed blende crystals from Trepča (Yugoslavia) to which they assign a pegmatitic-pneumatolytic origin with growth at elevated temperature and pressure. They reported the observation of some slip-step lines in addition to poorly developed growth spirals. In the extensive substructure on some crystal faces one can occasionally see step lines running along certain crystallographic directions and cutting across the growth steps. Two such lines parallel to a crystallographic direction can be seen in fig. 5, running from the pit at the left edge of the figure to the edge of the crystal on the bottom right of the figure. Several other such faint lines can be seen in other photographs, e.g. fig. 6. Votava *et al.* have in addition observed some faint lines, which are rows of etch pits, and which they have interpreted as polygonization lines (rows of Taylor dislocations).

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EXPLANATION OF PLATES III AND IV.

PLATE III.

FIG. 1. The entire tetrahedral face of a zinc blende crystal under low power using bright field illumination and mercury green light λ5461, showing a series of growth edges on which some broad and diffuse interference fringes due to a layer on the surface can be seen. ×10.

FIG. 2. A phase-contrast picture of a part of fig. 1, showing an hexagonal area which is remarkably smooth compared with the mottled crystal surface around it. ×75.

FIG. 3. The triangular growth terraces on the tetrahedral face of blende, using the phase-contrast microscope. Some inverted triangles in different stages of formation can be seen, e.g. one completed 'trigon' in the right middle of the bottom growth layer. ×75.

FIG. 4. A phase-contrast picture of another blende crystal, showing an extensive system of substructure which is quite shallow in depth (or height). ×45.

FIG. 5. A phase-contrast picture of another tetrahedral face of the same crystal as fig. 4, showing triangular pits in addition to the growth edges. ×30.

FIG. 6. A phase-contrast picture of the extensive substructure on a tetrahedral face of a blende crystal. ×60.

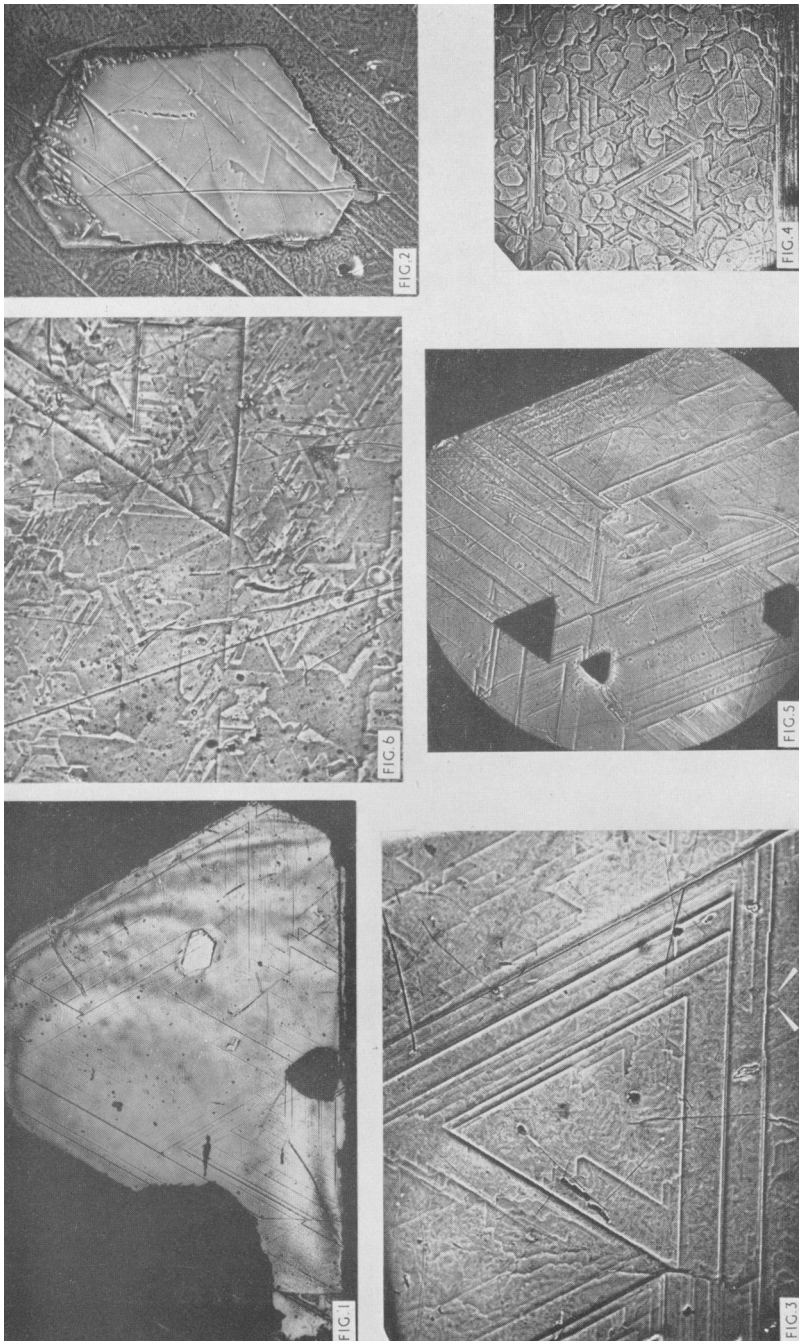
PLATE IV.

FIG. 7. A phase-contrast picture of a part of fig. 1, showing on the tetrahedral face of the blende crystal a number of growth spirals on the mottled background. Note that the spirals are all of the right-handed type. At the bottom of the figure small triangular markings can also be seen. ×140.

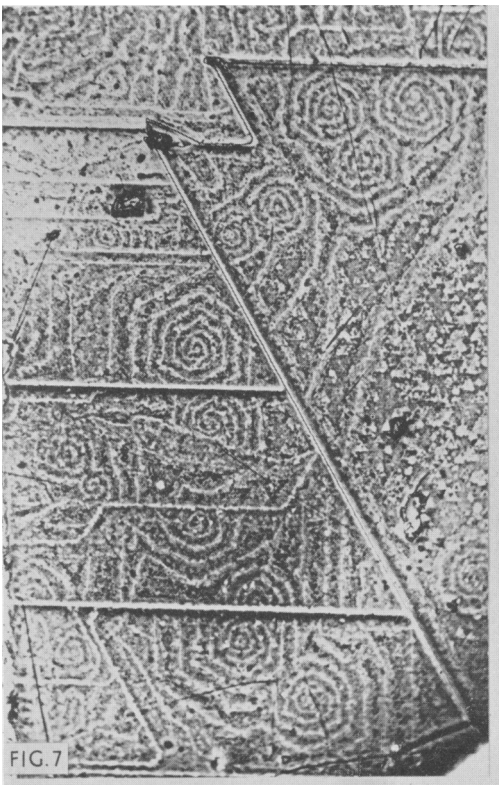
FIG. 8. A phase-contrast picture of a part of fig. 7 under higher power, showing a growth spiral. ×270.

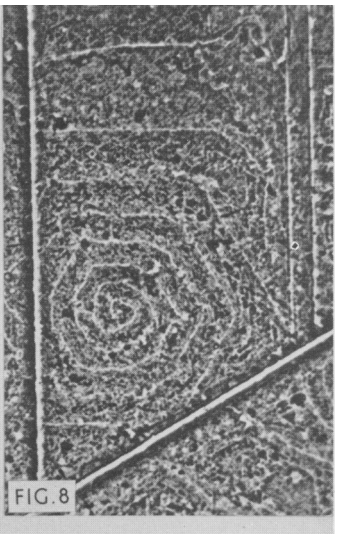
FIG. 9. A phase-contrast picture of a portion of the bottom of fig. 7, showing the triangular markings under higher power. ×440.

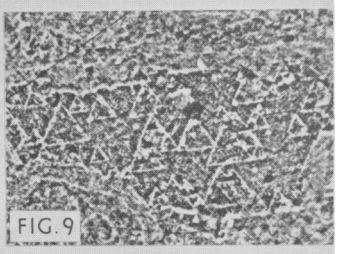
FIG. 10. A phase-contrast picture of another part of the tetrahedral face of fig. 1, showing a system of both left- and right-handed growth spirals together with the triangular markings on the mottled background. ×100.

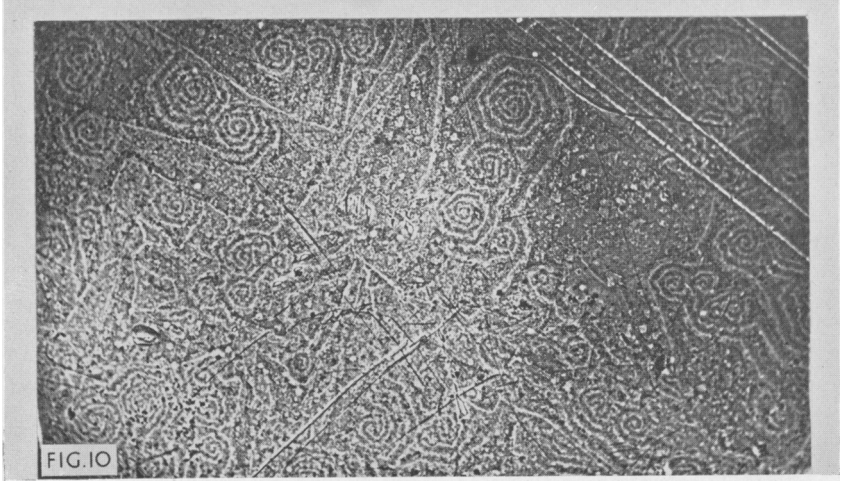


A. R. VERMA ON PHASE-CONTRAST MICROSCOPY OF BLENDE









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