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SURFACE STRUCTURES OF SPHALERITE CRYSTALS

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ABSTRACT

Surface structures of the (111), $(\bar{1}\bar{1}\bar{1})$ and (100) faces of sphalerite crystals from many localities were studied in detail, using an ordinary reflection and a phase contrast microscope. It was observed under low magnification that the (111) face is represented by the development of regular, equilateral triangular patterns and stepped but flat surfaces, whereas the $(\bar{1}\bar{1}\bar{1})$ face is characterized by deformed growth patterns and wavy or broken surfaces. On the (111) face, thin triangular growth layers, tables and simple spirals together with many slip lines were observed under the phase contrast microscope, whereas on the $(\bar{1}\bar{1}\bar{1})$ face, irregular, triangular or hexagonal growth layers and composite spirals were the main growth features. Slip lines were rarely observed on the latter face. It is considered that the essential and fundamental difference between the (111) and $(\bar{1}\bar{1}\bar{1})$ faces is the occurrence of slip lines on the former face and that because of the formation of slip lines during crystal growth, the former face assumes regular equilateral triangular growth features. It is also conjectured that the differences in growth mechanism between the two tetrahedral faces result in the difference in the development of the two faces. The {100} face shows spindle, rectangular and elliptical growth layers and spirals, all of which have two-fold symmetry axis in accord with the symmetry of the face.

INTRODUCTION

It is widely known that the surface characteristics of tetrahedral faces (111) and $(\bar{1}\bar{1}\bar{1})$ of sphalerite are distinctly different. This is inferred to be the result of the difference of atomic arrangement in the two faces. According to the well known explanation by Bragg (1937) and the experiments by Nishikawa and Matsukawa (1928) and Coster *et al.* (1930, 1933, 1934), the (111) face exhibits stepped surface with triangular markings and consists of Zn atoms only, whereas the $(\bar{1}\bar{1}\bar{1})$ has smooth surface and consists of S atoms only. Beyond this, however, the difference of the surface characteristics between the two faces has not been critically studied in detail. The drawing by Bragg as well as other figures in text books is not satisfactory in the light of present day science, and one might even wonder what the fundamental differences between the two faces are.

It is the purpose of the present work to show the essential characteristics of the surface structures and the differences between the two faces, through detailed observations of their surface structures using modern and sensitive methods of observation and measurement.

The surface structures of sphalerite crystals were studied previously

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using modern methods by Votava *et al.* (1953) and Verma (1956). Votava *et al.* observed two types of lines on the {111} face of sphalerite from Trepča, Yugoslavia; one type was considered to be minute etch pits formed at edge dislocation points arranged along polygonization lines, the other the boundaries of mosaic blocks. They also observed polygonal, but poorly developed spiral layers with step height of 500 Å. Verma studied the {111} faces of several crystals from Joplin, U.S.A., and showed growth spirals, the heights of which were estimated to be of molecular dimensions. Growth trigons were also observed on these faces. Both Votava *et al.* and Verma did not distinguish (111) and $(\overline{111})$, and therefore it is not certain whether the faces on which these spirals occurred were (111) or $(\overline{111})$. No special attention was paid to the differences between the two types of tetrahedral faces in their studies.

Recently, Hartman (1959, 1963) has discussed the morphology of sphalerite on the basis of polarization energy and concluded that the (111) face, consisting of S atoms only, develops larger, whereas $(\overline{111})$, consisting of Zn atoms only, is the smaller face. He denotes the former face as plus (111), and the latter as minus $(\overline{111})$. This is the reverse of the notation used by previous investigators. In this connection, discussion was carried on between Hartman and Sunagawa, through written communication, and both agreed to denote the Zn face as (111), and the S face as $(\overline{111})$. However, they could not reach an agreement as to the size of the two types of tetrahedral faces. According to our observations on some hundred crystals, it can be generally said that the larger faces show stepped, triangularly marked surfaces, which suggests that the face consists of Zn atoms only, if the conclusion by Nishikawa and Matsukawa (1928) is followed. In contrast, the smaller face exhibits, on most crystals, smooth and poorly marked surface, and is considered to be $(\overline{111})$ face consisting of S atoms only. This was also confirmed by x-ray investigations carried out on our specimens by Dr. Tokonami of the Solid State Physics Institute of Tokyo University, which will be reported elsewhere. Therefore, we will take, in this paper, the face showing stepped and triangularly marked surface as (111), which consists of Zn atoms, and the face exhibiting smooth surface as $(\overline{111})$, consisting of S atoms. Most of our specimens show that (111) is the larger face and $(\overline{111})$ the smaller. This observation conflicts with Hartman's explanation of the morphology of sphalerite, as well as with the results by Monier and Kern (1956), on which Hartman's explanation stands. The reason for this disagreement we will discuss elsewhere.

A large number of sphalerite crystals from the following localities were investigated in this study: Ani, Arakawa, Daira, Osaruzawa, Budo, Chichibu, Donsuiwa, Houei, Hosokura, Kamioka, Kunitomi, Kuratani, Noto, Obira, Ohizumi, Taihei and Tsunatori mines in Japan; Joplin in U.S.A. and Trepča in Yugoslavia. A brief description of the geology of these deposits is given in Table 1. They come from all sorts of origin, from high- to low-temperature hydrothermal origin, as well as metasomatic replacement origin. Most of the crystals have a tetrahedral habit with large (111) and small $(\bar{1}\bar{1}\bar{1})$, with or without (100), but some have an octahedral habit with large (111) and $(\bar{1}\bar{1}\bar{1})$. They are from 1 to 30mm in size.

OBSERVATIONS

Distinct differences can be noticed between the (111) and $(\bar{1}\bar{1}\bar{1})$ faces even under low magnification without phase contrast. The former face is characterized by the development of regular, equilateral triangular patterns, whereas the latter face is represented by the patterns varying from near hexagonal to irregular forms. Equilateral triangular patterns are seldom observed on the latter face. To the naked eye, the former face appears more stepped than the other face, which is flat and smooth. However, the surfaces of each growth layer are flatter on the (111) face than on the $(\bar{1}\bar{1}\bar{1})$ face, which shows a somewhat wavy surface under the microscope. Figures 1a, b are low magnification photomicrographs of the (111) and $(\bar{1}\bar{1}\bar{1})$ faces of the same crystal from the Kamioka mine. Clear differences between the two faces can be noticed even at a glance. A similar distinction between the two faces has been observed almost invariably on the crystals investigated, even on octahedral crystals from Trepča.

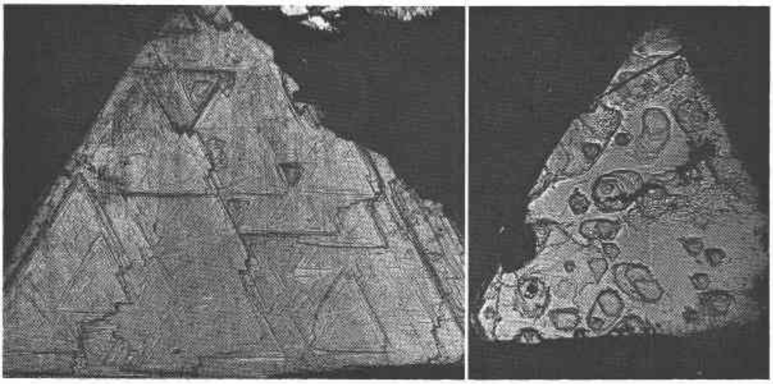
TABLE 1. TYPES OF DEPOSITS

Origin of Deposits	Name of Mines
Pyrometasomatic Deposits	Chichibu, Houei, Kamioka, Obira
Mesothermal veins	Trepča
Epithermal veins	Arakawa, Ani, Daira, Osaruzawa, Budo, Donsuiwa, Hosokura, Kuratani, Ohizumi, Tsunatori
Kuroko deposits[1]	Kunitomi, Noto, Taihei
Telethermal beds	Joplin

[1] Kuroko, or black ore deposits are bedded or massive type deposits of Cu, Zn, and Pb in Tertiary formations. The ore consists of chalcopyrite, sphalerite, galena and barite, and is considered to be of syngenetic origin. Kuroko deposits have been mainly found in northeastern Japan.

The triangular surface patterns of the (111) faces do not show noticeable variations by individual crystals and localities, at least under low magnification. In contrast to this $(\bar{1}\bar{1}\bar{1})$ faces show remarkable changes on crystals from different localities, although they show practically identical patterns on crystals in one hand specimen or from one locality. Under low magnification $(\bar{1}\bar{1}\bar{1})$ faces exhibit deformed triangular, nearly hexagonal, or irregular surface structures.

Under the phase contrast microscope, these faces show somewhat different characteristics. On the surface of the (111) face, a large number of triangular hills with steep sides, triangular tables with flat top surfaces, and triangular depressions are observed. Among these features, triangular depressions are formed at places where growth layers spreading from two or three directions remain unfilled. Thus the depressions are formed by the same mechanism as are trigons on the octahedral faces of diamond, as pointed out by Verma (1956) on sphalerite crystals from Joplin. The other features, *i.e.* triangular hills, tables and layers, are elevations that are growth features. In other words, they are hills and tables consisting of piles of thinner triangular growth layers.



(a) (b)

FIG. 1. Low magnification photomicrographs showing the difference of surface structures between (111) (a) and $(\bar{1}\bar{1}\bar{1})$ (b) faces of the same crystal of sphalerite from Kamioka mine, Japan. a—(111) ×6, b—$(\bar{1}\bar{1}\bar{1})$ ×11.

However, it is interesting to note that these thinner triangular growth features are not, in most cases, regular, equilateral triangles, but have truncated or curved corners (Fig. 2). This is observed especially on the thinner or smaller triangular layers, tables and hills. Even on the same surface, the larger triangular features with bigger step heights tend to show regular, equilateral triangles. This tendency shows that some sort of linear obstacles which have crystallographic directions parallel to $\langle 110 \rangle$ existed on the surface, and the spreading of triangular growth layers was stopped when they encountered the obstacles. The above resulted in the formation of regular, equilateral triangular patterns. Without assuming the existence of such linear obstacles, it is impossible to explain the above tendency as well as the remarkable development of the equilateral triangular growth patterns, since it is generally observed on wide variety of crystals that, when there are no obstacles, growth layers take on more irregular forms as they advance outerwards, even if they start as polygonal layers.

On the surfaces of triangular layers and tables of (111), other thinner growth features do not seem to appear in most cases. Their surfaces appear to be molecularly flat and smooth even under the phase contrast microscope. However, when their surfaces are investigated very carefully under high magnification, it is found on some crystals, especially on the crystals from the Daikoku Adit at the Chichibu mine, that many spiral layers with a very small step height occur on the surface of triangular layers and tables. Figure 3 is an example of these growth spirals. On the photomicrograph, the straight lines with wide white diffraction bands are the edges of thick triangular growth layers. The spirals occur only on the surface of such growth layers, and do not cross the edges of these layers. It suggests that the spirals are formed at the latest stage of crystal growth and that the spiral layers stop spreading when they arrive at these edges. This results in thickening of the triangular layers.

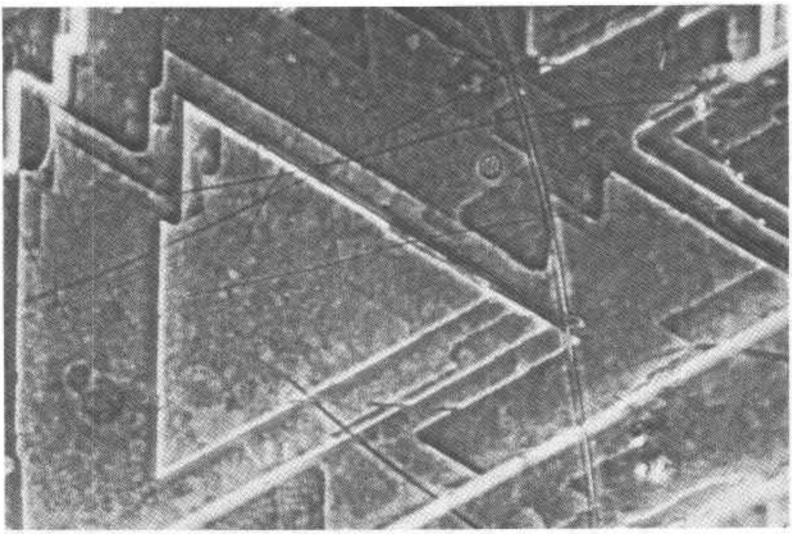


FIG. 2. Phase contrast photomicrograph showing characteristic growth features of (111) face. ×210.

On the phase contrast photomicrograph, the edges of the spirals appear as dark narrow lines, with no visible white diffraction band on either sides of the lines. This indicates two facts: 1. The step heights of the spiral layers are extremely small and are estimated to be of molecular dimensions; 2. Etching took place preferentially along the edges of the spiral layers forming ditches, which is the reason for the high visibility of such an extraordinarily thin spiral layer. It is also observed that minute etch pits are formed on the surface of spiral layers, and that their distribution is not uniform over the surface. Even on the surfaces of the spiral layers starting from a single dislocation point, both etched and non-etched surfaces are observed. In some cases, the surfaces of the two types occur alternately on a spiral pattern, that is the surfaces of the first, third and 2n+1th turns are etched whereas those of the second, fourth and 2nth turns are not etched. Etching seems to have taken place unevenly over the surface. It must have taken place selectively according to the different types of the atomic arrangement of the surfaces. In other words, the nature of the surfaces of these spirals is not uniform within the (111) face, but differs from place to place. This might be inferred to be caused by the uneven distribution of impurities near the crystal surfaces.

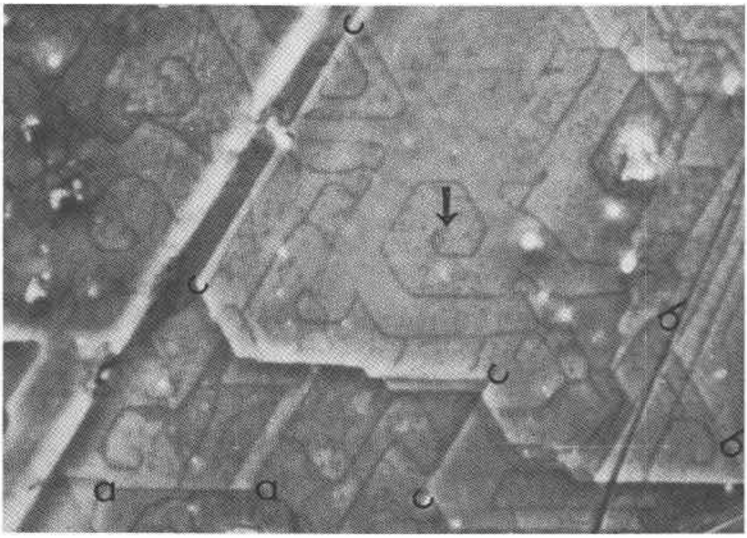


FIG. 3. Phase contrast photomicrograph showing typical spirals observed on the (111) face of sphalerite crystals from Chichibu mine, Japan. Slip lines are shown by the notation of a——a, b——b, etc. ×1000.

These spirals are apparently complicated, but can be analyzed as patterns formed by cooperation and interaction of spirals originating from independent single screw dislocations. This is shown schematically in

Fig. 4, in which solid points represent screw dislocation points. Many sorts of spiral morphology can be noticed in this figure; simple spirals, two spirals originating from single screw dislocation point, spirals with only a half turn, closed loops formed by two spirals originating from two screw dislocation points of the opposite sign, etc. They are all simple and typical spirals with wide spacings between the successive layers and small number of turns, and are not composite spirals originating from clusters of screw dislocations, which are widely observed on the $(\overline{11}1)$ face as well as on other minerals such as hematite (Sunagawa, 1962). Wide spacings between the successive layers of the spirals show that the spirals are formed under a low supersaturation condition. When these spirals take simple and polygonal forms, they are triangular with truncated corners in most cases. This morphology is in good accord with the symmetry of {111} face of sphalerite. However, a small number of spirals on the face takes regular hexagonal form, an example being shown by an arrow in Fig. 3. This suggests that both hexagonal and cubic polytypes coexist together in this crystal, since the morphology of growth spirals is strictly controlled by the symmetry of the crystal. This has been reported by one of the writers on several occasions on wide variety of crystals (Sunagawa, 1962, 1963a, 1964). Now, Strock (1955) and Czyzak and Manthurthil (1962) report that the coexistence of both hexagonal and cubic polytypes was noticed on many single crystals of synthetic ZnS. The former wrote that such a coexistence was observed only in synthetic ZnS and not in natural sphalerite. However, there is no reason that this sort of coexistence can not occur in natural crystals as well, and the present observations offer evidence of such coexistence in natural sphalerite crystals.

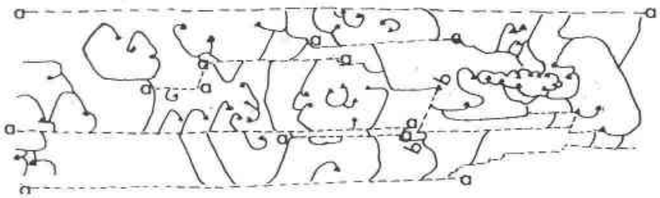


FIG. 4. Schematic drawing of spiral patterns. Dots show screw dislocation points. a—a, b—b, etc. show slip lines.

Another important feature observed on these crystals is straight lines which are slip lines formed during growth. These lines are shown by the notations of a—a, b—b, etc. in Figs. 3 and 4. They are straight and run in crystallographic orientations parallel to ⟨110⟩. They do not traverse over the surface, but run for a short distance. A small level difference can be noticed along the lines. They are lines with steps and not bands with some width, which suggests that they are slip lines and not twin lamellae, which are often observed in sphalerite. Spiral layers stop their advance when they arrive at these lines.

From these observations, it is concluded that the lines are slip lines formed during growth. It is also inferred that the other straight lines with larger step heights were originally the slip lines with a small level difference, but became thicker lines due to piling up of thinner layers which arrived at the lines and stopped their advance. This process is considered to be the main reason for the development of the regular, equilateral triangular growth patterns on the (111) face. As described, thin growth layers take on triangular form with truncated or curved corners in most cases, and not regular equilateral forms. From such growth layers, equilateral triangular patterns can not be expected to form by further growth, unless some sort of straight, linear obstacles control the advance of the growth layers. The slip lines formed during growth must have played the role of such obstacles. Because of the good development of such slip lines, the (111) face is characterized by the development of equilateral triangular patterns. On the $(\overline{111})$ face, slip lines do not occur as commonly as on the (111) face, which results in the formation of irregular growth patterns.

The difference in the development of slip lines during crystal growth between the (111) and $(\overline{111})$ faces was accounted for by Sunagawa (1963b) by the distortion in the crystal due to substitution of Zn atoms by Fe atoms. Only the Zn plane, *i.e.* (111), is distorted by this substitution, and hence exhibits good development of the slip lines, whereas $(\overline{111})$ will not be distorted and shows no development of slip lines. If no slip lines are formed during growth on the (111) face, surface structures of the face will be very different from those we observe now, and will be more or less similar to those on the $(\overline{111})$ face.

Here, it is necessary to define the term "slip lines." This term is used not in the strict sense that is generally used in metallurgy, as can be seen from the length of such lines. It implies a sort of line discontinuity with a level difference which has crystallographic direction. Such line discontinuity can be a stacking fault, a slip line or an edge dislocation. So far as it produces a straight line discontinuity with some length and a level difference, it is called a "slip line" in this paper.

The $(\overline{111})$ faces show quite different characteristics of surface structures from those on the (111) face. They are characterized by irregular and complicated growth layers and wavy or broken but not stepwise surfaces as (111). Their surface structures vary significantly from crystal to crystal and from locality to locality. Therefore, when they are observed under a phase contrast microscope, they exhibit various growth patterns, making a good contrast with the uniform and simple growth patterns that are characteristics of the (111) face. The following growth patterns are observed: irregular growth layers, circular growth layers, hexagonal growth layers, triangular growth layers, composite spirals, and spirals originating from the ends of misoriented portions on the surface. A few typical examples of the growth features are shown in Figs. 5a, b, c. Characteristic growth features of the $(\bar{1}\bar{1}\bar{1})$ faces that are different from the (111) are as follows.

1. Growth layers usually take irregular forms. Even when they take polygonal forms, their edges are neither regular nor straight as in the case of the (111) face.

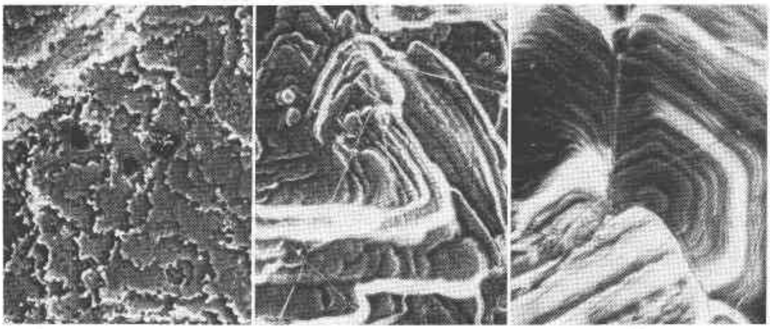

(a) (b) (c)

FIG. 5. Phase contrast photomicrographs showing characteristic growth features of $(\bar{1}\bar{1}\bar{1})$ faces. a—irregular growth layers, b—composite spirals, c—growth layers originating from the ends of misoriented portions. ×105.

2. The spacings between the successive layers are closer than the case of the (111) face As a result, growth pyramids occur more commonly than in the case of the (111), and triangular tables with flat top surface which are commonly observed on the (111) occur rarely.
3. In contrast to the stepped but flat surface of the (111), the $(\bar{1}\bar{1}\bar{1})$ face exhibits wavy or broken surfaces. Growth layers often originate from the corners of misoriented portions, and form composite spiral hillocks. Such features are not observed on the (111) face.
4. Growth spirals are observed more commonly on the $(\bar{1}\bar{1}\bar{1})$ than on the (111). However, they are always composite spirals originating from clusters of screw dislocations. No simple and typical spirals like those observed on the (111) have been found on the $(\bar{1}\bar{1}\bar{1})$.
5. Slip lines formed during growth are not commonly observed on the $(\bar{1}\bar{1}\bar{1})$, which makes a distinct contrast to the (111). This difference results in the difference of the surface structures between the two tetrahedral faces.

From these observations, the difference of the surface structures and the rate of development of the face between the two types of tetrahedral faces can be accounted for as follows. Because of the development of the slip lines during crystal growth only on the (111) face, this face exhibits regular equilateral triangular patterns, whereas irregular or deformed growth patterns are formed on the ($\overline{111}$) face, since slip lines are not formed on this face. Development of growth features such as composite spirals, close spacings between the successive layers, wavy or broken surfaces which provide the points for preferential growth on the ($\overline{111}$) face suggests that the rate of growth perpendicular to the face is high. This results in decreasing the surface area of the face as growth proceeds. The general tendency for the ($\overline{111}$) face to be smaller than the (111) face is explained by the above process, since on the latter face two-dimensional spreading of growth layers takes place more intensely than the rapid piling up of growth layers.

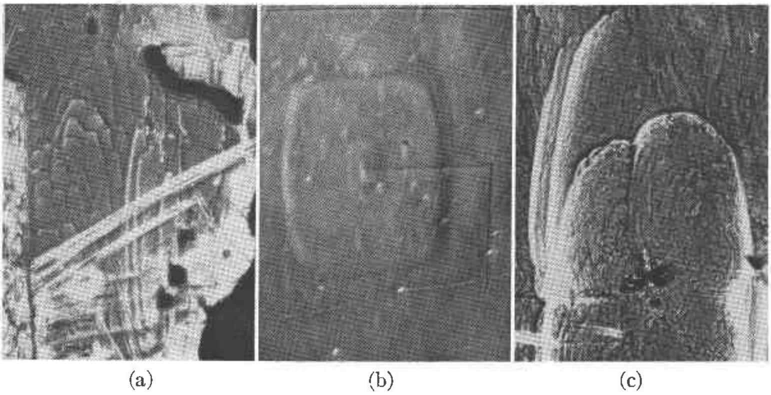


FIG. 6. Phase contrast photomicrographs showing characteristic growth features of (100) faces. a—spindle shaped tables, b—rectangular closed loop with two dislocation scarps, c—elliptical growth spirals. ×90.

The (100) face exhibits entirely different surface structures from the tetrahedral faces. Growth features appearing on the (100) always have two-fold symmetry, which is in good agreement with the atomic structure of the face. Three different types of surface structure are observed: spindle shaped tables, rectangular closed loops and elliptical growth hills. These are shown in Figs. 6a, b, c respectively. In all cases, elongation of the growth patterns is parallel to the elongation of (100) face, which usually appears in an elongated rectangular form. The spindle shaped tables have flat surfaces and consist of a few layers with a step height of some hundred Ångstroms. Many spindles occur on one face. It is observed on many spindles that straight lines cut the spindles parallel to their shorter side, *i.e.* [110], giving a small level difference and a small shift on their sides. Such straight lines occur frequently on the surface but do not run across the whole face. Similar straight lines parallel to the elongated direction have never been observed, nor lines parallel to [001]. Since the lines cut growth layers giving some effects on the latter, they must be slip lines which are formed during crystal growth.

Rectangular closed loops shown in Fig. 6b are formed from two spiral layers of the opposite signs. In one case, two parallel straight lines are observed to start from the center of the loop and run parallel to [110]. From the positions of white diffraction bands appearing along the lines, it is observed that both lines have level difference and that the one line has higher side on the left, whereas the other on the right, looking from the center of the loop. Following the same argument as Seager and Sunagawa's discussions (1962) on the movement of screw dislocations in hematite, these lines are dislocation scarps formed by the movement of screw dislocations of right and left hands after the cessation of crystal growth. The existence of these lines also proves that the rectangular loops are formed by spiral layers originating from two screw dislocations of opposite hands. On the surface of the loops, many minute spindle-shaped layers can be observed.

The third growth feature observed on the (100) face is composite spirals originating from clusters of screw dislocations. These spirals also have elongated forms parallel to the elongation of the face and take on irregular and rugged fronts. Their spacings between the successive layers are very narrow.

Conclusion

The surface structures of the (111) and $(\overline{111})$ faces of sphalerite are quite different from each other. The former face is represented by the remarkable development of regular, equilateral triangular patterns and stepped but flat surfaces, whereas the latter by more deformed growth patterns and wavy or broken surfaces, in spite of the flatter and smoother appearance than the former face to the naked eyes. On the former face, triangular growth layers, tables and occasionally pyramids, as well as typical simple spirals with step heights of molecular dimensions and a few turns occur, whereas on the latter face irregular, triangular or hexagonal growth layers, and composite spirals with narrow spacings are the dominant features. Many slip lines which are formed during crystal growth appear on the former surface, whereas rarely on the latter surface. Development of the slip lines is considered as determining the differences of the surface structures between the two faces. The dominant occurrence of composite spirals with narrow spacings and sometimes with big step heights on the $(\overline{111})$ face and not on the (111) face is considered to be the main cause for the smaller development of the $(\overline{111})$ face and the larger development of the (111) face. The (100) face shows entirely different surface structures from the two tetrahedral faces. Its surface structures are in good agreement with the atomic arrangement of the face.

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