STRUCTURAL REASONS FOR ORIENTED INTERGROWTHS IN SOME MINERALS

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INTRODUCTION

Many examples of oriented intergrowths are known.[1] In some mineral occurrences it seems to be almost the rule. The well known ilmenite lamellae along the octahedral planes of magnetite have been a subject for discussion for many years. On the other hand, the oriented intergrowth of silver and dyscrasite, which seems to be quite common, has been described only recently.[2] In other cases where oriented intergrowths might have been expected as in pyrrhotite and pentlandite none seem to exist. The case of tetrahedrite and chalcopyrite appears to be unusual. Oriented layers and crystal growth of chalcopyrite on tetrahedrite crystals have been mentioned frequently, but the microscopic oriented intergrowth of chalcopyrite and tetrahedrite has not been observed.

This paper deals with examples of oriented intergrowths so familiar to workers using the metallographic microscope. The writer is indebted to Prof. G. M. Schwartz of the University of Minnesota for assistance in the microscopic investigation of some of the intergrowths here described.

EXAMPLES OF INTERGROWTHS

There have been a number of suggestions in the literature[3] as to the reasons for oriented intergrowths. Some investigators lay considerable stress upon the similarity of the chemical composition of the intergrown minerals. This is justified, probably, in cases of such intimate intergrowths as will be here discussed,

[1] Müggie, O., Die regelmässingen Verwachsungen von Mineralien verschiedener Art, *Neues Jahrb., Beil. Bd.* **16,** 1903, p. 335.

[2] For literature see: Schwartz, G. M., Dyscrasite and the Silver Antimony Constitution Diagram, *Am. Mineral.*, vol. **13,** 1928, pp. 495–504.

[3] The references are numerous and widely scattered. Often the subject is merely touched upon in a few sentences. The first investigators who used X-ray data in the interpretation of oriented intergrowth seem to have been R. Gross and N. Gross (see under "Sphalerite and Chalcopyrite"). After this paper had gone to press the writer found M. L. Royer's "Recherches expérimentales sur l'épitaxie en orientation mutuelle de cristaux d'espèces differentes," *Bull. Soc. Min.*, Vol. **51,** No. 1–2, 1928. Royer describes chiefly experiments with artificial salts.

but it would not apply to the oriented growth of hematite in mica, for example. It seems to the writer, however, that in the common, natural, intergrowths at least one of the important elements of the two formulas should occur in both minerals. The reason most frequently advanced for oriented intergrowth is that the two planes which are in contact have very similar arrangements and spacings of atomic positions. The author would even go a step farther and suggests that in most cases these atomic or ionic positions are occupied by atoms or ions of the same element. The contact plane, therefore, would fit into the structure of one crystal as well as into that of the other. The linear differences in the spacing of the atoms in the two planes in which the crystals meet do not seem to be greater in any case than ten percent of the larger of the two structures that were examined.

Magnetite-Ilmenite and Magnetite-Hematite Intergrowths

Many writers have called attention to the microscopic ilmenite or hematite lamellae which occupy positions parallel to the octahedral planes of magnetite. Mügge[4] was one of the first to study these intergrowths. He suggested that the lamellae of ilmenite or hematite are basal plates (0001). This has been verified by the writer by employing reflected polarized light. This orientation of (0001) of ilmenite or hematite parallel to (111) of magnetite may be demonstrated on a polished section containing grains of magnetite cut parallel to (111). The ilmenite or hematite in such a section forms a more or less complete network or equilateral triangles. Extinction of the lamellae occurs whenever they are parallel to one of the vibration directions of the nicols. Ramdohr[5] describes a section of ilmenite in which magnetite lamellae parallel to (111) are in contact with (0001) planes of ilmenite. The writer[6] suggested three years ago that the orientation of ilmenite with respect to magnetite must be due to similarity of the contact plane. A study of the structures of the two minerals bears out this belief. Every third and seventh (111) structure plane of

[4] Über die Mikrostruktur des Magnetit und verwandter Glieder der Spinellgruppe und ihre Beziehungen zum Eisenoxyd, *Neues Jahrb., Beil. Bd.* **32**,, 1911, p. 511.

[5] Beobachtungen an Magnetit, Ilmenite, Eisenglanz, etc., *Neues Jahrb., Beil. Bd.*, **54**, A, 1926, p. 346.

[6] Magnetite-Martite-Hematite, *Econ. Geol.*, vol. **21**, 1926, p. 388.

magnetite consists of oxygen ions only. These have the arrangement shown in Fig. 1. The ilmenite structure according to Goldschmidt[7] and Zachariasen is very closely related to that of hematite. The distribution of the oxygen atoms seems to be practically

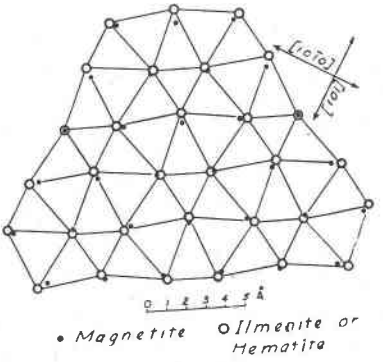

FIG. 1
The (0001) plane of O atoms of ilmenite or hematite superimposed on an O plane (111) of magnetite

identical in the two structures. Every third plane parallel to the base (0001) consists of O ions.[8] This arrangement is superimposed on the magnetite plane in Fig. 1. The crystallographic directions [110] of magnetite and [10$\bar{1}$0] of hematite (or ilmenite) have been observed to be normal to each other in the intergrowths described by Mügge.[9] These two directions are indicated in the structures planes of Fig. 1. They are also normal to each other in the crystal structures. Therefore crystallographic and structural relationships point to the conclusion that this oriented intergrowth is made possible by the sharing of one oxygen plane by both crystals. The spacing of the ions in this common plane is probably neither exactly that of hematite or ilmenite, nor that of magnetite, but about half way between the two values given. Any stresses set up at the contact plane could be gradually distributed over the ionic layers close to the plane.

[7] Goldschmidt, V. M., Geochemische Verteilungsgesetze der Elemente VIII, *Skrifter Utgitt av Det Norske Videnskaps—Akad.*, Oslo, I *Matem.—Natwrvid. Kl.*, 1926. p. 150.

[8] Structure of hematite: Ewald, P. P, and Hermann, C., *Strukturbericht*, 1913–1926, p. 242; *Zeit. f. Krist.*, attached to vols. **65, 66, 67, 68, & 69.**

[9] *Neues Jahrb., Beil. Bd.*, **16,** 1903, p. 347.

Hematite-Ilmentite Intergrowth

The structures of these two minerals are so similar in arrangement and spacing of the oxygen atoms that the frequent oriented intergrowth is not surprising. The two minerals usually intergrow parallel to (0001), but intergrowth parallel to $(10\bar{1}1)$ has also been noticed.[10] There is no reason why there could not be other orientations where structural resemblance is so complete.

Magnetite-Spinel Intergrowth

These two minerals are isomorphous. Their structures are the same, except for a slightly larger unit cell in magnetite. The well known oriented intergrowths of spinel lamellae parallel to the cubic (100) planes of magnetite are easily explained. Every second plane parallel to (100) is an O plane in both minerals. The O plane should become the plane of contact in preference to the others. The latter consist of ferrous or ferric Fe and Mg or Al ions, respectively. An exchange of Fe and Mg or Fe and Al would probably be necessary in the contact plane under those conditions.

Sphalerite-Chalcopyrite Intergrowth

R. Gross and N. Gross[11] determined the structure of chalcopyrite and noticed its resemblance to sphalerite.[12] The tetragonal character of chalcopyrite is due to the fact that in the sphalerite structure (taken as a structure type) every odd Zn (001) plane has been replaced by Cu, and every even one by Fe. The S positions have been shifted slightly in the direction of the *c*-axis. Gross explains the oriented growth of chalcopyrite on faces of sphalerite parallel to (100) by the similarity of the size and arrangement of the unit cell. He did not mention possible intergrowths along a mutual sulphur plane (100), as the writer has illustrated in Fig. 2. Since chalcopyrite is tetragonal the spacing of the S atoms in the plane parallel to the base (001) is slightly different from that parallel to the second order prism (100) which is shown in Fig. 2. The (001) plane of chalcopyrite, however,

[10] Ramdohr, P., *op. cit.*, p. 356.

[11] Die Atomanordnung des Kupferkieses und die Struktur der Berührungsflächen gesetzmässig verwachsender Kristalle, *Neues Jahrb., Beil. Bd.*, 48, 1923, pp. 128–134.

[12] For illustrations of the two structures see this Journal, vol. 14, 1929, pp. 184, 185.

agrees also with the cubic plane of sphalerite. Its S positions are indicated by crosses in Fig. 2.

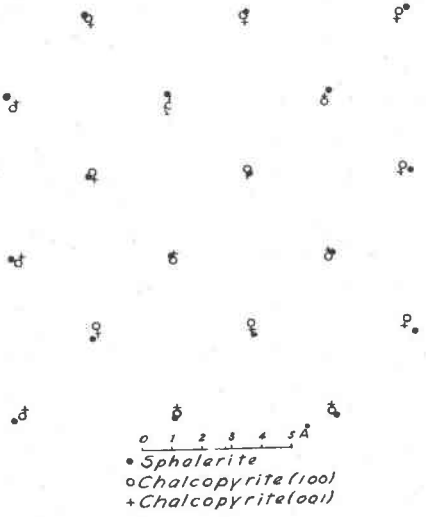

FIG. 2
The (100) plane of S atoms of sphalerite in contact with the (100) and (001) planes of chalcopyrite.

No mention was made by Gross of the intergrowth parallel to the (111) plane which is probably as common, if not more so, as that parallel to (100). Along (111) the close agreement of the two S planes is shown in Fig. 3. It is not quite correct however, to speak of the S atoms of chalcopyrite in Fig. 3 as being in one plane. On account of the tetragonal symmetry of the crystals the S atoms are not at the corners of equilateral triangles. Alternate rows of S atoms from top to bottom in Fig. 3 lie in the same plane. The two resulting parallel planes (111) of chalcopyrite, however, are so very close together that for the purpose of this discussion they may be considered as one.

It is significant that no microscopic intergrowth has been observed along the dodecahedral planes (the II order pyramid and I order prism of chalcopyrite) along which the spacing agrees as well as in the other planes. These planes contain half sulphur, half metal atoms. It is thought that the fact that the Zn atoms in sphalerite coincide with the Cu and Fe atoms of chalcopyrite in these planes prevents intergrowth or at least causes preferred

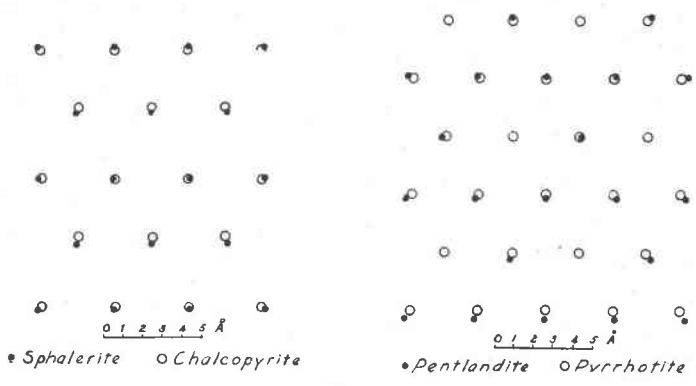

FIG. 3
Positions of S atoms in the (111) planes of sphalerite and chalcopyrite.

FIG. 4
Positions of S atoms in the (0001) plane of pyrrhotite
and in the first (111) S plane of pentlandite.

intergrowth along directions where complete chemical agreement exists.

CHALCOPYRITE-BORNITE AND BORNITE-CHALCOCITE INTERGROWTHS

Much has been published on the microscopic intergrowths of these minerals.[13] Their mutual planes of contact are the (111) planes for chalcopyrite and bornite, as well as for bornite and chalcocite. In his first manuscript the author had predicted that when the structure of bornite became known it would be found that its contact plane would be very similar in atomic spacing and arrangement to that of chalcopyrite and chalcocite, respectively. A few days after submitting the manuscript to the editor the writer received the description of the structure of bornite from Delft, Holland.[14] A study reveals that the arrangements of the S atoms in chalcopyrite and bornite are very similar. The spacing of the S atoms in the (111) planes of bornite is almost identical to that of sphalerite (3.84Å to 3.83Å). Fig. 3, therefore, can be used for showing the agreement of the (111) S planes in the

[13] See for example: Schwartz, G. M., Experiments bearing on bornite-chalcocite intergrowths, *Econ. Geol.*, vol. **23**, 1928, pp. 381–397.

[14] W. De Jong, Over de Kristalstructuren van Arsenopyriet, Borniet en Tetraëdriet, (Thesis) *Delft*, **1928.**

intergrowth of chalcopyrite and bornite as well as of chalcopyrite-sphalerite. The (111) Cu planes in bornite also agree closely with the (111) Cu-Fe planes of chalcopyrite. A decision, therefore, whether the common contact plane is a sulphur or metal plane cannot be made at present.

A comparison of the structures of bornite and cubic chalcocite[15] shows the same similarity for the (111) S planes and (111) Cu planes, respectively. The S as well as Cu atoms are arranged in equilateral triangular fashion in the (111) planes. In bornite the distances between S atoms (or Cu atoms) in these planes would be 3.84Å and in chalcocite it would be 3.95Å, a difference of approximately three percent for the two minerals. Again, it is impossible at present to decide whether the contact is along a common S or Cu (111) plane.

The fact that no microscopic intergrowth takes place along other than the (111) planes is also explainable by a study of the structures, for neither cubic nor dodecahedral planes of bornite are similar in atomic arrangement to chalcopyrite or chalcocite.

Chalcopyrite-Pyrrhotite Intergrowth

Oriented intergrowth of these two minerals does not seem to be very common, but it has been described by G. M. Schwartz.[16] It can be explained in the same way as the previous examples. The (0001) structure planes in pyrrhotite are S planes alternating with metal planes. The arrangement and spacing in the S planes is shown in Fig. 5. If this plane is superimposed on the S plane of chalcopyrite, in Fig. 3, the linear spacing agrees within 8 percent (3.73Å:3.43Å).

Chalcopyrite-Stannite Intergrowth

The oriented microscopic intergrowth of chalcopyrite in stannite has been described by G. M. Schwartz[17] and S. Reinheimer.[18] R. Gross and N. Gross[19] also mention it and show the structural

[15] Ewald, P. P., and Hermann, C., *op. cit.*, p. 150.

[16] A Sulphide Diabase from Cook County, Minnesota, *Econ. Geol.*, vol. 20, 1925, p. 264.

[17] Stannite, its Associated Minerals and Their Paragenesis, *Am. Mineral.*, vol. 8, 1923, p. 164.

[18] Chalkographische Untersuchungen an Zinnkies, *Neues Jahrb., Beil. Bd.*, 49, 1923, pp. 163–165.

[19] *Op. cit.*, p. 133. They give the wrong axial ratio for stannite.

similarity of the two minerals. The positions of the S atoms have not been determined as yet for stannite. The writer believes that their arrangement probably determines the intergrowth parallel to (001) or (100) in both minerals.

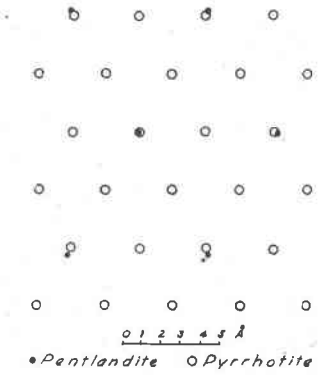

FIG. 5
Positions of S atoms in the (0001) plane of pyrrhotite and in the second (111) S plane in pentlandite.

CHALCOPYRITE-CUBANITE INTERGROWTH

The oriented intergrowth of these two minerals has been discussed a great deal. Ramdohr[20] in a recent paper summarizes and adds much new information concerning the lamellae of cubanite parallel to the (111) planes of chalcopyrite. The structure of cubanite, $CuFe_2S_3$, is still unknown, but it may be predicted that the plane intergrown with the (111) plane of chalcopyrite will have a very close resemblance to the latter.

SILVER-DYSCRASITE INTERGROWTH

This oriented intergrowth has been described several times.[21] Silver has the structure of a face-centered cube. The structure of dyscrasite, Ag_3Sb, has been determined very recently.[22] It is the close-packed hexagonal one. This is unusual, for the close packed

[20] Neue mikroskopische Beobachtungen am Cubanit (Chalmersit) und überlegungen über seine lagerstättenkundliche Stellung, *Zeitsch. f. prakt. Geol.*, vol. **36**, 1928, pp. 169–178.

[21] Schwartz, G. M., *Am. Mineral.*, vol. **13**, 1928, p. 495.

[22] Machatschki, F. Über die Kristallstruktur des blätterigen Dyscrasites von Andreasberg (Harz) und der künstlich dargestellen Legierung Ag_3Sb, *Zeit. Krist.*, vol. **67**, 1928, pp. 169–176.

hexagonal unit cell contains only two atoms in equivalent positions while a molecule of dyscrasite apparently contains four atoms three of which are equivalent. Machatschki, therefore, believes that Ag_3Sb is a solid solution similar to the hexagonal close-packed solutions of Ag-Zn, Ag-Sn, Ag-Cd, and Ag-In. It is difficult to understand, however, why such a solid solution should always have the same composition and a structure distinct from silver. Silver has no cleavage while dyscrasite has excellent basal cleavage similar to antimony. One is reminded by this property of so-called "layer lattices"[23]. Since the Sb atoms seem to have no definite positions assigned to them in the lattice, one is tempted to imagine that Sb atoms segregate in certain layers parallel to the base. Dyscrasite then would be composed of (0001) silver layers (containing some Sb atoms) alternating with a few layers containing an excess of Sb over silver. As Sb resembles Ag in mass as well as in radius it is doubtful, whether X-ray powder diagrams could record such discrepancies. Besides, Machatschki[24] mentions several unexplained anomalies in his investigation.

Regardless of how the Sb atoms are distributed the fact remains that the arrangement and spacing of the atomic positions in the (0001) plane of dyscrasite and in the (111) plane of silver are practically (within three percent) alike. Their contact plane would be a possible plane in both structures, especially since the cubic silver lattice can dissolve up to 14 percent of antimony.[25]

ABSENCE OF ORIENTED INTERGROWTHS IN PYRRHOTITE PENTLANDITE MIXTURES

So far we have been able to explain the occurrences of oriented intergrowths on the basis of internal structures of the minerals. The question now arises: Why are there no true oriented intergrowths in the mixtures of pyrrhotite and pentlandite, especially since pentlandite is supposed to be one of the components of the "unmixing" of a solid solution of (Fe, Ni)S? R. W. Van Der Veen[26] gives one illustration of pentlandite in pyrrhotite that seems to show some slight orientation, but the writer would

[23] Gruner, J. W., Crystal Structure Types, *Am. Mineral.*, vol. 14, 1929, pp. 173–187.

[24] *Op. cit.*, p. 174.

[25] Machatschki, F., *op. cit.*, p. 175.
Schwartz, G. M., *op. cit.*, p. 495.

[26] Mineragraphy and Ore Deposition, The Hague, 1925, Fig. 16.

hesitate to state definitely that it represents an oriented intergrowth. W. H. Newhouse[27] seems to have seen a similar intergrowth of pentlandite "sometimes extending into the pyrrhotite crystal from an intergranular mass of pentlandite." This may signify replacement along the parting planes of pyrrhotite, but not true oriented intergrowth.

Considerable differences exist in the two structures.[28] Pyrrhotite is hexagonal and more closely packed than pentlandite. The bonds or valence coördinates for each metal and S atom are six in number to six atoms of opposite charge. Odd numbered (0001) planes are metal; even numbered are S planes. The spacing of the atoms in these planes are shown in Figs. 4 and 5. The arrangement of S in cubic pentlandite in (111) planes is superimposed on pyrrhotite. It will be noticed that the S atoms shown almost coincide, but that there are "big holes" in the pentlandite structure. It will also be observed that the pentlandite S atoms in Fig. 5 are complementary to those in Fig. 4. The two together being equal to those of pyrrhotite. The sequence of the (111) planes in pentlandite is: metal plane, S plane (Fig. 4), S plane (Fig. 5), metal plane. The distance between the two S planes is twice that between S and metal planes. The good (111) cleavage of pentlandite probably would pass between the S planes. The arrangement of the S atoms seems to eliminate a S contact plane as a possibility. The arrangements of the metal atoms in the (0001) and (111) planes, respectively, are in excellent agreement, however. They may be superimposed as well as the S planes in Fig. 4, but with the "holes" now filled with atoms. Still a contact plane of metal atoms is improbable, for the forces acting on some of the atoms would be much greater on one side of the contact plane than on the other, as can be seen from a study of structure models. Since no other planes in the two minerals agree as well as those discussed, oriented intergrowths are improbable if not impossible.

[27] The equilibrium diagram of pyrrhotite and pentlandite and their relations in natural occurrences, *Econ. Geol.*, vol. 22, 1927, p. 296.

[28] Alsén, Nils, Röntgenographische Untersuchung der Kristallstrukturen von Magnetkies, Breithauptit, Pentlandit, Millerit und verwandten Verbindungen, *Geologiska Fören. i. Stockholm Förh.*, vol. 47, 1925, pp. 26–62.

CONCLUSIONS

Oriented intergrowths as seen especially under the metallographic microscope are discussed. It is found that intergrowth takes place only on those crystallographic planes in which the atomic arrangement and spacing are almost alike. Differences do not exceed a few percent. At least one of the chief chemical constituents (element or radical) of the two minerals is found in both. There is good reason to believe that one of the structural planes is shared by both minerals at the contact. In the examples investigated the common contact plane seems to be an oxygen or sulphur plane. Reasons are given for the probable non-existence of oriented intergrowths in mixtures of pyrrhotite and pentlandite.