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Crystallography of the Hexagonal Ferrites

This family of well-ordered inorganic compounds includes giant structures of "biological magnitude."

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From its primitive beginnings early in this century (*1*), x-ray crystallography, the study of crystal structures by means of x-ray diffraction, has steadily evolved into a highly sophisticated branch of science. A principal objective of x-ray crystallographers is the precise location of atoms in three-dimensional space, thereby defining the repeat pattern characteristic of a particular crystalline species. The problem may involve a material whose structure is unknown, in which case the atomic arrangement must truly be determined, or it may involve the refinement of a known structure. In either case, one is faced with the prospect of accurately measuring hundreds or thousands of diffracted x-ray intensities. Until recently, this process constituted a tedious, time-consuming, often frustrating effort, and the final set of data was relatively inaccurate. Today, however, stable x-ray sources, refined electronic counting systems, and automated x-ray diffractometers have essentially tamed this phase of x-ray crystallography. Nevertheless, if such were the only technological developments, the ambitious biological crystal structure projects recently accomplished (*2*) and those currently in progress would not have been possible. The concurrent development of large, high-speed digital computers provided the modus operandi for handling experimental diffraction data in the required manner. Hamilton (*3*) has recently presented a good description of these developments in x-ray crystallography.

For an unknown structure of reasonable size and complexity, the step from observed diffraction data to a working structure model is indeed large, a result of the inherent lack of phase information in the intensity data. Accordingly, indirect structure-solving methods are utilized whereby reasonable models are formulated and computer-based calculations (of structure factors and electron density functions) can be used to evaluate the validity of such models. Lengthy computations are frequently involved in deriving trial structure models. Recently, direct methods have been used in an attempt to solve the "phase problem" by applying algebraic and probability concepts (*4*). Such methods have been more successful with centrosymmetric crystals and are normally confined to relatively uncomplicated structures. Refinements of known structures are normally accomplished by fairly straightforward, albeit lengthy, iterative least-squares calculations. In any event, the capability afforded by high-speed digital computers with large-sized memory banks is essential to modern research in crystal structures. As the complexity of structures increases, this requirement of course, is increasingly more apparent.

The severest test of crystal structure determination arises in the case of biological materials. Such substances as ribonucleic acid (RNA), deoxyribonucleic acid (DNA), hemoglobin, lysozyme, and myoglobin have posed enormous structural problems, requiring the utmost in diffractometric and computer capability (*2*). Even with the benefit of these technological advances, such projects required literally years of effort on the part of a team of scientists. Inorganic materials have never presented as prohibitive a structure problem, principally because unit cell dimensions are considerably smaller and the number of symmetrically independent atoms which must be positioned is therefore drastically reduced (*5*). Whereas it is not uncommon for crystallographic unit cells of organic structures to attain volumes of 60,000 to 70,000 cubic angstroms, inorganic materials rarely exceed 2000 cubic angstroms (*6*).

The largest unit cell vectors observed in inorganic substances are found in so-called polytypic materials (*7*). In such structures, an invariant layer or block of atoms is regularly stacked along a given crystallographic direction so as to generate large superperiods along the stacking vector. Silicon carbide (SiC), for example, is known to exist in approximately 50 structural modifications (*7*); cell dimensions along the stacking vector range incrementally to approximately 1500 angstroms (*8*). Larger dimensions have been reported, but the supporting evidence is rather vague (*9*). The largest SiC modification with a known crystal structure (atoms spatially located) has an orthogonal stacking repeat pattern of approximately 990 angstroms and a unit cell volume of 8000 cubic angstroms (*10*). This is large by the standards of inorganic compounds but a far cry from the unit cell volumes of many organic compounds.

A variation on the polytypic theme is afforded by ordered stacking of two (or theoretically more) different kinds of invariant structural blocks. Such a mixed-layering is best exemplified by the so-called hexagonal ferrites (*11*),

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Table 1. Observed M_nS structures.

$M : S$ ratio	Stacking sequence	Hexagonal c (Å) (*22*)	Ideal stoichiometry
1 : 1	MS	32.845	$BaMe_2Fe_{16}O_{27}$
2 : 1	M_2S	84.11	$Ba_2Me_2Fe_{28}O_{46}$
4 : 1	M_4S	153.85	$Ba_4Me_2Fe_{52}O_{84}$
6 : 1	M_6S	223.4	$Ba_6Me_2Fe_{76}O_{122}$
•	•	•	•
•	•	•	•
•	•	•	•
∞	M	23.194	$BaFe_{12}O_{19}$

an extensive family (61 distinct members at present) of magnetic materials in which ordered stacking of two structural increments parlays the unit cell dimension along the stacking vector to a known maximum of 1577 angstroms (*12*). The corresponding unit cell volume is approximately 47,000 cubic angstroms. This is easily the largest known inorganic unit cell and constitutes a structural giant in the inorganic realm. The study of compounds that approach a "biological magnitude" is necessarily complicated by at least some of the problems formerly regarded as peculiar to complex organic compounds. Mounting unit cell size incurs difficulties in the resolution of x-ray diffraction data; the number of spatial models satisfying dimension and symmetry requirements increases astronomically. Fortunately, however, the hexagonal ferrites afford a mechanism for circumventing these problems. Upon suitable etching, they reveal extremely fine, characteristic networks of surface microfeatures observable by high-resolution electron microscopy (*13*). An understanding of the "code" of such features permits direct readout of crystal structures and has thereby enabled us to obtain unique structure solutions for these giant inorganic species (*12*).

Basic Features

The hexagonal ferrites, so named to differentiate them from the cubic, or spinel, ferrites, have attracted attention because of the following unique assemblage of magnetic properties (*14*): high permeability, high resistivity, and relatively narrow ferrimagnetic resonance linewidth at microwave frequencies; and large internal magnetic anisotropy fields. These properties permit the utilization of hexagonal ferrite crystals in electronic components operating at microwave and higher frequencies—a promising, relatively unexploited spectral region for communications and surveillance.

A basic feature of hexagonal ferrite structures is a layer of oxygen atoms arranged essentially in close-packed fashion, that is, each oxygen is surrounded by six other oxygen atoms in the plane. A second type of framework layer obtains when every fourth oxygen has a barium atom substituted for it, thus giving an ordered 1 : 3 ratio of barium to oxygen. These two layer types group, as shown schematically in Fig. 1, to form three basic building blocks or units, designated *S*, *M*, and *Y*. Block *S* has two oxygen layers; block *M* consists of five layers, one of which is the Ba-O type; block *Y* has six layers, with two adjacent ones containing barium. Heights and compositions are shown in Fig. 1; Me is usually divalent zinc, nickel, cobalt, or iron. These smaller cations occupy interstitial sites [normally tetrahedral and octahedral (*15*)]; their location is not critical to this discussion. Blocks *S*, *M*, and *Y* behave as integral structural units and stack along the *c* axis in a variety of ratios and permutations to form the extensive hexagonal ferrite family. Each particular assemblage of stacking units gives a discrete, characteristic, remarkably well-ordered structure, as evidenced by x-ray diffraction and electron microscopy.

Structure Groupings

The stacking elements (Fig. 1) show certain decided preferences. Block *M* is most commonly associated with the *Y* unit, and less often with unit *S*; block *Y* has yet to be seen in the same structure with an *S* unit, nor have all three units been found together. Thus known hexagonal ferrite structures fall into a limited *M–S* series (*16*) and a prolific *M–Y* group (*17*). The former series is expressed as M_nS, its members including structures in which a number (n) of *M* blocks combine with one *S* unit (*16*). Five such compounds have been observed, including end-member $BaFe_{12}O_{19}$. The latter phase, known as barium ferrite, consists entirely of *M* blocks; its structure has been refined by classical techniques (*18*). The M_nS phases are listed in Table 1. In phase M_4S, for example, four *M* blocks alternate with one *S* unit in a highly ordered manner along the *c* crystallographic vector. Since the chemical compositions of blocks *M* and *S* are known (see Fig. 1), the composition of phase M_4S is established on the basis of a knowledge of only one parameter, the subscript 4. Similarly, since dimensions and atomic positions (*18*) of the stacking elements are known, unit cell parameters and the crystal structure of phase M_4S can be determined, as in the previous case, from the subscript alone, if one has prior knowledge of the geometry involved in the interfacing of the blocks.

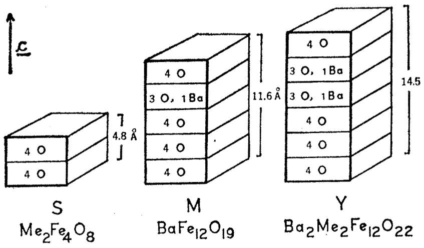

Fig. 1. Schematic presentation of the three discrete building blocks that stack along the *c* axis to form numerous, ordered, mixed-layer hexagonal ferrite structures; each block has the same cross-sectional dimensions and consists of individual layers with four oxygen atoms (4 O) or three oxygen atoms and one barium atom (3 O, 1 Ba).

With one possible exception (*19*), we have yet to observe more than one *S* unit in the base sequence of *M–S* structures. As a result, permutation of blocks is not a factor in establishing a stacking sequence: in phase M_4S, the sequences *MMMMS*, *MMMSM*, and so forth, degenerate into the same structure upon repetition. The largest *M–S* structure observed thus far is M_6S, with a hexagonal cell dimension of 223 angstroms along its stacking direction. (This dimension is obtained by summing the block heights and then tripling the value to achieve identity in a right-angle coordinate system.) Although 223 angstroms is an exceedingly large cell dimension for inorganic materials, the value is below average for hexagonal ferrites.

The second, and considerably more extensive, series of structures is designated M_pY_n (*17*). This series can conveniently be divided into several subgroups: M_2Y_n, M_4Y_n, M_6Y_n, and M_8Y_n. (An odd number of *M* blocks is symmetrically degenerate and doubles to an even number.) Fifty-six M_pY_n structures have been observed, including the end-member *Y* phase, one of the most common (and practical) hexagonal ferrites. This phase has the stoichiometry $Ba_2Me_2Fe_{12}O_{22}$

and consists entirely of Y blocks. Its crystal structure has been refined by classical means, and all atomic positions are accurately known (*20*).

M_2Y_n Structure Series

The M_2Y_n structures, of which 40 have been characterized, consist of two M blocks and n Y blocks. (The current maximum for n is 21.) The composition of a specific phase is immediately established when the value of n is known. Contrary to the situation in phases of the type M_nS, however, the crystal structure is not thereby uniquely defined because the permutation of blocks is now a factor in establishing a stacking sequence. Thus for M_2Y_4 phases, for example, $MMYYYY$, $MYMYYY$, and $MYYMYY$ describe different crystal structures, although all have the same composition. Each M_2Y_4 arrangement is associated with its own characteristic x-ray diffraction pattern. Such patterns show maxima in the same spatial positions, an indication of overall dimensional agreement; diffraction intensities differ markedly, however, an indication of substantial atomic rearrangement within the volumetric constraint. As input to the solution of structures, the following information is known: (i) the precise atomic positions in pure M and pure Y phases [from classical refinements (*18, 20*)]; (ii) the singular manner in which M and Y blocks interface along the stacking direction (from empirical evidence); and (iii) the fact that in the case of such mixed layering atomic positions within M and Y blocks remain relatively unchanged (from classical structure calculations). It follows that the only piece of information lacking for a complete, three-dimensional structure solution is the stacking sequence, that is, the sequence of stacked M and Y blocks.

A portion of the M_2Y_n series, incorporating stacking permutation as a mechanism for generating different structures, is shown in Table 2 (upper portion). Obviously, as the value of n increases, the number of stacking permutations also becomes larger. For M_2Y_{21}, the most complex phase of this type observed thus far, there are 11 different stacking permutations, that is, 11 unique arrangements for a one-dimensional sequence of two M blocks and 21 Y blocks. Although the basic stacking period of 328 angstroms leads to resolution difficulties in the x-ray diffraction experiment, the one-dimensional nature of the structure problem renders it amenable to standard treatment. Thus we need compute diffraction intensities for a maximum of only 11 models in order to compare with observed data and thereby determine the correct crystal structure.

If the hexagonal ferrite group were no more complex than this, it would pose no insurmountable structure problem for x-ray diffraction. These fascinating materials, however, contain M_4Y_n phases and compounds with even larger numbers of M blocks, with the result that several degrees of added complexity are introduced. This complication is occasioned by both larger unit cells and an increased number of possible structure models.

More Complex Structures

Twelve structures have thus far been characterized in the M_4Y_n series. Four M blocks combine with from 3 to 33 Y blocks; the series is included in Table 2 (lower portion). As in the case of the M_2Y_n structures, compositional characterization follows directly from a knowledge of the subscript n. Here again, however, permutation of structural blocks prevents unique characterization of the crystal structure. Although M_4Y_3, the simplest compound in this series, offers only four possible stacking arrangements, M_4Y_{33}, the most complex member, presents several thousand alternatives. The M_4Y_{33} member has the extraordinary stoichiometry $Ba_{70}Zn_{66}Fe_{444}O_{802}$; it has the largest unit cell (47,000 cubic angstroms) of any known inorganic material, containing over 4100 atoms. The c-axis cell dimension of 1577 angstroms introduces prohibitive difficulties in the resolution of experimental x-ray diffraction data. Furthermore, despite the one-dimensional nature of the structure problem, computer calculation of such a large number of stacking models remains an awesome prospect. Finally, were one ingeniously to obtain resolved diffraction data and subsequently struggle through the lengthy computational phase, he would arrive at several equally plausible an-

Table 2. Partial list of observed M_pY_n structures.

$M : Y$ ratio	Stacking sequence	Hexagonal c (Å) (*22*)	Ideal stoichiometry
2 : 1	MMY	113.16	$Ba_4Me_2Fe_{36}O_{60}$
2 : 2	$MYMY$	52.25	$Ba_6Me_4Fe_{48}O_{82}$
2 : 3	$MYMY_2$	200.4	$Ba_8Me_6Fe_{60}O_{104}$
2 : 4	$MYMY_3$	244.0	$Ba_{10}Me_8Fe_{72}O_{126}$
2 : 4	MY_2MY_2	81.32	$Ba_{10}Me_8Fe_{72}O_{126}$
•			•
•	(Plus 24 additional M_2Y_n structures)		•
•			•
2 : 12	MY_3MY_9	197.5	$Ba_{26}Me_{24}Fe_{168}O_{302}$
2 : 12	MY_4MY_8	592.5	$Ba_{26}Me_{24}Fe_{168}O_{302}$
2 : 13	$MYMY_{12}$	636.1	$Ba_{28}Me_{26}Fe_{180}O_{324}$
2 : 13	MY_6MY_7	636.1	$Ba_{28}Me_{26}Fe_{180}O_{324}$
2 : 15	$MYMY_{14}$	723.2	$Ba_{32}Me_{30}Fe_{228}O_{368}$
2 : 15	MY_4MY_{11}	723.2	$Ba_{32}Me_{30}Fe_{228}O_{368}$
2 : 15	MY_6MY_9	241.1	$Ba_{32}Me_{30}Fe_{228}O_{368}$
2 : 18	$MYMY_{17}$	854.0	$Ba_{38}Me_{36}Fe_{252}O_{434}$
2 : 18	MY_8MY_{10}	854.0	$Ba_{38}Me_{36}Fe_{252}O_{434}$
2 : 21	MY_3MY_{18}	327.5	$Ba_{44}Me_{42}Fe_{276}O_{500}$
2 : 21	$MYMY_{20}$	982.5	$Ba_{44}Me_{42}Fe_{276}O_{500}$
4 : 3	$MMYMYMY$	269.9	$Ba_{10}Me_6Fe_{84}O_{142}$
4 : 5	$MYMYMYMY_2$	357.0	$Ba_{14}Me_{10}Fe_{108}O_{186}$
4 : 8	$MYMYMY_3MY_3$	162.6	$Ba_{20}Me_{16}Fe_{144}O_{252}$
4 : 8	$MYMYMY_2MY_4$	487.8	$Ba_{20}Me_{16}Fe_{144}O_{252}$
4 : 8	$MYMY_2MY_2MY_3$	487.8	$Ba_{20}Me_{16}Fe_{144}O_{252}$
4 : 9	$MYMYMYMY_6$	531.4	$Ba_{22}Me_{18}Fe_{156}O_{274}$
4 : 10	$MMYMY_2MY_7$	191.6	$Ba_{24}Me_{20}Fe_{168}O_{296}$
4 : 10	$MYMY_2MY_2MY_5$	574.9	$Ba_{24}Me_{20}Fe_{168}O_{296}$
4 : 13	$MYMY_5MY_2MY_5$	705.7	$Ba_{30}Me_{26}Fe_{204}O_{362}$
4 : 13	$MY_2MY_4MY_2MY_5$	705.7	$Ba_{30}Me_{26}Fe_{204}O_{362}$
4 : 15	$MYMY_2MY_3MY_9$	792.9	$Ba_{34}Me_{30}Fe_{228}O_{406}$
4 : 33	$MY_6MY_{10}MY_7MY_{10}$	1577	$Ba_{70}Me_{66}Fe_{441}O_{802}$
6 : 13	$MYMYMYMY_2MY_3MY_5$	775.2	$Ba_{32}Me_{26}Fe_{228}O_{400}$
6 : 14	$MYMYMY_2MY_3MY_2MY_5$	818.8	$Ba_{34}Me_{28}Fe_{240}O_{422}$
8 : 27	$MMMY_4MY_7MYMYMY_6MY_8$	1455	$Ba_{62}Me_{54}Fe_{420}O_{746}$

swers rather than one unique solution.

Difficulties are further compounded by the occurrence of still more complex hexagonal ferrites (see the bottom of Table 2), two of the type M_6Y_n (M_6Y_{13} and M_6Y_{14}) and one of the type M_8Y_n (M_8Y_{27}). The latter has been observed in two different crystal specimens, each giving the same x-ray diffraction pattern. The M_8Y_{27} member, although not the largest, is the most complex hexagonal ferrite observed thus far by a diffraction technique. There are in excess of 400,000 permutations for the stacking of its 8 M and 27 Y blocks; the *c*-axis cell dimension is 1455 angstroms (*12*).

The number of hexagonal ferrite structures noted (61 to date) is certain to be increased as a result of additional research studies. Further x-ray diffraction investigation will undoubtedly reveal "missing" members of the groups described herein—structures with different block ratios or permutations—or even new series with novel block associations. One might well ask a few rather obvious questions at this point: Why do such immense structures form? What is the growth mechanism? How do the incremental building elements—be they atoms, layers, or blocks—"sense" these long-range, elaborate sequences and thereby propagate them in such an ordered fashion? These are questions that have perplexed students of stacking structures for many years. Although several theories have been proposed, none offers a full explanation of observed phenomena. Perhaps theories have tended to be too all-inclusive; specific explanations may apply to particular families of structures only. This aspect of the subject, however, requires an intensive treatment in its own right. The various theories are discussed by Verma and Krishna (*7*) and will not be considered herein. For our purposes it is sufficient to say that the hexagonal ferrites exist, that they comprise an extensive series of well-ordered, mixed-layer structures, including the largest known inorganic species, and that a *unique* solution of their more complex structures is beyond the combined capabilities of modern x-ray diffraction and computer procedures. Such structures, however, can readily be solved by high-resolution replica electron microscopy, as detailed in the following sections.

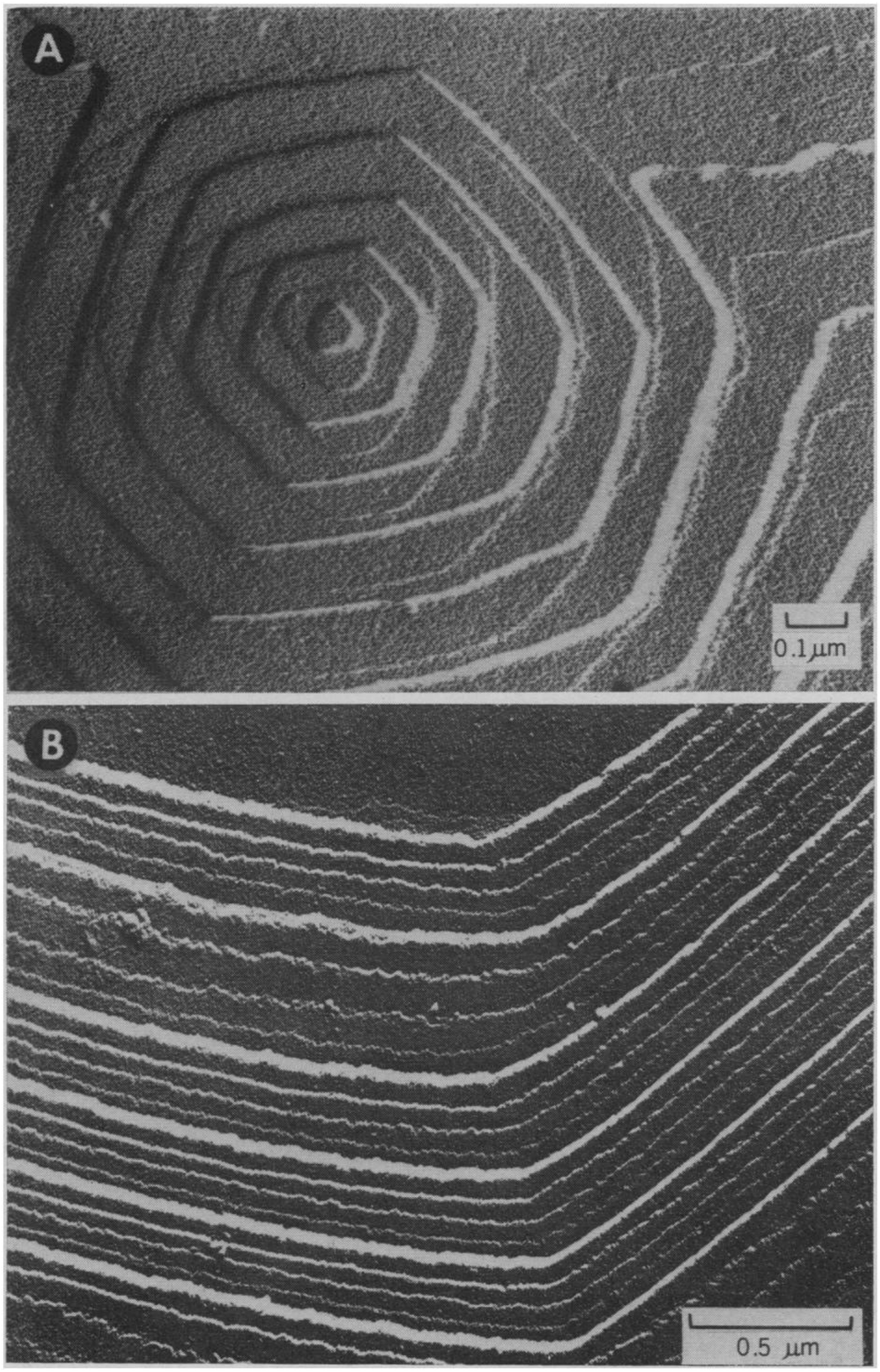

Fig. 2. Replica electron micrographs of portions of hexagonal ferrite basal surfaces etched with hydrochloric acid. (A) Two-step etch motif of an M_2Y_7 specimen in which the small step (26 angstroms) is an MY grouping and the large step (99 angstroms) is an MY_6 grouping (unique stacking sequence is $MYMY_6$). (B) Four-step etch motif of an M_4Y_{15} specimen in which the large step is an MY_9 grouping followed (reading downward from the top) by MY_3, MY_2, and MY (the repetitive stacking sequence is thus $MYMY_2MY_3MY_9$).

Electron Microscopy and Etching with Hydrochloric Acid

The capability of the electron microscope for extremely high magnification in conjunction with high resolution renders it an indispensable tool for observing *external* structural features on a scale beyond the capabilities of light microscopes. Studies of crystalline defect structures (dislocations and slip planes), the interpretation of micromorphological features, and the observation of imaged "lattice" planes have been used, along with similar procedures, to provide information related to *internal* crystal structures. Electron microscopy per se, however, has not been used as a direct structure-solving experimental tool, that is, as the means for determining relative atomic positions. Electron microscopy can be used to determine hexagonal ferrite crystal structures because of the peculiar mixed-layering nature of these crystals.

Hexagonal ferrite crystals react fairly readily with hydrochloric acid. Upon exposure to hot, 1 : 1 hydrochloric acid for several minutes, crystals are intricately etched on their basal faces (tabular faces normal to the *c* crystallographic direction). The etch patterns assume the form of fine terracing along the sides of gently sloping etch pits. Such surface structure can readily be observed if one views platinum-shadowed carbon replicas of the basal faces, using high-resolution electron microscopy (*13*). A typical etched surface is shown in the electron micrograph (Fig. 2A) of an M_2Y_n specimen. The steps revealed by etching consist of alternating large and small increments. Knowledge of the platinum shadowing angle and the absolute magnification allows a determination of the step heights as approximately 99 and 26 angstroms, respectively. The total, 125 angstroms, is the sum of the heights (along the *c* axis) of two M and seven Y blocks. Thus the specimen is an M_2Y_7 modification, and the two etch steps sum to give the primitive crystallographic repeat distance along the *c* axis. Furthermore, the smaller increment of 26 angstroms corresponds to one M and one Y block (MY), and the larger step represents one M and six Y blocks (MY_6). The stacking sequence is therefore $MYMY_6$, and this sequence constitutes the only additional piece of information needed for a complete structure determination. All M_2Y_n specimens show a repeat pattern of two steps (MY_x and MY_{n-x}) as a result of etching with hydrochloric acid. The two etch increments can be of equal height in cases such as MY_2MY_2, MY_4MY_4, and the like. In each instance where the same specimen has been examined by both electron microscopy and x-ray diffraction, crystal structures determined by the two techniques have been in complete agreement.

Specimens of the type M_nS, subjected to the same treatment, show one MS etch step and n—1 separate M increments. Thus, the M_4S phase has a repeat pattern of four steps: MS, M, M, and M. From the point of view of the crystal structure, however, such information is superfluous for the M_nS phases; no permutation of the stacking sequence is involved, and the structure is already established.

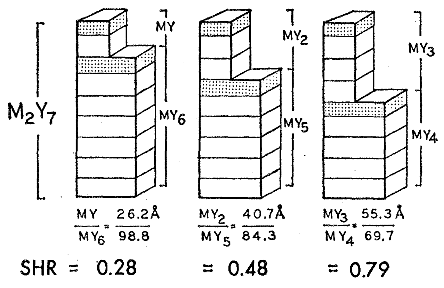

Fig. 3. Schematic presentation of the etch step-height ratio (SHR) method for differentiating stacking sequences within a given M_2Y_n group; the example shows three permutations of the M_2Y_7 grouping and their corresponding SHR's.

For M_4Y_n phases and more complex M–Y materials, since the number of stacking permutations can be very large, information gleaned by electron microscopy is usually critical to an efficient, unambiguous structure solution. Etched M_4Y_n specimens show four steps in the repeat pattern; each increment contains one M block, and the Y blocks are partitioned among the steps such that their total number is n. Figure 2B shows a portion of the etch structure for an M_4Y_n phase. The largest step (top of the micrograph) is an MY_9 increment. Subsequent steps correspond sequentially to MY_3, MY_2, and MY, after which the pattern repeats. Thus knowledge of absolute step heights leads to a direct solution of the stacking sequence in each case. Structures of the type M_6Y_n and M_8Y_n show an analogous pattern, with six and eight steps, respectively, in the primitive etch motif.

Etch Step-Height Ratios

This rather simple experimental procedure, however, is hampered by the fact that accurate determination of absolute step heights at the required levels of magnification and resolution is no simple matter. Experimental uncertainties in shadowing angle and magnification, and lateral irregularities in the steps themselves often lead to ambiguous results. Fortunately, however, the nature of the etch features affords a self-calibrating method that eliminates the need for measuring absolute step heights. This is accomplished by dealing with step-height ratios (SHR's) as shown in Fig. 3 for an M_2Y_7 structure. Having determined that the series is M_2Y_n from the two-step motif of the repetitive etch pattern, and that the structure is of the M_2Y_7 type from the *c*-axis dimension (from x-ray diffraction), in order to complete the task, one need only select one of the four following stacking sequences: MMY_7, $MYMY_6$, MY_2MY_5, and MY_3MY_4. The last three of these situations are shown schematically in Fig. 3. The two steps of $MYMY_6$ would be in the ratio of $MY/MY_6 =$ 0.28; for MY_2MY_5 and MY_3MY_4 the ratios are 0.48 and 0.79, respectively. Thus one need only measure the ratio of the two step heights to obtain a unique solution; neither magnification nor shadowing angle enters into the determination. Specimens from M_4Y_n and higher series are treated similarly.

The M_8Y_{27} structure, with a *c* dimension of 1455 angstroms, offers the most striking example of the power of the method. In this case, there are an estimated 400,000 permutations of eight M blocks and 27 Y blocks, an awesome prospect if one is trying to establish a unique stacking sequence. If one knows in advance the approximate number of layers in the basic repeat period (from an x-ray *c* dimension), SHR's readily lead to a stacking sequence of $MMMY_4MY_7MYMYMY_6$-MY_8. A unique structural solution is thus obtained from among a formidable array of geometric possibilities.

The SHR method has substantially augmented the list of structures that can be treated successfully by the electron microscopic approach to hexagonal ferrites (*21*). Nevertheless, even this experimental procedure has its limitations; it cannot cope with instances in which the crystallographic *c* dimension is too uncertain or cases in which relatively large MY_x steps are involved. In the group of M_2Y_{21} structures, for example, step-height ratios for MY_2-MY_{19} and MY_3MY_{18} are 0.14 and 0.20, respectively. Such fine distinctions are beyond the limitations of the SHR experimental method.

Nitric Acid Etching

A more detailed, and considerably more useful, etch structure can be realized on hexagonal ferrite basal surfaces by exposure to nitric acid rather than hydrochloric acid etchant. When specimens are refluxed in boiling, dilute nitric acid for approximately 30 minutes, MY_x steps are resolved into individual M and Y increments. The latter, 14.5 angstroms in height, are clearly visible on shadowed replica electron micrographs. The M steps measure 11.6 angstroms and are observable if sufficient care is exercised in the platinum shadowing stage of the specimen preparation procedure; this aspect is critical since the final platinum grain size limits attainable resolution.

Fig. 4A is a typical electron micrograph of a surface treated with nitric acid in the prescribed manner; this is an M_2Y_{21} phase. One can unmistakably discern a partitioning of the 21 Y blocks into a group of 20 alternating with a lone Y unit; single M increments are interleaved with the two Y groupings. Thus the stacking sequence is clearly $MYMY_{20}$, and an unambiguous structure solution is obtained. The case in point has only 11 possible stacking sequences, and, although the etch pattern is doubtless useful for a rapid, unique solution, it is not indispensable for solving the problem. On the other hand, the potential of the method can quickly be appreciated. No data on cell dimension, number of anion layers, magnification, or shadowing angle are required. One need only exert care in the preparation of suitable replicas for electron microscopy and then count the resolved M and Y etch steps until a primitive repeat sequence is established.

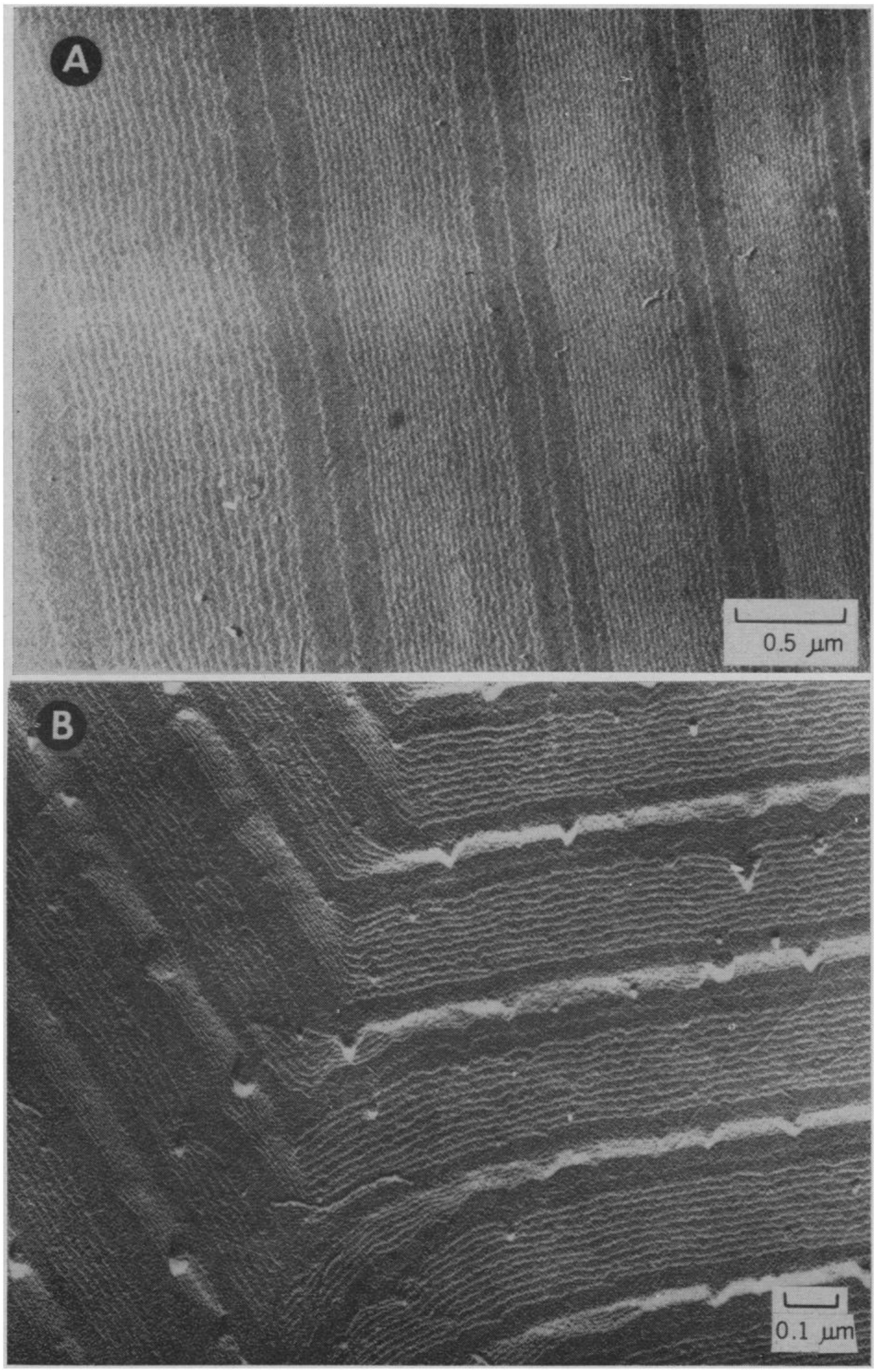

Fig. 4. Replica electron micrographs of portions of hexagonal ferrite basal surfaces etched with nitric acid. (A) Etch motif of an M_2Y_{21} specimen showing a partitioning of its 21 individual Y increments (14.5 angstroms each) into a group of 20 and a lone Y unit; single M steps (11.6 angstroms each) are disposed on either side of the isolated Y unit; the repetitive stacking sequence is thus $MYMY_{20}$. (B) Etch motif of the M_4Y_{33} phase showing a partitioning of its 33 individual Y steps (14.5 angstroms each) into four groups with 10, 6, 10, and 7 increments (reading downward from the top); single M units (11.6 angstroms each) are interleaved with the four Y groupings; the repetitive stacking sequence is thus $MY_6MY_{10}MY_7MY_{10}$.

Figure 4B shows the resolved M–Y step structure on the surface of the M_4Y_{33} phase; the latter, as already noted herein, has a hexagonal c dimension of 1577 angstroms, and its hexagonal cell volume of approximately 47,000 cubic angstroms houses over 4100 atoms. Etching with hydrochloric acid does not permit one to distinguish between step MY_6 and step MY_7 and erroneously indicates an M_2Y_n structure. Treatment with nitric acid, however, clearly reveals (Fig. 4B) an M_4Y_n motif and a stacking sequence of $MY_6MY_{10}MY_7MY_{10}$. In this case, as with M_8Y_{27}, the structure can be "seen" and its existence confirmed by x-ray diffraction; that is, one-dimensional c-axis x-ray diffraction profiles, although poorly resolved, show cell dimensions consistent with those deduced from electron microscopy.

Larger "Structures"

Once one has established a clear correlation between structures determined by x-ray diffraction, the standard technique, and those established by electron microscopy, a new tool in this sense, one can then seek structures solely by the latter method. Using such an approach, we have studied a large number of hexagonal ferrites and observed, among other things, repeat stacking sequences even larger than those noted above. In so doing, however, one is immediately faced with a basic problem bordering on the philosophic: When does an atomic array constitute an ordered crystal structure? How many times must a stacking sequence repeat itself before it defines a unit cell? Normally, this question is answered by noting the degree of coherency with respect to the diffraction of x-rays, but the new procedure has dispensed with a diffraction approach.

To avoid fruitless entanglement, we have arbitrarily established a criterion of six successive repeat periods: If an etch motif is repeated six times in succession, the associated unit cell is accepted as characterizing a valid structure. Depending upon the stacking sequence within a primitive repeat group, the requirement for six successive, identical ensembles corresponds to either two, three, or six complete hexagonal unit cells. Structures designated as "observed" by the electron microscopic procedure had to satisfy this requirement; such structures have been noted with hexagonal *c* dimensions up to 4000 angstroms. As a matter of fact, the observable size limit is set not by specimen stacking sequences, but rather by the openings of copper grids (70 micrometers square) used as supporting substrates in the electron microscope. The ultimate size attainment for the unit cells of these inorganic giants has therefore not yet been established.

Summary and Conclusions

The hexagonal ferrites form an unusual group of complex, ferrimagnetic oxides embodying some 60 known crystal structures. These include phases for which the structural unit cell is larger than that in any known inorganic materials. The various hexagonal ferrite modifications fall into two distinct structural series, each formed by the ordered interlayering (stacking) of two discrete building blocks; these blocks stack along the *c* crystallographic axis in varying ratios and varying permutations to form strictly coherent, reproducible crystal structures. This mixed-layering aspect of the hexagonal ferrites permits direct, visual observation of the sequence of their subunit-cell stacking elements, after etching, by means of electron microscopy. The sequence of stacked blocks in such structures constitutes the only information lacking for a complete, three-dimensional structure determination. Direct access to this information provides an immediate, unique solution of the crystal structure problem in each case and thereby avoids the dilemmas of a classical diffraction approach to such large unit cells. Ferrite structures with hexagonal *c* dimensions of 1455 and 1577 angstroms have been uniquely solved by direct electron microscopic readout of surface etch features.

One must exercise caution, however, in generalizing these findings to other materials. The method is successful in the case of the hexagonal ferrites because these are mixed-layer structures, wherein the building blocks react at different rates to a specific etchant. Mixed-layer systems are not uncommon in crystallography, and it is likely that similar techniques can be developed for other such materials. Regardless of the validity of this prognosis, however, it is quite evident that high-resolution replica electron microscopy is a most promising tool for the direct observation of surface structure on an ultramicro scale. During the studies reported here replica resolution capability was improved to about 10 angstroms; final resolution is limited by the particle size of the platinum shadowing material. Careful control of experimental conditions during replica preparation or an alternate choice of shadowing material, or both, might reasonably improve the resolution by a factor of 2. This resolution is within the range of most unit cell dimensions and approaches interatomic distances in solid-state materials. The potential of such an experimental capability needs no elaboration.

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