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MIXED-LAYER POLYTYPES RELATED TO MAGNETOPLUMBITE

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ABSTRACT

Thirteen new, discrete rhombohedral and hexagonal layer structures, of the type $Ba_wZn_yFe_wO_z$, have been identified during an *x*-ray diffraction study of "hexagonal ferrite" single crystals. They consist of an ordered *c*-axis stacking of two five-anion-layer substituted magnetoplumbite units ($BaFe_{12}O_{19}$; *M*) with a variable number of closely related six-layer units ($Ba_2Zn_2Fe_{12}O_{22}$; *Y*). An M_2Y_n series (n = 1–10) is generated, in which all unit cells have a common basal section ($a = 5.88$ Å) and hexagonal *c* varies up to 505.4 Å. For a given $M_2:Y_n$ ratio, *mixed-layer polytypes* form by permutation of the M and Y units along *c*. Well-resolved Weissenberg patterns and 00·1 diffractometer traces were obtained. The latter furnished relative intensities for use with one-dimensional structure-factor calculations to establish stacking structures from among qualifying models.

INTRODUCTION

Although principal unit cell vectors exceeding tens of Ångstroms are common in organic crystallography, they are rare among inorganic species. Most of the exceptions are contained in polytypic systems, particularly the silicon carbide family. At least a dozen SiC structures have *c* dimensions in excess of 100 Å; the largest polytype with an established crystal structure (Mitchell, 1954) has a value of approximately 990 Å. The present study has disclosed members of a considerably more complex quasi-polytypic system, $Ba_wZn_xFe_yO_z$, with *c* dimensions challenging those of the largest SiC modifications. These structures are related to the rare natural species magnetoplumbite.

The mineral magnetoplumbite was described by Aminoff (1925) from Långban, Sweden. Ideally $PbFe_{12}O_{19}$, it crystallizes as a hexagonal layer structure (Adelsköld, 1938). The Ba-substituted synthetic analogue, $BaFe_{12}O_{19}$, is known as barium ferrite and has become a commercially important ferrimagnetic material. The addition of certain divalent transition metal cations was shown to form five additional layer structures (Braun, 1957; Smit and Wijn, 1959), closely related to barium ferrite, the group being collectively termed "hexagonal ferrites" (as opposed to the cubic, spinel ferrites). Subsequent single-crystal *x*-ray studies on flux-grown material revealed five more phases (Kohn and Eckart, 1964a, b) and showed that all the hexagonal ferrites then known fell into two distinct series of polytypic stacking structures. Each series consists of a *c*-axis stacking of different ratios of two anionic building blocks. Three blocks are involved in all; the one common to both systems is barium ferrite itself, *i.e.*, it has the magnetoplumbite structure. It was pointed out that one series offered the likelihood of generating many new structures by changing the sequence of stacking elements while keeping their ratio unchanged. Since then, Weissenberg and single-crystal diffractometer studies have disclosed 13 such permutation structures, extending the series to larger ratios of stacking elements and raising the number of known hexagonal ferrites to 24. The present paper describes the new structures and discusses the polytypic stacking relationships whereby they are generated.

GENERAL RELATIONSHIPS

The magnetoplumbite structure has a *c*-axis repeat block of five oxygen layers, *one* of which contains Pb (or Ba in the case of barium ferrite) substituting for every fourth oxygen atom. This is shown schematically in Fig. 1. The positions of the smaller Fe^{3+} ions can be neglected for these stacking discussions. The five(-anion)-layer block, designated M, is doubled to form the ten-layer hexagonal unit cell of magnetoplumbite or barium ferrite. Similarly, there is a block having six anion layers, *two* of which contain Ba substituting for every fourth oxygen (Fig. 1). This block is designated Y; it is tripled along *c* to give the hexagonal unit cell of rhombohedral $Ba_2Zn_2Fe_{12}O_{22}$ (so-called Y phase). The latter is one of the original hexagonal ferrites (Braun, 1957); no natural equivalent is yet known. Here again cation positions other than Ba are neglected.

The M and Y blocks, compositionally $BaFe_{12}O_{19}$ and $Ba_2Zn_2Fe_{12}O_{22}$ respectively, comprise the stacking elements of the principal hexagonal

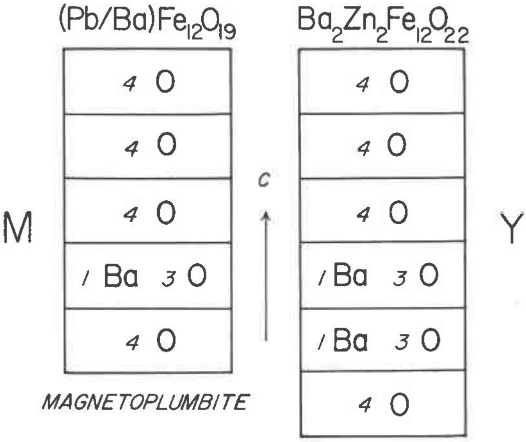

FIG. 1. Schematic drawing of the anion layer make-up of magnetoplumbite, $PbFe_{12}O_{19}$ (isostructural with barium ferrite, $BaFe_{12}O_{19}=M$) (left) and $Ba_2Zn_2Fe_{12}O_{22}=Y$ (right).

ferrite series, designated M_2Y_n. Including structures reported herein, it contains 19 members, derived by a *c*-axis stacking of two M blocks and one to ten Y blocks (hence M_2Y_n). The remaining hexagonal ferrites comprise an M_nS series (Kohn and Eckart, 1964b), in which S is a two-layer spinel block, $Zn_2Fe_4O_8$. This series is not pertinent to the present paper, since it does not permit the generation of new structures by stacking permutation.

M_2Y_n SERIES

The M_2Y_n series, complete through an M:Y ratio of 2:10, is shown in Table 1. Adjacent groups of structures differ by one Y block or six anion layers. Since the series is concerned with the generation of structures by ordered, one-dimensional stacking, the analogy with polytypism is obvious, hence the use of polytypic symbols (Ramsdell, 1947) to describe the hexagonal ferrites. The number of anion layers is that in the primitive repeat unit. In some cases, the cell is thereby complete along *c*, and the primitive repeat unit corresponds to the true *c*-axis identity period. Such structures are hexagonal (hence H in the symbol). In other cases, the primitive repeat unit is rhombohedral (hence R) and must be tripled to achieve identity along hexagonal *c*. The structure symbol, then, gives the number of anion layers in the hexagonal (simple or triply-primitive) unit cell.

Structures indicated by a single asterisk in Table 1 had previously been identified (Braun, 1957; Smit and Wijn, 1959; Kohn and Eckart, 1964a). They involve stacking of *different* M:Y ratios and are therefore of different compositions. To differentiate them from true, compositionally-invariant polytypes, they were termed mixed-layer structures (Kohn and Eckart, 1964a). Not until discovery of the structures reported herein (double asterisks in Table 1) was it conclusively demonstrated that, for a given M:Y ratio, the stacking elements could be permuted to generate additional species. Within each M:Y group the composition is unchanged; the structures are therefore true polytypes and, since the stacking elements differ, are termed *mixed-layer polytypes*. Note that, beginning with M:Y=2:4, different structures are possible (and some have been observed) with the same symmetry and number of layers in the *c*-axis identity period. They are differentiated by adding letter subscripts (first used in SiC; Ramsdell and Kohn, 1952) as shown in Table 1.

There are 35 possible structures in the M_2Y_n series for M:Y ratios through 2:10. The system, of course, extrapolates to the Y phase itself as end member. The possible stacking permutations are given in Table 1. Nineteen of these have so far been identified. With the exception of 48R,

TABLE 1. M_2Y_n SERIES

M:Y	Anion layers	Stacking Permutations	Structure Symbol
2:1	16	M — M Y	48R*
2:2	22	M — M Y_2	66R
		M Y M Y	22H*
2:3	28	M — M Y_3	28H
		M Y M Y_2	84R*
2:4	34	M — M Y_4	$102R_a$
		M Y M Y_3	$102R_b$*
		M Y_2 M Y_2	34H**
2:5	40	M — M Y_5	$120R_a$
		M Y M Y_4	40H*
		M Y_2 M Y_3	$120R_b$**
2:6	46	M — M Y_6	$46H_a$
		M Y M Y_5	$138R_a$*
		M Y_2 M Y_4	$138R_b$**
		M Y_3 M Y_3	$46H_b$
2:7	52	M — M Y_7	$156R_a$
		M Y M Y_6	$156R_b$**
		M Y_2 M Y_5	52H**
		M Y_3 M Y_4	$156R_c$**
2:8	58	M — M Y_8	$174R_a$
		M Y M Y_7	$58H_a$**
		M Y_2 M Y_6	$174R_b$**
		M Y_3 M Y_5	$174R_c$**
		M Y_4 M Y_4	$58H_b$**
2:9	64	M — M Y_9	$64H_a$
		M Y M Y_8	$192R_a$
		M Y_2 M Y_7	$192R_b$**
		M Y_3 M Y_6	$64H_b$**
		M Y_4 M Y_5	$192R_c$
2:10	70	M — M Y_{10}	$210R_a$
		M Y M Y_9	$210R_b$
		M Y_2 M Y_8	$70H_a$
		M Y_3 M Y_7	$210R_c$
		M Y_4 M Y_6	$210R_d$**
		M Y_5 M Y_5	$70H_b$

* Previously known structures; ** new structures.

structures involving contiguous M blocks are noticeably absent from the observed species. Whether such structures actually are more rare remains to be seen. The possible stacking permutations for the 58-layer group ($M:Y = 2:8$) are shown schematically in Fig. 2. Note that the last structure, $58H_b$, has an equipartition of its eight Y blocks. The result is a systematic absence in the single-crystal x-ray patterns, use of which is made in assigning stacking models to new structures. This is discussed further in the next section.

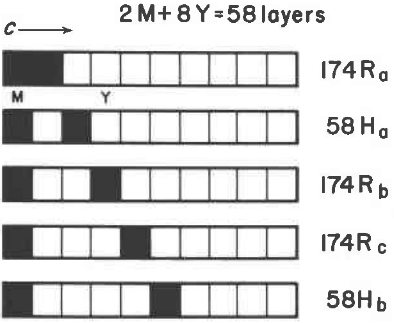

FIG. 2. Schematic drawing of the five c-axis stacking permutations for the 58-layer, M_2Y_8 group of structures.

EXPERIMENTAL PROCEDURES

Crystals were grown from an $NaFeO_2$ flux. Details of the preparation procedure have been given elsewhere (Savage and Tauber, 1964). Specimens are typically black, lustrous, tabular, 1–3 mm across, with well-developed basal faces and fairly prominent first-order pyramid zones.

Zero-level, a-axis Weissenberg patterns served to distinguish between hexagonal and rhombohedral symmetry and to determine the number of anion layers in the c-axis identity period. The $h0\cdot l$ Weissenberg pattern (FeK) for $64H_b$ ($P\bar{3}m1$, $c = 153.96$ Å) is shown in Fig. 3. The prominent central lattice line is c^*. Similarly discrete, well-resolved reflections were obtained for all of the structures described herein. Crystals showing evidence of new structures, or those for which the identity period could not be established with certainty, were studied further on a three-circle, single-crystal, x-ray diffractometer. Since the intent was to reveal c-axis stacking relationships and not to determine complete crystal structures, diffractometer patterns were confined to $00\cdot l$ series.

Portions of $00\cdot l$ traces for the four observed structures in the 58-layer group are shown in Fig. 4. Such patterns, typical of those obtained for all of the new structures, served to establish the identity period with certainty, to give accurate c dimensions, and for the measurement of intensities for use with structure-factor calculations. The patterns in Fig. 4 have the same peak spacing but differ considerably in relative intensities. These differences reflect the juxtaposition of M and Y blocks depicted in Fig. 2. Note that the diffraction pattern for $58H_b$ shows an absence of alternate reflections. This is due, as mentioned above, to the equipartition of the Y blocks, which introduces a c glide plane in $h0\cdot0$ and deletes $hh\cdot l$ reflections when l is odd. Note also in Fig. 4 that as the number of Y blocks approaches an equipartition between the two M blocks (Fig. 2), the odd $00\cdot l$'s (1 and 3, 9 and 11) become weaker relative to the even $00\cdot l$'s (2, 10). The strongest reflection (10) is $00\cdot116$ for the hexagonal structures and $00\cdot348$ for the rhombohedral modifications. Pending structure-factor confirmation, this intensity behavior was successfully used to assign stacking sequences to structures giving new patterns.

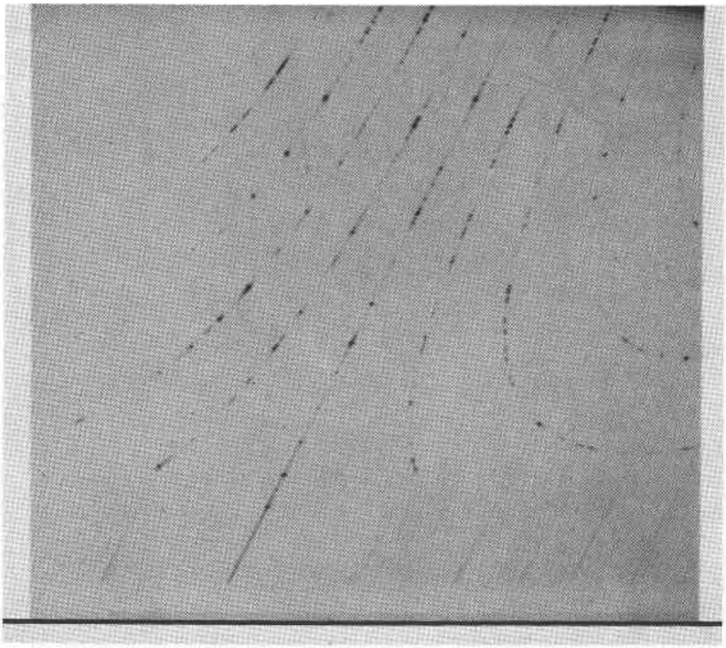

FIG. 3. $h0\cdot l$ Weissenberg pattern of $64H_b$ ($c=153.96$ Å, $a=5.88$; $P\bar{3}ml$). The prominent central lattice line is c^*, (FeK radiation; actual size).

Integrated intensities were obtained by standard fixed-time techniques using a θ-2θ scan and open x-ray optics. When the number of layers in the basic repeat group exceeded 52, however, diffraction peak overlap, even with FeK radiation, led to erratic results. For larger structures, therefore, a slit system was used and peak heights measured. The latter were corrected by applying an empirical function relating peak heights to integrated intensities.

MIXED-LAYER POLYTYPES

The single-crystal *x*-ray studies resulted in identification of 13 new hexagonal ferrites and in establishment of mixed-layer stacking permutation as a valid mechanism for the generation of multiple structures. In general, several examples were found of each new structure. Some of the crystals showed a single modification throughout; the typical specimen, however, was a syntactic intergrowth of two structures. The 13 new species are listed in Table 2, together with unrefined reliability factors resulting from the $00 \cdot l$ structure-factor calculations. For purposes of brevity, complete listings of calculated and observed structure factors have not been included. Where more than one stacking model satisfied identity period and symmetry requirements, structure factors were computed for each arrangement (*a* through *d*; Table 1) using atomic positions generated from those in the M and Y stacking elements. The lowest R-factors are italicized in Table 2; results were deemed sufficient to confirm the assigned stacking sequence in each case. No attempt was made at this stage to refine the structures or to extend the work beyond a one-dimensional stacking investigation.

TABLE 2. SUMMARY OF RELIABILITY FACTORS

Structure	No. $00 \cdot l$'s	R-factors (%) for model:			
		a	b	c	d
34H	68	*19.4*	—	—	—
$120R_b$	75	46.4	*23.3*	—	—
$138R_b$	86	37.7	*22.3*	—	—
$156R_b$	112	39.4	*25.1*	45.1	—
52H	113	*22.2*	—	—	—
$156R_c$	115	62.1	58.2	*26.9*	—
$58H_a$	127	*20.8*	—	—	—
$174R_b$	127	42.8	*22.4*	38.4	—
$174R_c$	124	50.6	38.8	*22.8*	—
$58H_b$	127	—	*20.2*	—	—
$192R_b$	141	43.2	*23.2*	43.5	—
$64H_b$	139	47.7	*20.1*	—	—
$210R_d$	153	59.9	55.5	46.1	*25.6*

Structural and compositional data are summarized in Table 3. M:Y ratios range from 2:4 to 2:10. Three of four possible structures (Table 1)

TABLE 3. COMPOSITE DATA FOR THE NEW M_2Y_n STRUCTURES

M:Y	Anion layers	Structure symbol	Space group	Hexagonal c (Å)		Ideal Formula
				Obs.	Calc.	
2:4	$(34)_1$	34H	$P6_3/mmc$	81.32	81.32	$Ba_{10}Zn_8Fe_{72}O_{126}$
2:5	$(40)_3$	$120R_b$	$R\bar{3}m$	287.55	287.55	$Ba_{12}Zn_{10}Fe_{84}O_{148}$
2:6	$(46)_3$	$138R_b$	$R\bar{3}m$	331.09	331.12	$Ba_{14}Zn_{12}Fe_{96}O_{170}$
2:7	$(52)_3$	$156R_b$	$R\bar{3}m$	374.68	374.70	$Ba_{16}Zn_{14}Fe_{108}O_{192}$
2:7	$(52)_1$	52H	$P\bar{3}m1$	124.89	124.90	$Ba_{16}Zn_{14}Fe_{108}O_{192}$
2:7	$(52)_3$	$156R_c$	$R\bar{3}m$	374.68	374.70	$Ba_{16}Zn_{14}Fe_{108}O_{192}$
2:8	$(58)_1$	$58H_a$	$P\bar{3}m1$	139.42	139.43	$Ba_{18}Zn_{16}Fe_{120}O_{214}$
2:8	$(58)_3$	$174R_b$	$R\bar{3}m$	418.25	418.28	$Ba_{18}Zn_{16}Fe_{120}O_{214}$
2:8	$(58)_3$	$174R_c$	$R\bar{3}m$	418.25	418.28	$Ba_{18}Zn_{16}Fe_{120}O_{214}$
2:8	$(58)_1$	$58H_b$	$P6_3/mmc$	139.42	139.43	$Ba_{18}Zn_{16}Fe_{120}O_{214}$
2:9	$(64)_3$	$192R_b$	$R\bar{3}m$	461.89	461.85	$Ba_{20}Zn_{18}Fe_{132}O_{236}$
2:9	$(64)_1$	$64H_b$	$P\bar{3}m1$	153.96	153.95	$Ba_{20}Zn_{18}Fe_{132}O_{236}$
2:10	$(70)_3$	$210R_d$	$R\bar{3}m$	505.42	505.42	$Ba_{22}Zn_{20}Fe_{144}O_{258}$

have been found for M:Y=2:7 and four of five for M:Y=2:8. The largest structure observed ($210R_d$) requires 210 anion layers for identity along c and has a c dimension of 505.4 Å. This is indeed a large vector for an inorganic species. An impression of the enormity of the cells can be obtained from Fig. 4 when one realizes that these are $00\cdot l$ traces with a relatively long x-ray wavelength (FeK_α), yet the diffraction peaks are separated by only 1.4° in the 2θ range 105° to 120°. Calculated c dimensions were obtained by summing values for 22H (M Y M Y; 52.271 Å) and the appropriate number of Y blocks (43.577/3 Å). The probable error for observed dimensions is $\pm.01\%$. The remarkable agreement between observed and calculated values shows little if any dimensional interaction between blocks. All structures have a common basal section, with an a dimension of 5.88 Å.

Rhombohedral structures all have the same space group, $R\bar{3}m$. The hexagonal space group is either $P6_3/mmc$, if the Y blocks are equally divided, or $P\bar{3}m1$ otherwise.

The ideal formula, corresponding to the composition of the basic repeat group, is derived by summing the stoichiometries of the M and Y blocks according to the prescribed ratio. The formulas are clearly unorthodox, but when one understands the stacking principles relating the many hexagonal ferrite structures and the enormity of the unit cells, the stoichiometry becomes more realistic.

At this juncture, there appears to be nothing sacred about two M blocks in association with a variable number of Y blocks. Other series

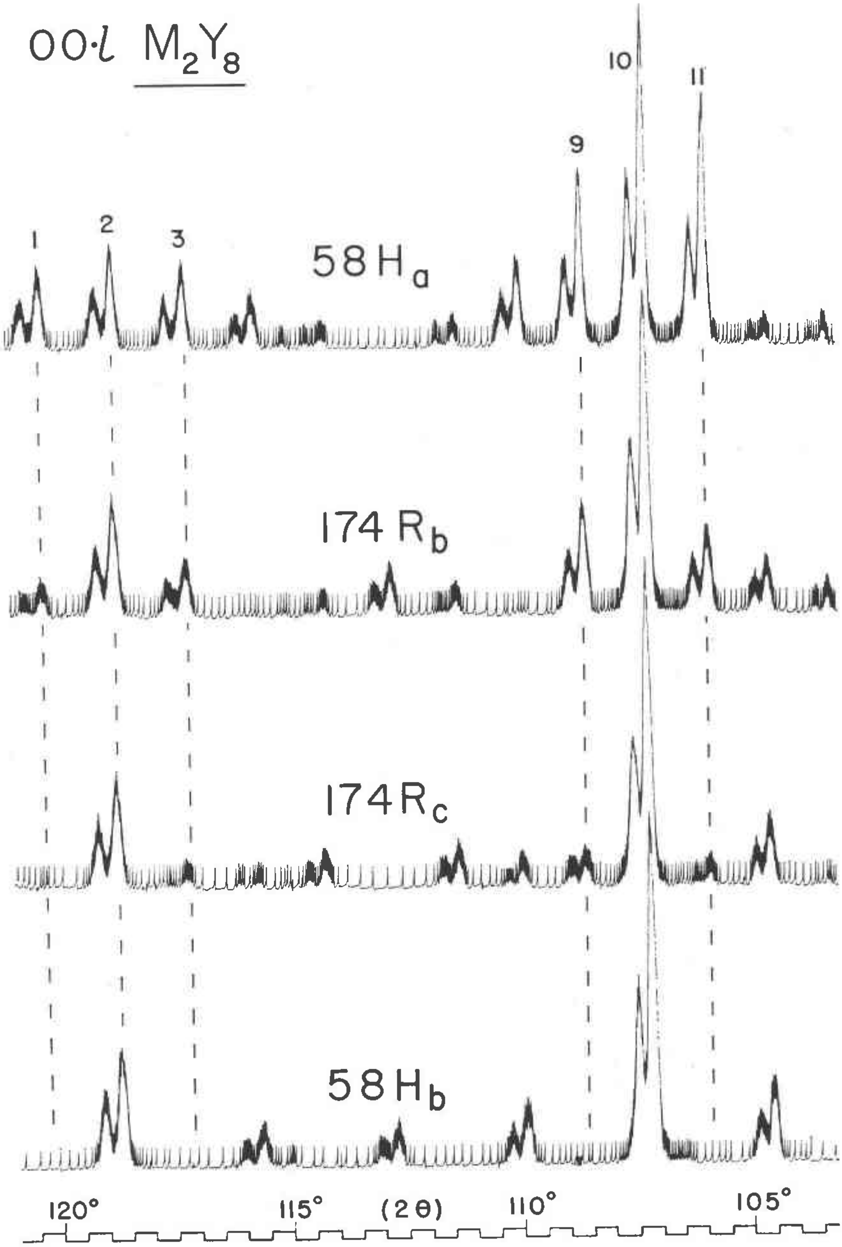

FIG. 4. Analogous portions of the 00·*l* single-crystal diffractometer patterns for the four observed structures in the 58-layer, M_2Y_8 group. See text for discussion and symbol explanation. Filtered FeK radiation.

might very well be expected with a different number of M blocks. Current single-crystal studies are being conducted in the general M-Y system on Zn-containing material and on crystals with other cations (*e.g.*, Mn, Co, Cu, Ni) nominally in place of Zn. The hexagonal ferrites have already outshone other inorganic, multiple-structure systems in structural and compositional complexity. It can safely be said that they will soon exceed even silicon carbide in number and size of characterized structures.

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